spectrum and this situation may result in a nonconvergent behavior of the perturbation expansion. However, the success of the model proves the ability of the QDMBPT to derive the logic and structure of an effective Hamiltonian which remains efficient beside the radius of convergence of the QDMBPT used to establish it, provided that the high orders are tempered through a diminution of $|\lambda|$.

Anyway the EVB Hamiltonian seems a very promising tool. It gives accurate results at a very low cost; diagonalization of moderate matrices (up to 12 atoms), built according to a very simple logic, gives results very close to the full π CI result. The model has been used elsewhere[14] to predict the evolution of the $^1A_g \rightarrow {}^1A_g$ forbidden transition in the series of linear polyenes and the N dependence of the lowest allowed transition energy in odd polyenes.

The demonstration of the aromaticity rule for cyclic polyenes has been achieved in a highly correlated model, and its physical content as a collective circular movement of electrons supports the interpretation of aromaticity that is due to ring currents. This example illustrates the power of the QDMBPT applied to the VB problem.

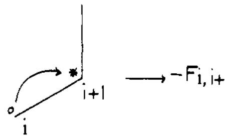
The analysis of the resulting wave function (i.e., the component of the exact wave function on the neutral subspace of the VB theory) shows the importance of spin alternation (assumed and verified by the ASMO method[16]). The picture of the electronic structure of the molecule, as it arises from our EVB model, is somewhat different from the usual MO description, in terms of filling canonical delocalized MO's or coupled electron pairs in localized bond MO's. The "faithful couple" of the electron pair[17] is replaced by a dance of electrons of opposite spins, permuting their positions through instantaneous ionic pairs; that dance is far from being disordered since some basic figures (regular spin alternation) are dominant (at least locally) and since some collective movements such as the ring currents along the circles appear to play a prominent role.

IV. Appendix. Sign of the Full Spin Permutation Matrix Element of Order $N = 2n$ for an N-Membered Ring

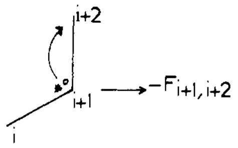
One must prove that, ϕ_1 and ϕ_2 being the two neutral determinants with full spin alternation

$$(\phi_1|H^{\text{eff}}|\phi_2) = (1\bar{2}3...\bar{2}n|\bar{H}^{2n}|\bar{1}2\bar{3}...2n\rangle > 0\ \forall n$$

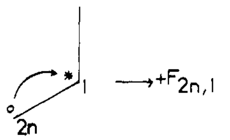
The $2n$th-order perturbative process generating this effective interaction goes through (multi) ionic intermediate determinants which will be written according to the following rules: the AO's appear in their natural (cyclic) sequence; when two electrons are on the same center, the β-spin AO will be put in second position. The determinant 2^+6^- will be written $|1\bar{3}4\bar{5}6\bar{6}\bar{7}8]$. Let us examine the signs of the matrix elements associated with the $2n$ circular electron jumps, allowing for ϕ_2 to be reached from ϕ_1; as already noted each electron only jumps to the neighboring position. The negative signs will be associated to jumps of the β-spin electron from i to $i + 1$ such as

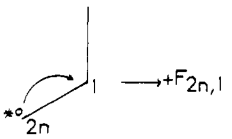


But it must necessarily be followed by another jump



also associated with a negative sign. The only exception concerns the events on the last $[2n - 1]$ bond for which





The $2n$th-order spin-exchange process therefore corresponds to a negative numerator. Since the denominator $(-\Delta E)^{2n-1}$ is negative at the same order, the resulting contribution is necssarily positive.

Registry No. 1, 106-99-0; **2**, 1120-53-2; **3**, 4095-06-1; **4**, 115-11-7; **5**, 71-43-2; **6**, 5291-90-7; **7**, 13753-03-2; **8**, 497-20-1; **9**, 3227-90-5; **10**, 80673-42-3; **11**, 926-56-7; **12**, 63943-67-9; **13**, 513-81-5; **14**, 32796-95-5; **15**, 108-38-3; **16**, 502-86-3; **17**, 52385-09-8; **18**, 924-71-0.

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Electron-Transfer Catalysis. Radical Chain Mechanism for the Ligand Substitution of Metal Carbonyls

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Abstract: A novel chain process for the ligand substitution of metal complexes is revealed by bulk and transient electrochemical methods. The large turnover numbers that are obtained for the ligand substitution of the tris(acetonitrile) complexes of molybdenum and tungsten carbonyls with phosphines and isocyanides underscore the electrocatalytic phenomenon. The efficient chain process derives from the substitution lability of the cation radicals, which are formed by the one-electron oxidation of metal carbonyls and subsequently undergo rapid electron transfer, as in Scheme II. The driving force for ligand substitution is related to the relative stabilities of the cation radicals. Electron-transfer equilibria between these cation radicals can be evaluated from the standard reduction potentials $E°$ or the cyclic voltammetric peak potentials E_p. The initiation of the chain process is finely tuned to the value of $E°$ and E_p for the various metal carbonyls. The effectiveness of metal carbonyls as catalysts in the enhanced oxidation of nucleophiles such as triphenylphosphine is also described.

Ligand substitution of the octahedral complexes of the transition metals is usually considered to proceed via the even-numbered, 16- and 18-electron intermediates.[1,2] Thus the displacement of ligands from a series of group 6B metal carbonyls $LM(CO)_5$ by

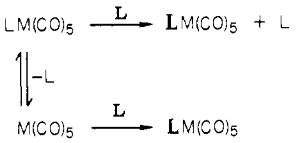
0002-7863/82/1504-3034$01.25/0

Table I. Electrocatalytic Substitution Reactions of Carbonylmetal Complexes[a]

$L_nM(CO)_{6-n}$ (mmol)	added ligand L (mmol)	temp, °C	electrode potential, V[b]	charge passed, far mol^{-1} [c]	product (yield,[d] isolated yield)
fac-$(MeCN)_3W(CO)_3$ (0.16)	*t*-BuNC (0.96)	0	0.1	6×10^{-2}	*fac*-$(BuNC)_3W(CO)_3$ (87%, 68%)
fac-$(MeCN)_3Mo(CO)_3$ (0.14)	Ph_3P (1.1)	22	0.1	9×10^{-3}	$(MeCN)_{1.5}(Ph_3P)_{1.5}Mo(CO)_3$[e]
cis-$(py)_2Mo(CO)_4$ (0.14)	BuNC (0.55)	0	0.4	1.9×10^{-1}	*cis*-$(BuNC)_2Mo(CO)_4$ (80%, 67%)
cis-$(py)_2W(CO)_4$ (0.16)	Ph_3P (0.16)	0	0.4	1.2×10^{-1}	*cis*-$(py)(Ph_3P)W(CO)_4$ (98%, 68%)
cis-$(MeCN)_2W(CO)_4$ (0.10)	Ph_3P (0.57)	22	0.2–0.4	7×10^{-2}	$(Ph_3P)_2W(CO)_4$ (--, 71%)
cis-$(MeCN)_2W(CO)_4$ (0.32)	Ph_3P (0.32)	22	0.2	5×10^{-2}	*cis*-$(MeCN)(Ph_3P)W(CO)_4$ (102%, 84%)
cis-$(MeCN)_2W(CO)_4$ (0.14)	BuNC (0.35)	22	0.2	1.3×10^{-1}	*cis*-$(BuNC)_2W(CO)_4$ (84%, --)
$(MeCN)W(CO)_5$ (0.098)	Ph_3P (0.19)	22	0.5	1.3×10^{-1}	$(Ph_3P)W(CO)_4$ (98%, --)
$(py)W(CO)_5$ (0.17)	Ph_3P (1.1)	0	0.9	1.1[g]	$(Ph_3P)W(CO)_5$ (69%, --)[g]
$(py)W(CO)_5$ (0.099)	*t*-BuNC (0.5)	22	0.7	0.47	$(t\text{-}BuNC)W(CO)_5$ (64%, --)[j]
$(MeCN)Cr(CO)_5$ (0.26)	Ph_3P (0.38)	25	0.7	0.58[h]	$(Ph_3P)Cr(CO)_5$ (≤11%, --)[h]
$(py)Cr(CO)_5$ (0.064)	Ph_3P (0.61)	22	0.7	1.05[i]	$(Ph_3P)Cr(CO)_5$ (≤10%, --)[i]

[a] Reactions performed in 10–15 mL of MeCN containing 0.1 M TEAP subsequent to purging with argon in a preparative electrolysis cell. Contents stirred with a magnet. [b] Volts vs. saturated NaCl SCE. [c] Based on faradays required for complete consumption of $L_nM(CO)_{6-n}$ unless noted otherwise. [d] Yield determined by quantitative infrared spectrophotometry. [e] Ligand stoichiometry based on elemental analysis of the precipitated product. [f] Mixture of cis and trans isomers precipitated from solution. [g] 29% of starting material recovered. [h] 87% of $(MeCN)Cr(CO)_5$ recovered. [i] 90% of starting $(py)Cr(CO)_5$ reisolated. [j] 28% of $(py)W(CO)_5$ reisolated.

Scheme I



phosphines and arsines **L** have been reported to involve competitive dissociative and associative pathways, as summarized in Scheme I.[3-6] Nitrogen-centered ligands L which serve as σ donors are particularly good leaving groups. Consequently, such derivatives are versatile synthetic precursors.[7-10]

We wish to report a series of similar ligand substitutions that proceed via a catalytic chain process. In this study, we have focused our attention on the ligand substitutions of group 6B metal carbonyls bearing pyridine (py) or acetonitrile (MeCN) ligands by the structurally distinctive nucleophiles, triphenylphosphine and *tert*-butyl isocyanide. Electrochemical methods are employed for the production of the 17-electron cation radicals required for the initiation of the chain process.

Results

I. Chain Process for the Ligand Substitution of Metal Carbonyl Complexes. Products and Stoichiometry. The bis(acetonitrile) and bis(pyridine) complexes of tungsten carbonyl, $(MeCN)_2W(CO)_4$ and $(py)_2W(CO)_4$, respectively, are stable to ligand substitution by triphenylphosphine at 25 °C. However, the phosphine substitution is effected rapidly if a set of platinum electrodes [E] is inserted into the acetonitrile solution (containing 0.1 M tetraethylammonium perchlorate TEAP as supporting electrolyte) and a slight potential of 0.2 V is applied.[11] For example, the results in Table I show that the monosubstitution products are obtained in high yields within 15 min, when an equimolar amount of triphenylphosphine is present, i.e.,

$$cis\text{-}L_2W(CO)_4 + PPh_3 \xrightarrow{[E]} cis\text{-}L(Ph_3P)W(CO)_4 + L \quad (1)$$

where L = MeCN, C_6H_5N(py). The electrocatalytic nature of the substitution is readily deduced by coulometry during bulk electrolysis at controlled potential. From the measurement of the amount of current (faradays) passed through the solution, a turnover number (TN) in excess of 20 equiv of substitution products per electron obtains for eq 1.

In the presence of excess triphenylphosphine, the bis(acetonitrile) complex undergoes two sequential substitutions.

$$cis\text{-}(MeCN)_2W(CO)_4 + 2PPh_3 \xrightarrow{[E]} trans\text{-}(Ph_3P)_2W(CO)_4 + 2MeCN \quad (2)$$

Thus the nearly quantitative formation of *cis*-$(Ph_3P)(MeCN)W(CO)_4$ in the first stage presented in eq 1 was accompanied by an increase in the electrode potential from 0.2 to 0.4 V. Continued application of this electrode potential resulted in the formation of the disubstitution product in eq 2, which precipitated from solution predominantly as the trans isomer. The passage of 0.07 faraday per mol of $(MeCN)_2W(CO)_4$ indicated a turnover number in excess of 15 for the substitution of both ligands. By contrast, the bis(pyridine) analogue $(py)_2W(CO)_4$ did not undergo further ligand substitution of the monosubstituted $(py)(Ph_3P)W(CO)_4$ in the presence of excess triphenylphosphine.

$$(py)(Ph_3P)W(CO)_4 + PPh_3 \xrightarrow{[E]} (Ph_3P)_2W(CO)_4 + py \quad (3)$$

The substitution products in the examples above (and in the later studies) were characterized by comparison with authentic samples that were synthesized by independent methods described in the Experimental Section.

Multiple substitution of both pyridine ligands in the molybdenum carbonyl, *cis*-$(py)_2Mo(CO)_4$, is effected simultaneously by *tert*-butyl isocyanide at 0.40 V.

$$cis\text{-}(py)_2Mo(CO)_4 + 2BuNC \xrightarrow{[E]} cis\text{-}(BuNC)_2Mo(CO)_4 + 2py \quad (4)$$

It is important to note that the substitution reaction in eq 4 proceeds at an appreciable rate even without the application of an electrode potential, if the components are merely mixed without the exclusion of air. However, when special precautions are taken, the uncatalyzed substitution is quite slow. For example, when a solution of *cis*-$(py)_2Mo(CO)_4$ under argon is prereduced at −0.5 V to remove adventitious (oxidized) impurities, no substitution by either *tert*-butyl isocyanide or triphenylphosphine could be observed, even after 1 h. Application of a slight positive electrode potential to the solution then leads to the rapid electrocatalytic process in eq 4. If a slight negative potential is reapplied during the course of electrocatalysis, ligand substitution is again inhibited.

In a similar manner, the ligand substitution of the highly air sensitive tris(acetonitrile) complex *fac*-$(MeCN)_3Mo(CO)_3$ could be completely inhibited by a prereduction at −0.5 V prior to the addition of triphenylphosphine. The passage of only 0.009 faradays per molybdenum (TN > 100) is sufficient to catalyze the sub-

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(11) All potentials are given in volts relative to saturated NaCl SCE.

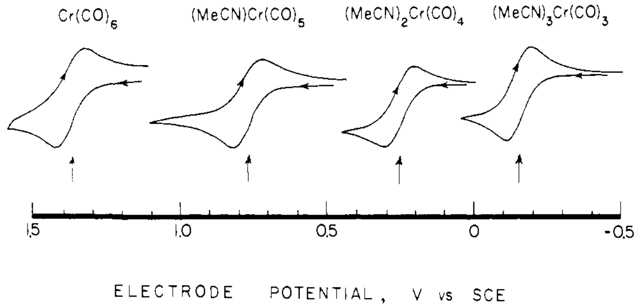

Figure 1. Single-scan cyclic voltammograms of the series of chromium carbonyls $(MeCN)_nCr(CO)_{6-n}$ in acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate at 25 °C.

stitution process, the termination of which is signaled by the complete separation of the product within 2 min. Elemental analysis of the precipitate is consistent with the empirical formula $(MeCN)_{1.5}(Ph_3P)_{1.5}Mo(CO)_3$, suggesting that it is a mixed crystal of the mono- and disubstituted products. Incomplete substitution no doubt arises from the insolubility of this mixed crystal. Indeed, the soluble tris(*tert*-butyl isocyanide) derivative is the principal product derived from the electrocatalytic substitution of the tris(acetonitrile) complex of tungsten carbonyl, i.e.,

$$(MeCN)_3W(CO)_3 + 3BuNC \xrightarrow{[E]} (BuNC)_3W(CO)_3 + 3MeCN \quad (5)$$

The efficiency of the electrocatalytic substitution is highly dependent on the ligand and the metal. As an example, the monoacetonitrile tungsten carbonyl $(MeCN)W(CO)_5$ undergoes catalytic substitution by triphenylphosphine at 0.5 V with a turnover number of at least 8.

$$(MeCN)W(CO)_5 + Ph_3P \xrightarrow{[E]} (Ph_3P)W(CO)_5 + MeCN \quad (6)$$

However, the corresponding monopyridine complex $(py)W(CO)_5$ affords a 70% yield of the phosphine derivative $(Ph_3P)W(CO)_5$ only after more than 1 faraday of charge is passed through the solution; i.e., TN < 1. (Acetonitrile)chromium carbonyl affords little or no substitution product even after a substantial amount of current has flowed through the solution.

$$(MeCN)Cr(CO)_5 + Ph_3P \xrightarrow{[E]} (Ph_3P)Cr(CO)_5 + MeCN \quad (7)$$

II. Cyclic Voltammetry of Metal Carbonyl Complexes. In order to probe the electrocatalysis, we initially examined the anodic properties of the various transition-metal carbonyls in the absence of added ligands. Cyclic voltammetry was carried out with a stationary platinum microelectrode in acetonitrile solutions containing 0.1 M tetraethylammonium perchlorate (TEAP) as the supporting electrolyte. Two distinctive types of limiting electrochemical behavior can be observed for metal carbonyl complexes.

Reversible Oxidation. The cyclic voltammograms in Figure 1 all exhibit a well-defined anodic wave together with the coupled cathodic wave on the reverse scan. In most cases both the peak current ratio $i_P(a)/i_P(c)$ and the potential separation Δ of the anodic and cathodic waves at scan rates of 200 mV s^{-1} correspond to the expected values for the reversible electrochemical couple, e.g.,

$$(Ph_3P)_2Cr(CO)_4 \rightleftharpoons (Ph_3P)_2Cr(CO)_4^+ + e \quad (8)$$

The electrochemical standard reduction potentials E° for these substituted metal carbonyls are listed in Table II.[12] It is noteworthy that the successive replacement of CO ligands by acetonitrile in chromium hexacarbonyl leads to a progressive lowering of the standard reduction potential. Indeed, the difference in E° between the hexacarbonyl complex $Cr(CO)_6$ and the corresponding tris(acetonitrile) derivative $(MeCN)_3Cr(CO)_3$ is in excess of 1.4 V or 30 kcal/mol! The standard reduction potentials are also strongly dependent on the nature of the ligand and the metal. Thus in the series of mono- and disubstituted chromium carbonyls $LCr(CO)_5$ and $L_2Cr(CO)_4$, the magnitudes of E° are substantially lower for the nitrogen-centered ligands MeCN and C_5H_5N than for the phosphine ligand, Ph_3P.[13] In the tris(acetonitrile) complexes, the standard reduction potentials for the metal centers decrease in the order Mo > W > Cr.

Table II. Reversible Cyclic Voltammetric Data for Metal Carbonyl Complexes[a]

$L_nM(CO)_{6-n}$	E_p,[a] V[b]	E°, V[b]	$i_p(a)/i_p(c)$[c]
$Cr(CO)_6$[d]	1.86	1.36	1.1
$(Ph_3P)Cr(CO)_5$	1.11	1.05	1.0
$(MeCN)Cr(CO)_5$	0.82	0.77	1.0
$(py)Cr(CO)_5$	0.80	0.74	1.1
trans-$(Ph_3P)_2Cr(CO)_4$	0.58	0.55	1.1
cis-$(MeCN)_2Cr(CO)_4$	0.29	0.24	1.0
cis-$(py)_2Cr(CO)_4$	0.35	0.28	1.0
fac-$(MeCN)_3Cr(CO)_3$	−0.09	−0.14	1.0
fac-$(MeCN)_3Mo(CO)_3$	0.26	0.21	1.0
fac-$(MeCN)_3W(CO)_3$	0.18	0.12	1.0
cis-$(t\text{-}BuNC)_2W(CO)_4$	0.81		2.4
fac-$(t\text{-}BuNC)_3W(CO)_3$	0.75		2.3
ferrocene (reference)	0.37	0.31	1.0

[a] At a platinum electrode in acetonitrile solutions containing ~10^{-3} M metal carbonyl and 0.1 M TEAP at 25 °C. Scan rates = 200 mV s^{-1}. [b] Potentials relative to E° of ferrocene equal to 0.31 V vs. saturated NaCl SCE. [c] Ratio of anodic and cathodic peak currents. [d] Compare with ref 14.

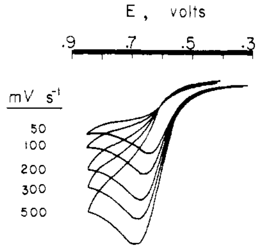

Figure 2. Single-scan cyclic voltammogram of $(MeCN)(Ph_3P)W(CO)_4$ in acetonitrile containing 0.1 M TEAP at various scan rates.

Irreversible Oxidation. The single-sweep cyclic voltammogram of the tungsten complex $(MeCN)(Ph_3P)W(CO)_4$ in Figure 2 is characterized by an anodic wave showing a well-defined current maximum but no coupled cathodic wave on the reverse scan, even at rates up to 10 V s^{-1}. An inspection of the details of the sweep dependence reveals that the current in the foot of the anodic wave is independent of the sweep rate. Such a behavior suggests that electron transfer from this tungsten carbonyl is electrochemically unidirectional, i.e., irreversible.[15] Suffice it to mention here that the absence of the reverse electron-transfer step derives from the rapid decomposition of the cation, i.e.,

$$(MeCN)_2W(CO)_4 \xrightarrow{-e} (MeCN)_2W(CO)_4^+ \xrightarrow{\text{fast}} \text{etc.} \quad (9)$$

Such an electrochemical EC mechanism is known in a variety of other organometal systems showing irreversible CV behavior.[16,17] Indeed, at the peak potential E_p of a totally irreversible CV wave, the rate of electron transfer is given by[18]

$$k(E_P) = 2.18[D\beta n\mathcal{F}v/RT]^{1/2} \quad (10)$$

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[12] Standard reduction potentials obtained by electrochemical methods include a work term. For a discussion, see: Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.*, in press.

[13] For $(Ph_3P)_2W(CO)_4$, reference is made only to the trans isomer.

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Table III. Irreversible Cyclic Voltammetric Data for Metal Carbonyl Complexes[a]

metal carbonyl	E_p, V[b]	metal carbonyl	E_p, V[b]
$(Ph_3P)W(CO)_5$	1.23	*cis*-$(Ph_3P)(CH_3CN)W(CO)_4$	0.65
$(t\text{-}BuNC)W(CO)_5$	1.18	*cis*-$(MeCN)_2W(CO)_4$	0.58
$(MeCN)W(CO)_5$	1.02	*cis*-$(py)_2W(CO)_4$	0.55
$(py)W(CO)_5$	1.01	*cis*-$(t\text{-}BuNC)_2W(CO)_4$	0.81
trans-$(Ph_3P)_2W(CO)_4$	0.75	*cis*-$(t\text{-}BuNC)_2Mo(CO)_4$	1.00
cis-$(Ph_3P)(py)W(CO)_4$	0.69	*cis*-$(py)_2Mo(CO)_4$	0.60

[a] In acetonitrile solution containing 0.1 M TEAP at 25 °C. [b] Anodic peak potential in volts vs. saturated NaCl SCE, as measured at a uniform sweep rate of 200 mV s^{-1}.

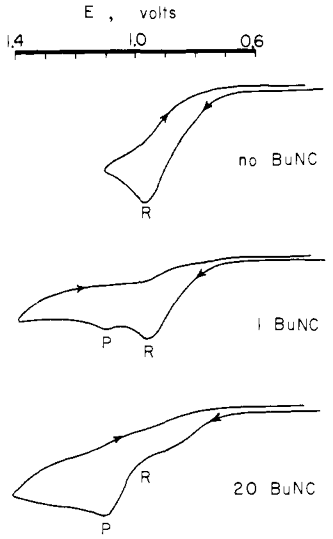

Figure 3. Cyclic voltammograms of 1.0×10^{-3} M $(py)W(CO)_5$ in the presence of various amounts of added *tert*-butyl isocyanide, as measured at 200 mV s^{-1} in acetonitrile containing 0.1 M TEAP at 25 °C: (a) no *t*-BuNC present; (b) 1 equiv of *t*-BuNC; (c) 20 equiv of *t*-BuNC added. Note: R and P refer to the CV peak potentials of the $(py)W(CO)_5$ reactant and $(t\text{-}BuNC)W(CO)_5$ product, respectively.

where D is the diffusion coefficient, β the transfer coefficient for the electrode process, n the number of electrons transferred in the rate-limiting step, and v the scan rate. $\mathcal{F}$ is the Faraday constant, and R and T have their usual significance. According to eq 10, the location of the CV peak E_p in an irreversible electrochemical process directly relates to the activation process for electron transfer when the sweep rate and the other parameters in the right side of the equation are constant.[19,20] As such, the tabulation of the CV peak potentials E_p in Table III represents measures of the ease of oxidation of substituted metal carbonyl complexes that show irreversible electrochemical behavior. In accord with this expectation, it is noteworthy that the structural trends for the reversible $E°$ in Table II parallel those for the irreversible E_p in Table III.[21,22]

III. Transient Electrochemical Behavior of Metal Carbonyl Complexes in the Presence of Nucleophiles. Coulometry together with product isolation in Table I have established the phenomenon of electrocatalysis in the substitution of metal carbonyls by nucleophiles. We now wish to describe the cyclic voltammograms associated with this transient electrochemical behavior. In the course of this study, we also observed that various metal carbonyls are capable of efficiently inducing the oxidation of triphenylphosphine at potentials substantially less than its oxidation potential.

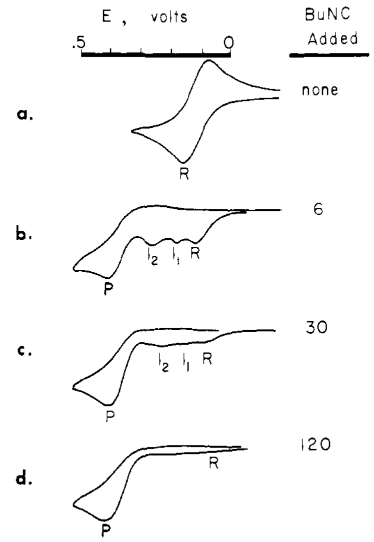

Figure 4. Cyclic voltammetric studies of multiple-ligand substitution of 1.0×10^{-3} M $(MeCN)_3W(CO)_3$ in acetonitrile containing 0.1 M TEAP: (a) no additive; (b) 6 equiv of *t*-BuNC; (c) 30 equiv of *t*-BuNC; (d) 120 equiv of *t*-BuNC. All cyclic voltammograms recorded at a constant scan rate of 200 mV s^{-1}. R, I, and P refer to the CV peak potentials of the reactant, intermediates, and product, respectively, as described in the text.

Electrocatalysis in the Substitution of a Single Ligand. The cyclic voltammogrm of the monopyridine complex $(py)W(CO)_5$ in MeCN at a sweep rate of 200 mV s^{-1} consists of a single irreversible wave shown in Figure 3a. However, when 20 equiv of *tert*-butyl isocyanide is added to a solution containing 1.0×10^{-3} M $(py)W(CO)_5$, the CV wave at $E_p = 1.01$ V is absent, being replaced by a new irreversible wave with $E_p = 1.18$ V corresponding to that of the substitution product $(t\text{-}BuNC)W(CO)_5$ shown in Figure 3c.[25] When smaller amounts of *tert*-butyl isocyanide are employed, both waves can be observed in the cyclic voltammogram (see Figure 3b). Since the CV wave of $(py)W(CO)_5$ in Figure 3a arises from its oxidation to the cation, the phenomenon in Figure 3c is associated with its rapid interception by added ligand, i.e.,

$$(py)W(CO)_5 \xrightarrow{[E_p]} (py)W(CO)_5^+ + e \qquad (11)$$

$$(py)W(CO)_5^+ + t\text{-}BuNC \xrightarrow{\text{fast}} (t\text{-}BuNC)W(CO)_5^+ + py \qquad (12)$$

Isolation of the *tert*-butyl isocyanide complex $(t\text{-}BuNC)W(CO)_5$ in excellent yields after bulk electrolysis at 0.70 V indicates that the substitution process in eq 12 is rapid.

The electrocatalytic substitution by triphenylphosphine of the monopyridine and monoacetonitrile complexes of tungsten carbonyl, $(py)W(CO)_5$ and $(CH_3CN)W(CO)_5$, are more difficult to interpret solely on the basis of the CV experiment, since their anodic waves listed in Table III are not cleanly separated from the anodic wave of triphenylphosphine with $E_P = 1.3$ V. In the presence of added Ph_3P, the anodic wave at $E_p = 1.02$ V for $(MeCN)W(CO)_5$ was absent. However, the cyclic voltammogram of $(py)W(CO)_5$ appeared to be unaffected by the presence of added triphenylphosphine. In neither case could a CV wave corresponding to the product $(Ph_3P)W(CO)_5$ be clearly discerned owing to the presence of the phosphine wave. Nonetheless,

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(18) Klingler, J. R.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 4790.

(19) The transfer and diffusion coefficients of these related metal carbonyls are assumed to be the same. See ref 16.

(20) Partial reversibility is also observed in some cases. See also: Pletcher, D. *Chem. Soc. Rev.* **1975**, *4*, 471.

(21) None of the metal carbonyl complexes employed in this study are reducible at potentials greater than −0.5 V vs. SCE.

(22) Values of E_p are not trivially related to the thermodynamic $E°$ of the oxidation process since electrode kinetics,[23] and in some cases, chemical kinetics[24] affect the location of the current peak.

(23) Nicholson, R. S. *Anal. Chem.* **1965**, *37*, 1351.

(24) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706.

(25) A slight shift in E_p is predicted for an electrode oxidation followed by a chemical reaction. See ref 24.

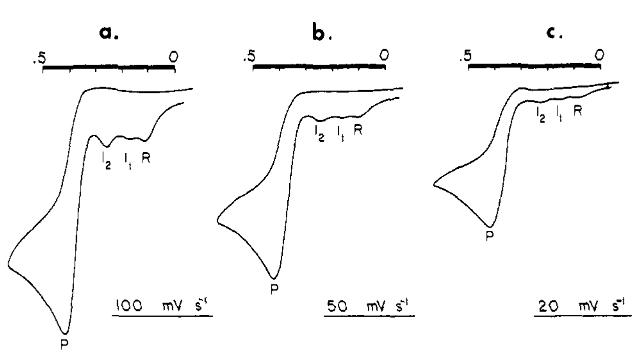

Figure 5. Sweep rate dependence of the intermediates in the cyclic voltammogram of 1.0×10^{-3} M $(MeCN)_3W(CO)_3$ with 6 equiv of *tert*-butyl isocyanide in acetonitrile containing 0.1 M TEAP at 25 °C. Sweep rates: (a) 100 mV s^{-1}, (b) 50 mV s^{-1}, and (c) 20 mV s^{-1}.

preparative-scale electrolysis in Table I demonstrates that both complexes undergo ligand substitution with Ph_3P at these electrode potentials.

Electrocatalysis in Multiple Ligand Substitutions. The cyclic voltammogram of the tris(acetonitrile) complex of tungsten carbonyl *fac*-$(MeCN)_3W(CO)_3$ is illustrated in Figure 4a. The reversible character of the one-electron wave at $E° = 0.12$ V is absent when the cyclic voltammogram is obtained of a similar solution but containing 6 equiv of added *tert*-butyl isocyanide. Furthermore, the cyclic voltammogram in Figure 4b taken at the same sweep rate shows that the anodic current maximum at $E_p = 0.18$ is significantly diminished.[25,26] The presence of incrementally more *tert*-butyl isocyanide leads to further diminution of this CV wave (Figure 4c) and finally its disappearance altogether (Figure 4d). The cyclic voltammogram in Figure 4d corresponds to that of an authentic sample of *fac*-$(MeCN)_3W(CO)_3$. A closer inspection of the cyclic voltammogram in Figure 4b reveals the presence of two additional waves. Indeed, the irreversible waves with $E_p = 0.17$ and 0.25 V can be readily ascribed to the mono- and disubstituted intermediates $(t\text{-}BuNC)(MeCN)_2W(CO)_3$ and $(t\text{-}BuNC)_2(MeCN)W(CO)_3$, respectively.

The transient formation of the partially exchanged intermediates is clearly brought out in Figure 5, which shows the cyclic voltammograms of the same solution of $(MeCN)_3W(CO)_3$ and *tert*-butyl isocyanide at different sweep rates: (a) 100 mV s^{-1}, (b) 50 mV s^{-1}, and (c) 20 mV s^{-1}. The disappearance of the CV waves for the reactant, as well as the partially exchanged intermediates at the slowest sweep rate recorded in Figure 5c, results from the complete conversion to the fully exchanged product $(t\text{-}BuNC)_3W(CO)_3$[26b] (compare with Figure 4d).

Electrocatalytic behavior of the cyclic voltammogram is also observed for the bis(acetonitrile) complex of the molybdenum carbonyl $(py)_2Mo(CO)_4$, which exhibits an irreversible wave with $E_p = 0.60$ V. Thus the current-induced chain reaction was apparent upon the addition of 6 equiv of *tert*-butyl isocyanide. First, the anodic peak current of $(py)_2Mo(CO)_4$ decreased by more than 80% and was accompanied by a slight shift in the anodic peak potential to 0.51 V. Second, the appearance of a new wave is attributable to the bis(isocyanide) derivative *cis*-$(t\text{-}BuNC)_2Mo(CO)_4$ with $E_p = 1.00$ V. The latter was verified by the preparative-scale electrolysis at a controlled potential of 0.4 V, followed by isolation of *cis*-$(t\text{-}BuNC)_2Mo(CO)_4$ in 67% yield. The presence of the monoisocyanide intermediate was not clearly discerned in the cyclic voltammogram owing to the partial overlap of the CV of the reactant with that of the product. Indeed, the intermediates formed during the multiple electrocatalytic substitution may not be readily observed during cyclic voltammetry, unless there is a sizeable window between the potentials (E_p) of the reactant and the product. For example, the intermediate in the electrocatalytic substitution of $(MeCN)_2W(CO)_4$ by added triphenylphosphine in eq 1 is not cleanly delineated in the cyclic voltammogram. Although the peak current arising from $(MeCN)_2W(CO)_4$ decreased from 40 μA to less than 3 μA attendant upon the introduction of triphenylphosphine, the new wave at $E_p = 0.83$ V may be attributed to either the monophosphine or bis(phosphine) product, $(Ph_3P)(MeCN)W(CO)_5$ or $(Ph_3P)_2W(CO)_4$, as judged by the values of E_p in Table III. The isolation of the monophosphine product in high yield by controlled-potential electrolysis in eq 2 provides the direct evidence that it is more than a transitory intermediate.

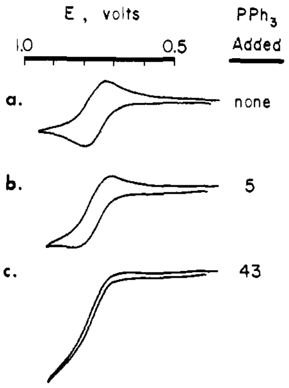

Figure 6. Cyclic voltammogram of 1.0×10^{-3} M $(MeCN)Cr(CO)_5$ showing the catalytic oxidation of triphenylphosphine. (a) Reversible CV of $(MeCN)Cr(CO)_5$ only. Partially reversible CV of the same solution but containing (b) 5 equiv of Ph_3P and (c) 43 equiv of Ph_3P at uniform scan rates of 50 mV s^{-1}.

Catalysis in the Electrochemical Oxidation of Nucleophiles. The chromium carbonyls $(py)Cr(CO)_5$ and $(MeCN)Cr(CO)_5$ are characterized in Table II by reversible electrode processes with $E°$ between 0.3 and 0.8 V. However, in the presence of added triphenylphosphine, each cyclic voltammogram changes from a reversible one-electron wave to that which can be characterized as irreversible. For example, the reversible CV in Figure 6a for the monoacetonitrile complex $(MeCN)Cr(CO)_5$ with $E° = 0.75$ V is replaced by the quasi-reversible wave in Figure 6b upon the addition of triphenylphosphine. In the presence of additional Ph_3P (43 equiv), the coupled cathodic wave has almost completely disappeared. (Note the scan rate is held constant.)

The elongated shapes of the CV waves in Figure 6b and 6c have been described by Nicholson and Shain[24] for the general case, in which the electrode process consists of a reversible charge transfer followed by the chemical regeneration of the reduced species (case VII in their paper[24]). For the system examined in this study, the mechanism is

$$(MeCN)Cr(CO)_5 \rightarrow (MeCN)Cr(CO)_5^+ + e \quad (13)$$

$$(MeCN)Cr(CO)_5^+ + PPh_3 \rightarrow (MeCN)Cr(CO)_5 + [Ph_3P]^+ \quad (14)$$

where $[Ph_3P]^+$ represents the oxidation products of triphenylphosphine (vide infra). The overall process in eq 13 and eq 14 corresponds to the carbonylmetal-induced oxidation of triphenylphosphine. Such a formulation can be readily verified in several ways. First, the exponential disappearance of Ph_3P was observed by continuously monitoring its concentration by chromatography during bulk electrolysis at a controlled current. After completion, the chromium carbonyl $(py)Cr(CO)_5$ could be recovered in 94% yield. During this period, the electrode potential remained relatively invariant. Second, the same results were obtained in the bulk electrolysis at a controlled potential in Figure 7 showing the sharp falloff in the concentration of Ph_3P. Again, most of the $(py)Cr(CO)_5$ could be recovered intact after most of the phosphine was consumed.

A similar electrocatalytic oxidation of triphenylphosphine occurred at 0.8 V when $(MeCN)Cr(CO)_5$ was present. However, the bis(acetonitrile) analogue $(MeCN)_2Cr(CO)_4$, with a more negative potential, did not induce ligand oxidation, and the cyclic

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(26) (a) The magnitude of the observed decrease in i_p for $(MeCN)_3W(CO)_3$ is not expected for an EC process involving oxidation followed by a simple irreversible chemical reaction. (b) Indeed a catalytic consumption of $(MeCN)_3W(CO)_3$ in the vicinity of the electrode is indicated.

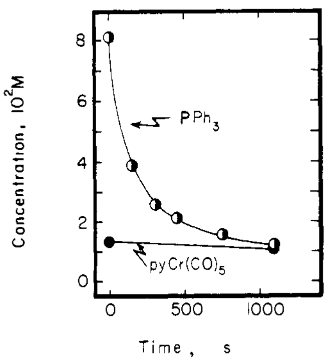

Figure 7. Bulk electrolysis of 1.3×10^{-2} M (py)Cr(CO)$_5$ and 8.1×10^{-2} M Ph$_3$P in acetonitrile at a constant potential of 0.69 V vs. NaCl SCE.

voltammogram was unaffected by the presence of Ph$_3$P.

Discussion

Ligand substitution of metal carbonyls $L_nM(CO)_{6-n}$ is tantamount to an exchange process:

$$L_nM(CO)_{6-n} + nL \rightleftharpoons L_nM(CO)_{6-n} + nL \qquad (15)$$

For the systems examined in this study, the equilibrium lies in the direction in which the nitrogen-centered ligands, L = pyridine and acetonitrile, are replaced by the ligands **L** = Ph$_3$P and *t*-BuNC, respectively.[27]

Such ligand substitutions as those included in Table I are facilitated with remarkable ease when only a trickle of current is passed through the solution. Since the conversion of metal carbonyl far exceeds the faradays of charge, a chain mechanism must pertain to these ligand substitutions. Indeed, they show the earmarks of a conventional chain process in that substitution can be either deliberately inhibited or initiated simply by reversing the flow of the current.

Two questions arise immediately about this electrode-assisted substitution. How is the direction of ligand substitution related to the thermal exchange in eq 15? What is the mechanism of such an unusually facile ligand substitution?

The Nature of Electrocatalysis. We begin the discussion by emphasizing that the electrochemical process can be carried out with turnover numbers in excess of 100. As such, the electrode is only a means of initiating the catalytic cycle and by itself supplies no net input of energy.[28] Indeed, those metal carbonyls such as (MeCN)$_3$Mo(CO)$_3$, which undergo chain substitution with long kinetic chain lengths, can be triggered by either chemical or electrochemical initiation. In fact, the chemical initiation (particularly by adventitious air) may be so facile as to obscure the chain character of ligand substitution.[29] The kinetic chain length for ligand substitution of most of the metal carbonyls examined in this study is rather limited, however, and electrochemical initiation provides a unique method for continuously generating the active species required for the chain process. Since the electrochemically induced process is truly catalytic, it only facilitates the ligand substitution and does not alter the course of the thermal process in eq 15. It is important to emphasize this point, since such a chain process is to be distinguished from the conventional ligand substitution of metal carbonyls induced by light, in which the direction of eq 15 is determined by the photostationary equilibrium.[30]

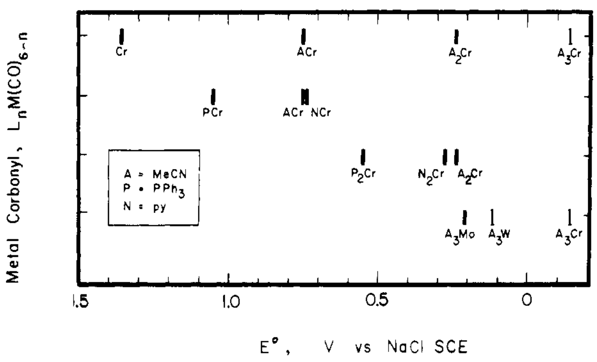

Figure 8. Effect of the nature of and the number of noncarbonyl ligands L on the standard reduction potentials $E°$ of substituted chromium carbonyls, $L_nCr(CO)_{6-n}$.

Redox Equilibria among Metal Carbonyls. Electrocatalysis is most effective when the ligand substitution in eq 15 proceeds in the direction to produce the metal carbonyl with the more positive oxidation potential. The results in Tables II and III illustrate the dependence of both $E°$ and E_p, respectively, on the nature and number of the noncarbonyl ligands L and the identity of the metal M. Metal carbonyls bearing phosphine or isonitrile ligands are more difficult to oxidize than those bearing an equivalent number of pyridine or acetonitrile ligands on the same metal carbonyl. Phosphines, isocyanides, and carbonyl ligands are considered to be better π acids than nitrogen-centered ligands such as pyridine and acetonitrile.[31] Accordingly, the significant differences in $E°$ and E_p for various metal carbonyls largely relate to the ability of ligands L to stabilize the carbonylmetal cation formed upon one-electron oxidation, i.e.,[35]

$$L_nM(CO)_{6-n} \rightarrow L_nM(CO)_{6-n}^{+} + e \qquad (16)$$

As the number of carbonyl ligands is decreased and replaced by ligands which are poorer π acids, the metal carbonyls become progressively more easily oxidized, as schematically represented in Figure 8.

A singularly useful conclusion to be derived from the foregoing observations is that the driving force for the reduction of the carbonylmetal cation A$^+$ by the metal carbonyl B is favored in the following sense:

$$\underset{A^+}{L_nM(CO)_{6-n}^{+}} + \underset{B}{L_nM(CO)_{6-n}} \rightarrow \underset{A}{L_nM(CO)_{6-n}} + \underset{B^+}{L_nM(CO)_{6-n}^{+}} \qquad (17)$$

when M = Cr, L = Ph$_3$P and L = py, MeCN; when M = Mo, L = Ph$_3$P, *t*-BuNC and L = py, MeCN; and when M = W, L = Ph$_3$P, *t*-BuNC and L = py, MeCN. The same conclusion applies to metal carbonyls with mixed ligands, e.g.,

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[27] Quantitative data regarding such equilibria are unfortunately not available.

[28] (a) For a recent discussion of electrocatalysis in other systems, see: Saveant, J. M. *Acc. Chem. Res.* **1980**, *13*, 323. (b) Various types of electrocatalysis can be described. In the chain process for ligand substitution, the *turnover number* (TN) referred to in this study is synonymous with *current efficiency*. For the enhanced phosphine oxidation in eq 13 and 14, electrocatalysis refers to the change (i.e., decrease) in the potential required for oxidation.

[29] A number of ligand exchange reactions reported in the literature which involve easily oxidized substrates and extremely mild conditions may proceed by the chain process.[7-10]

[30] See: (a) Adamson, A. W.; Fleischauer, P. D. "Concepts in Inorganic Photochemistry"; Wiley: New York, 1975. (b) For substitution in metal carbonyls, see: Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979. Bock, C. R.; Koerner von Gustorf, E. A. *Adv. Photochem.* **1977**, *10*, 221. See also: (c) Schwenzer, G.; Darensbourg, M. Y.; Darensbourg, D. J. *Inorg. Chem.* **1972**, *11*, 1967. (d) Incorvia, M. J.; Zink, J. I. *Ibid.* **1977**, *16*, 3161 and references therein.

[31] The relative π acidities of various ligands have been deduced from the carbonyl stretching frequencies ν_{CO} of substituted metal carbonyls.[32] Empirical correlations exist between E_p and ν_{CO}[33] or force constants[34] for a homologous series of metal carbonyls.

[32] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980; p 1070.

[33] (a) Connelly, N. G.; Demidowicz, Z.; Kelly, R. L. *J. Chem. Soc., Dalton Trans.* **1975**, 2335. (b) Connelly, N. G.; Kelly, R. L. *J. Organomet. Chem.* **1976**, *120*, C16.

[34] Connelly, N. G.; Kitchen, M. D. *J. Chem. Soc., Dalton Trans.* **1977**, 931.

[35] This implies that the neutral metal carbonyls differ less in energy than the corresponding cations.

$$(Ph_3P)_2W(CO)_4^+ + (Ph_3P)(MeCN)W(CO)_4 \rightarrow (Ph_3P)_2W(CO)_4 + (Ph_3P)(MeCN)W(CO)_4^+ \quad (18)$$

$$(Ph_3P)(MeCN)W(CO)_4^+ + (MeCN)_2W(CO)_4 \rightarrow (Ph_3P)(MeCN)W(CO)_4 + (MeCN)_2W(CO)_4^+ \quad (19)$$

Carbonylmetal Cation Radicals as Reactive Intermediates. We now wish to describe how the foregoing delineation of electron exchange between metal carbonyl species relates to the mechanism of the electrocatalysis of ligand substitution. Before doing so, it is important to emphasize that the mediation of the electrode in the initiation process demonstrates that it is directly responsible for the generation of the catalytically active species. As such, the applied potential at which electrocatalysis commences is determined by the potential at which the metal carbonyl is readily oxidized (see Table I). Indeed, the cyclic voltammetric studies described in Figures 3–5 provide conclusive evidence that the cation radical $L_nM(CO)_{6-n}^+$ derived from the one-electron oxidation of the diamagnetic metal carbonyl is readily converted by added nucleophile **L**.

Let us first consider the reversible charge transfer at $E°$

$$(MeCN)_3W(CO)_3 \xrightleftharpoons{[E°]} (MeCN)_3W(CO)_3^+ + e \quad (20)$$

to afford the cation radical, which disappears in the presence of added **L** only to show up as the substitution product in Figures 4 and 5. Clearly, the cation radical must have undergone ligand exchange on the CV time scale:

$$(MeCN)_3W(CO)_3^+ + 3\mathbf{L} \rightarrow \mathbf{L}_3W(CO)_3^+ + 3MeCN \quad (21)$$

The catalytic cycle can be completed by electron transfer between the product cation radical and the reactant metal carbonyl, i.e.,

$$\mathbf{L}_3W(CO)_3^+ + (MeCN)_3W(CO)_3 \rightarrow \mathbf{L}_3W(CO)_3 + (MeCN)_3W(CO)_3^+, \text{ etc.} \quad (22)$$

The net effect of eq 21 and 22 is the electrocatalysis of the ligand substitution:

$$(MeCN)_3W(CO)_3 + 3\mathbf{L} \xrightarrow{[E]} \mathbf{L}_3W(CO)_3 + 3MeCN \quad (23)$$

The reversible charge transfer in eq 20 thus constitutes only the initiation step for the catalytic cycle.

The same basic mechanism also pertains to the initial charge transfer in Figure 3a, which is electrochemically irreversible, i.e.,

$$(py)W(CO)_5 \xrightarrow{[E_p]} (py)W(CO)_5^+ + e \quad (24)$$

However short the lifetime of the cation radical in eq 24, it is sufficient to be intercepted by the added ligand **L**. Thus the sequence of steps in eq 25 and 26 can constitute the catalytic cycle

$$(py)W(CO)_5^+ + \mathbf{L} \rightarrow \mathbf{L}W(CO)_5^+ + py \quad (25)$$

$$\mathbf{L}W(CO)_5^+ + (py)W(CO)_5 \rightarrow \mathbf{L}W(CO)_5 + (py)W(CO)_5^+, \text{ etc.} \quad (26)$$

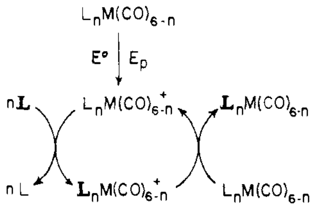
for the ligand substitution in eq 27.

$$(py)W(CO)_5 + \mathbf{L} \xrightarrow{[E]} \mathbf{L}W(CO)_5 + py \quad (27)$$

In both systems, the rate of chain initiation is determined by the electrode potential $E°$ or E_p applicable to the metal carbonyls, as listed in Table II or III. In other words, for a particular system, electrocatalysis is critically tuned by the electrode potential of the metal carbonyl.

Chain Mechanism for Ligand Substitution. The mechanism for electrocatalysis is schematically represented by the catalytic cycle in Scheme II. This formulation underscores the equivalence between electrode-assisted and chemically induced methods for the initiation of the ligand substitution, particularly of those processes with long kinetic chain lengths. We hasten to add that the reduction potentials of the product are more positive than the potential $E°$ or E_p at which electrocatalysis is effectively initiated. Accordingly, it is also posssible (and quite likely) for the catalytic cycle to be completed by electron transfer at the electrode potential $E°$ or E_p, i.e.,

Scheme II



$$\mathbf{L}_nM(CO)_{6-n}^+ + e \xrightarrow{[E]} \mathbf{L}_nM(CO)_{6-n} \quad (28)$$

Such an electrode process will be particularly beneficial for ligand substitutions in Scheme II with short kinetic chain lengths. In this regard, electrocatalysis of ligand substitution is unique, and cannot be easily replaced by an equivalent chemical method.

It follows from the mechanistic formulation in Scheme II that the efficiency of the catalytic cycle is determined primarily by the ligand substitution of the cation radical, i.e.

$$L_nM(CO)_{6-n}^+ + n\mathbf{L} \rightarrow \mathbf{L}_nM(CO)_{6-n}^+ + nL \quad (29)$$

First, the rate of the substitution in eq 29 must be rapid in relationship to other competing modes of decomposition of the cation radical, especially the transient ones. Second, the electrode potential of the substitution product $\mathbf{L}_nM(CO)_{6-n}$ should be more positive than that of the reactant $L_nM(CO)_{6-n}$ in order to provide adequate driving force for the substitution. Results obtained from independent experiments indeed support both of these criteria.

Substitution Lability of Cation Radicals. There is ample precedence in the extant literature[36] for the lability of odd-electron species toward substitution to exceed that of their diamagnetic precursors in a large number of organometallic systems. In studies more germane to metal carbonyls, Pletcher and co-workers[14,37] found the cation radical $Cr(CO)_6^+$ to be substantially more persistent in the trifluoroacetic acid than in the more nucleophilic acetonitrile. Furthermore, the substitution of CO ligands by phosphines and phosphites is accelerated in several cobalt and iron carbonyl complexes upon one-electron reduction.[38] The cyclic voltammetric data presented by Rieger et al. in the latter study indicated rapid substitution in the anion radical. As odd-electron intermediates, carbonylmetal ion radicals are related to the uncharged 17-electron species that have been identified as the substitution-labile species in a number of reported ligand exchanges.[39] The radical produced by the reversible homolytic scission of the Mn–Mn bond is responsible for ligand exchange in $[Ph_3PMn(CO)_4]_2$.[40–43] In a series of elegant studies, Brown and co-workers[44–47] have demonstrated the chain substitution of $HMn(CO)_5$, where M = Re, Mn, to form $HMn(CO)_4L$ via the paramagnetic $Mn(CO)_5$. Similarly substitution of $HM(CO)_3Cp$, where M = Mo, W, involves the analogous radicals $M(CO)_3Cp$.[48] Furthermore, the radical $Co(CO)_4$ is the substitution-labile species in the chain reactions of $Cl_3SnCo(CO)_4$ and $Co_2(CO)_8$ with L = phosphines and arsines to form $[Co(CO)_3L_2]^+SnCl_3^-$ and

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(36) For some leading references, see: Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(37) Pickett, C. J.; Pletcher, D. *J. Chem. Soc., Dalton Trans.* **1976**, 636.

(38) Bezems, G. J.; Rieger, P. H.; Visco, S. *J. Chem. Soc., Chem. Commun.* **1981**, 265.

(39) See ref 36, p 184 ff, for a recent summary.

(40) Dewitt, D. G.; Fawcett, J. P.; Pöe, A. *J. Chem. Soc., Dalton Trans.* **1976**, 528.

(41) Fawcett, J. P.; Jackson, R. A.; Pöe, A. *J. Chem. Soc., Chem. Commun.* **1975**, 733.

(42) Fawcett, J. P.; Pöe, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1302.

(43) Fawcett, J. P.; Pöe, A.; Twigg, M. V. *J. Organomet. Chem.* **1973**, *51*, C17.

(44) Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095.

(45) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 947.

(46) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527.

(47) Byers, B. H.; Brown, T. L. *J. Organomet. Chem.* **1977**, *127*, 181.

(48) Hoffman, H. W.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 613.

$[LCo(CO)_3]_2$, respectively.[49,50]

The driving force for the ligand exchange between cation radicals in eq 29 is largely determined by the relative stabilities of the cation radicals.[35] Such thermochemical measurements are presently unavailable. Nonetheless, a qualitative indication of the driving force can be deduced from the electron-transfer equilibria in eq 17–19. Thus the largest driving force for ligand exchange is expected between pairs of metal carbonyls with the largest difference in $E°$ or E_p. Such systems are represented in this study by the conversion of tris(acetonitrile) complexes of tungsten and molybdenum to the tris(phosphine) derivatives. Indeed, the highest turnover numbers reported in Table I correspond to such ligand substitutions. The substitution processes in these systems are so facile as to exchange all three acetonitrile ligands in rapid succession. By contrast, the ligand substitution of the bis(acetonitrile) complex $(MeCN)_2W(CO)_4$ can be interrupted at an intermediate state of exchange with phosphine. It is noteworthy that the anodic E_p of the half-substituted $(MeCN)(Ph_3P)W(CO)_4$ differs from that of the disubstituted product $(Ph_3P)_2W(CO)_4$ by only 0.1 V.[51] It follows from the same line of reasoning that electrocatalysis will not occur if E_p of the product is less than that of the reactant, even though the overall ligand substitution may be favored. For example, let us consider the electrocatalysis of the reaction between the norbornadiene (NB) complex of tungsten carbonyl and acetonitrile.

$$(NB)W(CO)_4 + 2MeCN \rightarrow (MeCN)_2W(CO)_4 + NB \tag{30}$$

Although ligand exchange as written in eq 30 is thermodynamically favorable, the anodic peak potential $E_p = 0.58$ V of the product $(MeCN)_2W(CO)_4$ is actually less than the E_p of $(NB)_2W(CO)_4$ (0.92 V). Thus the absence of electrocatalysis for eq 30, even after prolonged passage of current through the solution, is not surprising. The microscopic reverse process for eq 30 is contrathermodynamic. In accord with expectations, the cyclic voltammogram of $(MeCN)_2W(CO)_4$ is unaffected by the presence of added norbornadiene, despite its less positive E_p relative to that of $(NB)_2W(CO)_4$.

Mechanism of Ligand Exchange in Cation Radicals. Although the driving force for exchange of metal carbonyl cation radicals can provide a measure of the electrocatalytic efficiency, it sheds no light on the mechanism of the exchange step itself. The two principal mechanisms, which are related to those described in Scheme I for the neutral precursor, merit some consideration.

Ligand substitution of the cation radical by the direct S_N2 displacement is an associative process. As such, it proceeds via a 19-electron intermediate or transition state, e.g.,

$$LM(CO)_5^+ + \mathbf{L} \rightarrow [\mathbf{L}LM(CO)_5^+] \rightarrow \mathbf{L}M(CO)_5 + L \tag{31}$$

The alternative 2-step, dissociative mechanism involves the loss of ligand L to afford the 15-electron cation prior to reaction with the added nucleophile.

$$LM(CO)_5^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M(CO)_5^+ + L \tag{32}$$

$$M(CO)_5^+ + \mathbf{L} \xrightarrow{k_2} \mathbf{L}M(CO)_5^+ \tag{33}$$

Cyclic voltammetric studies show that the oxidation of the tris(acetonitrile) complexes of both tungsten and molybdenum is electrochemically reversible at sweep rates as high as 10 V s^{-1}. Such measurements do not exclude the dissociative mechanism in eq 32 and 33, but they do place a lower limit on the rate constant k_1 for the dissociation in eq 32.[52] Pending the quantitative evaluation of k_1, we are unable at this juncture to rigorously establish either mechanism. It is worth noting, however, that the bis(acetonitrile) and tris(acetonitrile) complexes of chromium are inert to phosphine substitution upon electrocatalysis, despite the favorable values of their reduction potentials. Such an observation would qualitatively accord with the associative mechanism, in which the 19-electron intermediate or transition state would be disfavored owing to steric limitations at the chromium center.[53]

Catalytic Electrochemical Oxidation of Triphenylphosphine. The electrochemical oxidation of phosphines catalyzed by metal carbonyls also relates to the participation of cation radicals in electron-transfer equilibria. For example, the change in the reversible cyclic voltammogram of $(py)Cr(CO)_5$ upon the addition of Ph_3P in Figure 6 results from the electron transfer in eq 34.

$$(py)Cr(CO)_5^+ + Ph_3P \rightarrow (py)Cr(CO)_5 + Ph_3P^+ \tag{34}$$

Since this oxidation occurs at a potential $E° = 0.75$ V, which is substantially less than that ($E_p = 1.3$ V) at which Ph_3P alone is readily oxidized, it contributes overall to an enhanced anodic process, i.e.

$$Ph_3P \xrightarrow{[E°]} Ph_3P^+ + e \tag{35}$$

Products derived from the phosphine cation radical have been described earlier.[54] It is noteworthy that *tert*-butyl isocyanide (with a relatively large positive E_p of 2.13 V) did not affect the cyclic voltammogram of $(MeCN)Cr(CO)_5$.

The enhanced oxidation of triphenylphosphine depends on the facility of the electron-transfer step in eq 34, which appears to be endergonic at first sight. Such an electron transfer is possible, however, if it proceeded via an inner-sphere mechanism.[55] Indeed the utilization of the latter may provide the mechanistic basis for a general class of enhanced electrode processes, which we hope further studies will provide.

Summary and Conclusion

The one-electron oxidation of metal carbonyls in the presence of nucleophiles leads to an enhanced rate of ligand substitution. The chain process can be initiated electrochemically and deliberately inhibited by reversing the flow of current. The electrocatalytic process involves the concurrence of three vital steps, viz., electron-transfer initiation

$$LM \rightarrow LM^+ + e$$

with the two reactions in the propagation cycle

$$LM^+ + \mathbf{L} \rightarrow \mathbf{LM}^+ + L$$

$$\mathbf{LM}^+ + LM \rightarrow \mathbf{LM} + LM^+, \text{ etc.}$$

where LM and **LM** refer to the metal complex and its substitution product, respectively.

The role of the cation radicals LM^+ and LM^+ as prime intermediates is demonstrated by the cyclic voltammetric studies in Figures 3–5. As such, the reduction potential of LM determines the rate of initiation at a given applied potential. The efficiencies of both steps in the propagation cycle are also determined in large part by the relative reduction potentials of LM and **LM** or by the anodic CV peak potentials for irreversible systems. The rate of ligand substitution of the cation radicals LM^+ by nucleophiles **L** represents an important aspect of the chain process. As odd-electron intermediates, they are indeed related to a variety of other labile 17-electron radicals.

The electrochemical syntheses of metal carbonyl complexes described in this study are catalytic. There are other electrochemical procedures for the synthesis of metal carbonyls. For

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(50) See also: Fabian, B. D.; Labinger, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 2239.

(51) See Table III.

(52) Actually, it requires that the quantity $(k_1/k_{-1})[(v/26)/(k_1 + k_{-1})]^{1/2}$ be less than ~0.1, where v is the scan rate in mV s^{-1} (see ref 24).

(53) However, it should be noted that the rates of isomerization for both the 17- and 18-electron analogues of $M(CO)_2(P\text{-}P)_2$ follow the order Cr < Mo < W. In this series, chromium is the most kinetically inert carbonylmetal complex, and the isomerization of the 17-electron is faster than that of the 18-electron counterpart. See: Bond, A. M.; Grabaric, B. S.; Jackowski, J. J. *Inorg. Chem.* **1978**, *17*, 2153 and related papers.

(54) For a detailed description of the complex mixture of products derived from Ph_3P^+, see: Schiavon, G.; Zecchin, S.; Cogoni, G.; Bontempelli, G. *Electroanal. Chem. Interfac. Electrochem.* **1973**, *48*, 425.

(55) (a) See: Fukuzumi, S.; Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2928 for the energetics of inner-sphere electron transfer. (b) Alternatively, a significant overpotential may be responsible for the large value of E_p for triphenylphosphine.

example, the cathodic reduction of various transition-metal salts of vanadium, chromium, manganese, iron, cobalt, nickel, etc., under a carbon monoxide pressure affords metal carbonyls.[56-60] Likewise, transition-metal anodes under pressurized CO afford metal carbonyls at the cathode.[57-61] The latter method has been applied to the preparation of a variety of phosphine-substituted derivatives of group 6B and iron carbonyls.[58,60] Cathodic reduction of $M(CO)_6$ and $(R_3P)_nM(CO)_{6-n}$ in the presence of amines and phosphines produces substitution products at the anode.[62,63] Whether any of these processes proceed via similar or related chain mechanisms remains to be determined by further studies.

Experimental Section

Materials. Reagent grade acetonitrile was repurified by distillation from calcium hydride, followed by stirring over potassium permanganate and sodium carbonate at room temperature for 24 h. The mixture was filtered, and distilled at reduced pressure. It was then redistilled from phosphorus pentoxide, followed by a final fractional distillation from calcium hydride through a 19-plate bubble cap (Oldershaw) column. The purified solvent was stored under argon. Fisher Spectranalyzed grade acetone and methylene chloride were used without purification. Tetrahydrofuran was distilled from benzophenone ketyl and stored under argon. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium perchlorate (TBAP) were used as received from G. F. Smith Chemical Co. The following compounds were prepared by literature procedures: $(CO)_5Cr(py)$,[64] $(CO)_5Cr(MeCN)$,[65] *cis*-$(CO)_4Cr(MeCN)_2$,[66] $(CO)_5Cr(PPh_3)$,[67] *trans*-$(CO)_4Cr(PPh_3)_2$,[68] *cis*-$(CO)_4Cr(py)_2$,[69] *fac*-$(CO)_3Cr(MeCN)_3$,[70] *cis*-$(CO)_4Mo(py)_2$,[69] *fac*-$(CO)_3Mo(MeCN)_3$,[70] $(CO)_5W(py)$,[64] $(CO)_5W(MeCN)$,[66] $(CO)_5W(PPh_3)$,[67] *cis*-$(CO)_4W(MeCN)_2$,[71] *cis*-$(CO)_4W(py)_2$,[69] $(CO)_5W(t\text{-}BuNC)$,[72] *cis*-$(CO)_4W(t\text{-}BuNC)_2$,[72] *fac*-$(CO)_3W(MeCN)_3$,[70] and *trans*-$(CO)_4W(PPh_3)_2$.[68]

Electrochemical Measurements. Electrochemistry was performed with a Princeton Applied Research Model 173 potentiostat equipped with a Model 176 current-to-voltage converter, which provided a feedback compensation for ohmic drop between the working and reference electrodes. The high impedance voltage amplifier (PAR Model 178) was mounted external to the potentiostat to minimize the length of the connection to the reference electrode for low noise pickup. Cyclic voltammetry was performed in a cell of conventional design.[73] The voltammograms were recorded on a Houston Series 2000 X-Y recorder. Bulk coulometry was carried out in a three-compartment cell equipped with two side arms, which permitted sampling and the insertion of a magnetic stir bar. The working electrode consisted of a platinum gauze. Oxidations were performed in the current-controlled mode at 0.5 or 1.0 mA. Substantially less than the diffusion-limited current was desired for the initiation of the chain reactions. In a few examples, electrode passivation was encountered during oxidation (the potential rapidly rose to approximately 2.0 V). This problem was remedied by briefly applying a reducing potential at 10 mA.

Control Reactions. In all cases, no substitution reaction was observed in the absence of anodic oxidation, provided the following precautions were observed. A solution of the carbonylmetal substrate in MeCN containing 0.1 M TEAP was reduced under an argon atmosphere at −0.5 V vs. SCE in the electrolysis cell prior to introduction of the added ligand. The current was allowed to flow for approximately 30 min, during which time it decayed from approximately 10 mA to ~10 μA, as the trace impurities were reduced. The phosphine or isocyanide was added while the reducing potential was maintained. No substitution occurred (as indicated by the infrared spectrum) for at least 1.5 times the duration of the oxidation-induced reaction.

Reactions of $(CO)_5CrL$ and $(CO)_5WL$ with PPh_3 (L = py, MeCN). Pentacarbonyl(pyridine)chromium (17 mg, 0.064 mmol) was dissolved in approximately 9 mL of argon-purged MeCN containing 0.1 M TEAP and triphenylphosphine (160 mg, 0.61 mmol). An oxidizing current of 1 mA was passed through the solution for 6470 s. The anolyte was diluted to 15 mL with a solution of MeCN containing 0.1 M TEAP and analyzed by quantitative IR spectrophotometry. The only carbonyl species present was $(CO)_5Cr(py)$ (0.058 mmol, 90% recovery), which exhibited strong absorptions at 1930 and 1870 cm^{-1}. The yields based on the IR analysis were accurate to within ±5–10% and were determined with molar absorptivities evaluated with standards prepared at concentrations comparable to the diluted anolyte.

The controlled-potential electrolysis at 0.69 V of a mixture of pentacarboxyl(pyridine)chromium (25 mg, 0.092 mmol), triphenylphosphine (150 mg, 0.57 mmol), and 0.1 M TEAP in 7 mL of MeCN proceeded with an initial current of ~20 mA. (In the absence of the chromium complex, less than 0.2 mA could be passed through the solution at the same potential. The latter indicated that the direct oxidation of phosphine at this electrode potential is negligible.) The progress of the electrolysis was monitored by cyclic voltammetry and by gas chromatography on a Varian Model 3700 FID chromatograph. Aliquots (0.20 mL) were removed and diluted with a solution (0.20 mL) of 0.013 M bibenzyl. The analysis for triphenylphosphine was carried out on a $^1/_8$ × 2 ft stainless steel column containing Chromosorb W with no liquid phase. Temperature programming was carried out at 45 °C min^{-1} between 100 and 260 °C. After 2200 s, more than 80% of the triphenylphosphine had disappeared. The analysis of the unreacted pentacarbonyl(pyridine)chromium was effected by quantitative IR spectrophotometry. Despite sampling losses, 87% of the chromium carbonyl was accounted for. A minute absorption at 2062 cm^{-1} may be attributed to $(CO)_5Cr(PPh_3)$, which places an upper limit of an 11% yield on this product.

The reaction between $(CO)_5W(py)$ and PPh_3 was performed in a similar manner. After passage of current corresponding to 1.06 faradays mol^{-1} of the tungsten complex, both the starting material (29%) and $(CO)_5WPPh_3$ (69%) were observed by IR analysis. Since the absorptions overlapped extensively, the yields were obtained by evaluating the absorptions at 1933 and 1893 cm^{-1} and using the equations

$$A^{1933} = (\epsilon b_{\text{W-py}}{}^{1933})[\text{W–py}] + (\epsilon b_{\text{W-PPh}_3}{}^{1933})[\text{W–PPh}_3]$$

$$A^{1893} = (\epsilon b_{\text{W-py}}{}^{1893})[\text{W–py}] + (\epsilon b_{\text{W-PPh}_3}{}^{1893})[\text{W–PPh}_3]$$

where ϵb = molar absorptivity times the optical path length of the IR cell.

Similarly, the reaction between *t*-BuNC and $(CO)_5W(py)$ was performed with a passage of 1 mA (corresponding to 0.47 faradays mol^{-1} on the basis of the tungsten complex). The substitution product $(CO)_5W(t\text{-}BuNC)$ was formed in 64% yield, and 28% of the starting tungsten complex was recovered. Since the absorption bands of these compounds overlapped, the IR spectrophotometric yields were obtained in a fashion analogous to that described above for the reaction of PPh_3 with $(CO)_5W(py)$. The absorbances at 1948 and 1892 cm^{-1} were employed.

The oxidation of a solution containing $(CO)_5W(MeCN)$ (36 mg, 0.098 mmol) and triphenylphosphine (50 mg, 0.19 mmol) commenced at 0.45 V vs. SCE. The electrode potential increased sharply to 0.8 V after 1500 s. The starting complex was completely consumed, and the spectrophotometric yield of $(CO)_5W(PPh_3)$ was 98%.

Reaction of *cis*-$(CO)_4WL_2$ with PPh_3 (L = MeCN, py). The bis(acetonitrile)tungsten complex (39 mg, 0.1 mmol) and triphenylphosphine (150 mg, 0.57 mmol) reacted to form *cis*-$(MeCN)(PPh_3)W(CO)_4$ quantitatively upon oxidation at 0.5 mA for 900 s. (The potential rose from 0.2 to 0.4 V.) The potential increased to 0.7 V after oxidation for an additional 1500 s. IR spectroscopy showed that the monophosphine complex had been consumed. During the latter part of the oxidation, $(PPh_3)W(CO)_4$ precipitated from solution as light yellow microcrystals (60 mg, 71% yield). The product consisted predominantly of the trans isomer, as revealed by the comparison of the IR spectrum

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with that of an authentic sample. (A single strong absorption was observed at 1890 cm^{-1} in $CHCl_3$.) The monophosphine complex was conveniently isolated after a mixture of 0.32 mmol of $(CO)_4W(MeCN)_2$ and 0.32 mmol of triphenylphosphine was electrolyzed for 600 s at 1 mA. The yield of *cis*-$(MeCN)(PPh_3)W(CO)_4$ was 102% by IR analysis. The product precipitated as yellow microcrystals upon the addition of deoxygenated water (0.16 g, 84% yield). It was recrystallized from a mixture of CH_2Cl_2 and hexane to afford 0.12 g of lustrous needles. The IR and ^1H NMR spectra were in agreement with the published spectra.[74]

The reaction between equimolar amounts (0.16 mmol) of *cis*-$(py)_2W(CO)_4$ and PPh_3 was performed similarly. It afforded a 98% yield of *cis*-$(py)(PPh_3)W(CO)_4$ by IR analysis. Precipitation with water gave a bright yellow product in 68% yield. It was characterized by its IR spectrum.[30c] The reaction of *cis*-$(py)_2W(CO)_4$ (66 mg, 0.14 mmol) with excess PPh_3 (79 mg, 0.3 mmol) gave *cis*-$(py)(PPh_3)W(CO)_4$ quantitatively after electrolysis for 1200 s at 1 mA. The IR spectrum showed that no further substitution occurred after 4200 s of additional oxidation. No $(PPh_3)_2W(CO)_4$ was formed.

Reactions of *cis*-$(CO)_4W(MeCN)_2$, *fac*-$(CO)_3W(MeCN)_3$, and *cis*-$(CO)_4Mo(py)_2$ with *t*-BuNC. The reaction of *cis*-$(CO)_4W(MeCN)_2$ (53 mg, 0.14 mmol) with excess *t*-BuNC (29 mg, 0.35 mmol) required electrolysis for 1800 s at 1 mA. It afforded, after precipitation with water, 53 mg (84% yield) of *cis*-$(t\text{-}BuNC)_2W(CO)_4$ as a cream-colored solid. The IR spectrum of the product was identical with that of the authentic compound prepared independently.

Excess *t*-BuNC (80 mg, 0.96 mmol) and *fac*-$(CO)_3W(MeCN)_3$ (61 mg, 0.16 mmol) reacted with complete substitution of the acetonitrile ligand (87%, IR yield). The substitution required oxidation for 2000 s at 0.5 mA. The product *fac*-$(CO)_3W(t\text{-}BuNC)_3$ was isolated in 68% yield by precipitation with water as a yellow solid. The IR spectrum was identical with that reported previously.[9]

Reaction of *cis*-$(py)_2Mo(CO)_4$ (51 mg, 0.14 mmol) and *t*-BuNC (46 mg, 0.55 mmol) afforded an 80% yield by IR analysis of *cis*-$(t\text{-}BuNC)_2Mo(CO)_4$. The electrolysis required 2600 s at 1 mA. The product was isolated (35 mg, 67%) by precipitation with water and identified by comparison of the IR spectrum with the published spectrum.[9]

Reaction of *fac*-$(CO)_3Mo(MeCN)_3$ with PPh_3. Triphenylphosphine (300 mg, 1.1 mmol) was added, under an argon backflush, to a solution of the subject molybdenum carbonyl (42 mg, 0.14 mmol) in 10 mL of MeCN containing 0.1 M TEAP which was "stabilized" with a reducing current. No reaction was apparent after 1 h. This system could not be monitored readily by IR analysis since the substitution occurred readily in the solution cell. A short application of an oxidizing current (120 s at 1 mA) induced the complete precipitation of the product which is quite insoluble in MeCN. Anal. Calcd for $(CH_3CN)_{1.5}[(C_6H_5)_3P]_{1.5}Mo(CO)_3$: C, 62.4; H, 4.3; P, 7.3. Found: C, 61.5; H, 4.5; P, 7.2.

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Registry No. *fac*-$(MeCN)_3W(CO)_3$, 30958-95-3; *fac*-$(MeCN)_3Mo(CO)_3$, 17731-95-2; *cis*-$(py)_2Mo(CO)_4$, 16742-99-7; *cis*-$(py)_2W(CO)_4$, 16743-01-4; *cis*-$(MeCN)_2W(CO)_4$, 29890-10-6; $(MeCN)W(CO)_5$, 15096-68-1; $(py)W(CO)_5$, 14586-49-3; $(MeCN)_{c}r(CO)_5$, 15228-38-3; $(py)Cr(CO)_5$, 14740-77-3; $(Ph_3P)Cr(CO)_5$, 14917-12-5; *trans*-$(Ph_3P)_2Cr(CO)_4$, 38800-75-8; *cis*-$(MeCN)_2Cr(CO)_4$, 29890-09-3; *cis*-$(py)_2Cr(CO)_4$, 24354-36-7; *fac*-$(MeCN)_3Cr(CO)_3$, 22736-49-8; *cis*-$(t\text{-}BuNC)_2W(CO)_4$, 42401-92-3; *fac*-$(t\text{-}BuNC)_3W(CO)_3$, 42401-95-6; $(Ph_3P)W(CO)_5$, 15444-65-2; $(t\text{-}BuNC)W(CO)_5$, 42401-89-8; *trans*-$(Ph_3P)_2W(CO)_4$, 16743-03-6; *cis*-$(Ph_3P)(py)W(CO)_4$, 38496-28-5; *cis*-$(Ph_3P)(MeCN)W(CO)_4$, 18078-18-7; *cis*-$(t\text{-}BuNC)_2Mo(CO)_4$, 37584-08-0.

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Matrix Infrared Spectrum of the H_3N--HF Hydrogen-Bonded Complex

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Abstract: Codeposition of Ar/NH_3 and Ar/HF samples at 12 K produced new absorptions at 3401, 1920, 1679, 1093, and 916 cm^{-1}, which are due to reaction products. Concentration studies and evaporation from solid NH_4HF_2 identify the 1920-cm^{-1} absorption as due to a 1:2 complex ammonium bifluoride species and the other four product bands as the 1:1 hydrogen-bonded complex. Isotopic substitution (DF, $^{15}NH_3$, ND_3) supports assignment of the 3041- and 916-cm^{-1} bands to the ν_s stretching and ν_l librational motions of the HF submolecule in the complex and the 1679- and 1093-cm^{-1} bands to the ν_4^c and ν_2^c vibrations of the NH_3 submolecule in the complex, respectively. The argon-to-nitrogen matrix shift in ν_s for the H_3N--HF complex shows that the complex is relatively polar, in agreement with theoretical calculations.

Hydrogen bonding is an important phenomenon in many biological and chemical systems and has been studied a great deal by experimental and theoretical methods.[1,2] Hydrogen fluoride is useful in the study of hydrogen bonding because it forms strong hydrogen bonds and HF and DF are straightforward to synthesize; in addition HF complexes give simple vibrational spectra and are light enough for meaningful theoretical work. Studies of HF complexes with the π systems of acetylene and ethylene in solid argon have produced strong stretching modes at 3747 and 3732 cm^{-1} for the HF submolecule in the complex (ν_s).[3] The shift in ν_s from the H–F value, $\Delta\nu_s$, is a useful indicator of the strength of the hydrogen bond, and a study of complexes between HF and methyl-substituted amines has demonstrated a linear correlation between the proton affinity of the base and the shift of the HF stretching fundamental for these complexes.[4]

The purpose of this study is to characterize the 1:1 complex between hydrogen fluoride and ammonia in solid argon by its infrared spectrum. Infrared spectra of ammonia in inert gas matrices have been thoroughly investigated,[5,6] and a complex between ammonia and hydrogen chloride has been identified in solid nitrogen.[7] The ammonia–hydrogen fluoride complex has

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