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15 Years of Reductive Coupling: What Have We Learned?

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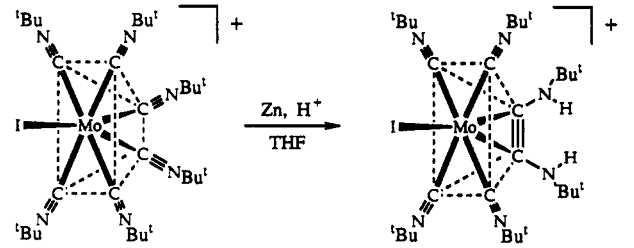
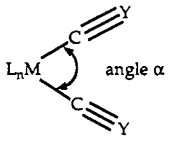
"...The molecular geometry is very similar to that of the starting $[(RNC)_6MoI]^+$ cation with one major difference. In the product there is a bond between the two carbon atoms on the edge opposite the capped face." [1]



The chemical transformation shown above was unexpected. Our previous studies of the structure and reactivity of high-coordinate transition metal complexes had afforded synthetic routes to seven-coordinate alkyl isocyanide complexes of Mo(II) and W(II).[2] An attempt to reduce $[Mo(CNBu^t)_6I]^+$ to the homoleptic molybdenum(0) species $[Mo(CNBu^t)_6]$ resulted instead in the isolation of a dark red product, $[Mo(^tBuHNC{\equiv}CNHBu^t)(CNBu^t)_4I]^+$. This complex proved to be structurally similar to the starting material except that two isocyanide ligands had been coupled reductively to form a bis(alkylamino)acetylene ligand.[1] Since our interest in the chemistry of high-coordinate transition metal species was fueled in part by the expectation of unusual chemical reactivity, we were delighted with the result. In particular, it seemed possible that the newly discovered reductive coupling reaction might have been the consequence of just such a "high coordination effect". A simple explanation for the unusual reactivity was that an increase in coordination number above 6 diminished the C–M–C angle (α) and the nonbonded C···C distance between adjacent linear ligands (see drawing), thus promoting C–C bond formation. This explanation was especially appealing since, as our results were being written for publication, we received a preprint of a manuscript from colleagues at Cornell reporting calculations which demonstrated that a small, positive orbital overlap population existed between adjacent carbon atoms of the ligands on the unique edge of the capped trigonal prism.[3] We speculated that addition of electrons as well as a Lewis acid to stabilize the product, resulted in the coupling of two adjacent ligands.



Angle α and C···C distance decrease as the number of ligands at the metal center increases above six.

The discovery of the isocyanide coupling reaction also suggested the exciting possibility that a similar transformation with CO ligands might be feasible, affording a dihydroxyacetylene complex. The fuel crisis of the 1970s spawned significant research into the selective conversion of carbon monoxide into C_2 oxygenates. We therefore wondered whether high-coordinate transition metal complexes might be good catalysts for the conversion of CO into ethylene glycol precursors. In order to pursue this possibility, we decided to explore the reaction system thoroughly. Our goals included (1) discovering the factors that promoted the isocyanide coupling reaction; (2) extending the coupling to other early transition metals and unsaturated linear ligand combinations, especially two CO molecules; and (3) elucidating the reaction mechanism and determining what role, if any, high coordination numbers played in forming the new C–C bond.[4]

Subsequent research along these lines has met most of these objectives. Carbonyl coupling was accomplished, as well as cross coupling of CO with CNR. The mechanistic details of these reactions have been elucidated by isolating and characterizing intermediates in the coupling reaction sequence as well as by investigating the kinetics of the critical C–C bond-forming step. The factors promoting these reactions have now largely been elucidated. In hindsight, we see that several details of the initially surprising isocyanide coupling reaction can be understood by applying the principles that govern many other reactions in organometallic chemistry, principles which themselves were evolving during the course of our work. Our goal in this Account, however, is to give the reader a sense of the historical development of the chemistry. As the story unfolds, we hope the reader will share our pleasure in the discovery of the fascinating intermediate complexes, including highly reduced organometallic and

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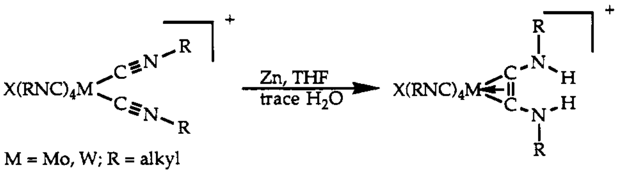
electron-rich heterocarbyne species, and of unprecedented ligands such as coordinated dihydroxyacetylene. Pinpointing the factors involved in the actual C–C bond-forming step has proven to be surprisingly difficult. Like so many questions of mechanism, we find in the end that we may never know the complete answer. It is certain, however, that the truth is more complicated, and far more interesting, than we first surmised 15 years ago.

Scope of the Isocyanide Reductive Coupling Reaction. The reductive coupling of isocyanide ligands at seven-coordinate molybdenum(II) and tungsten(II) centers proved to be relatively general. Conversion of two isocyanide ligands into a bis(alkylamino)acetylene functionality was readily effected by heating a solution of $[M(CNR)_6X]^+$ (M = Mo, R = alkyl, X = halide or cyanide; M = W, R = Bu^t) and zinc metal in THF containing a trace amount of water (eq 1).[5] Two



(1)

M = Mo, W; R = alkyl
X = halide or CN⁻

isocyanide ligands in the homoleptic $[Mo(CNBu^t)_7]^{2+}$ cation could also be reductively coupled, but the reaction required a prior dealkylation step (eq 2).[6] Seven-coordinate molybdenum(II) complexes containing bipyridine or phosphine as well as isocyanide ligands also underwent the coupling reaction.[7,8]

$$[Mo(CNBu^t)_7]^{2+} \xrightarrow{\Delta} [Mo(CNBu^t)_6(CN)]^+ \xrightarrow[\text{trace } H_2O]{\text{Zn, THF}} [Mo(^tBuHNC{\equiv}CNHBu^t)(CNBu^t)_4(CN)]^+ \quad (2)$$

Perhaps even more instructive were complexes where no coupling reactions were observed. Lower-coordinate, low-valent complexes such as $[Fe(CNR)_5]$ and $[Pt(CNR)_4]$ failed to undergo reductive coupling reactions when subjected to the conditions shown in eq 1.[5,9,10] Attempts to couple the more electron deficient aryl isocyanide ligands in $[Mo(CNAr)_6X]X$ also failed. Indeed, the formation of $[Mo(RHNC{\equiv}CNHR)(CNR)_4X]X$ was found to be directly related to the ease of electrochemical oxidation of the precursor complexes.[11] This knowledge allowed us to understand why dealkylation was required for the chemistry shown in eq 2, since the cyanide complex $[Mo(CNBu^t)_6(CN)]^+$ is oxidized at a potential 530 mV less positive than $[Mo(CNBu^t)_7]^{2+}$.[11]

Attempts to extend the reaction to more electropositive metal centers, such as $[M(CNBu^t)_6X]^{2+}$ (M = Tc, Re), resulted only in reduction of the metal complex (eq 3).[12] Furthermore, when $[ReCl_2(PMePh_2)_2(CNBu^t)_3]^+$ was treated in a similar manner, a six-coordinate aminocarbyne complex was isolated (eq 4).[13,14] These

$$\underset{M = Tc,\ Re}{[M(CNBu^t)_6X]^{2+}} \xrightarrow[\text{trace } H_2O]{\text{Zn, THF}} [M(CNBu^t)_6]^+ \quad (3)$$

$$[Re(CNBu^t)_3(PMePh_2)_2Cl_2]^+ + Zn \xrightarrow[\text{trace } H_2O]{\text{THF}} [Re({\equiv}CNHBu^t)(CNBu^t)_2(PMePh_2)_2Cl]^+ \quad (4)$$

reactions were initially thought to be competing pathways which prevented ligand coupling. We soon realized, however, that they were instead early indications of the true reductive coupling pathway.

At this point in our studies, although we did not know the mechanism of the reaction, we had sufficient information to formulate some working hypotheses. The geometric similarity between the starting complexes and the products suggested that precursors with seven-coordinate, capped trigonal prismatic geometries might be the best candidates for reductive coupling. The failure of lower-coordinate species to undergo similar coupling reactions supported this concept of a high coordinate effect, as did theoretical considerations.[15] A low-valent transition metal species was deemed necessary, as evidenced by the failure to couple ligands in more highly oxidized complexes. Finally, the presence of a Lewis acid, or electrophile, was believed to be necessary to facilitate isolation of a stable coupled product. The true meaning of these early empirical observations eventually unfolded, as detailed below, in large measure due to the extension of this chemistry to achieve the coupling of the isoelectronic substrate, carbon monoxide.

Discovery of the CO Coupling Reaction. With some understanding of the factors that promoted reductive coupling of two isocyanide ligands, the process of extending the coupling reaction to two CO molecules was made considerably easier. In particular, we were able to eliminate the vast majority of transition metal carbonyl complexes as unlikely to undergo the coupling reaction. After an initial and unsuccessful foray into group VI carbonyl systems, we concentrated our efforts on the $[M(CO)_2(dmpe)_2Cl]$ (M = Nb, Ta) complexes,[16] for they, of all the metal carbonyl complexes known at the time, most closely met our requirements as governed by the empirical observations listed above. More reducing reaction conditions were employed, which required a corresponding change in Lewis acid in order to avoid hydrogen formation. Lewis acids that form strong bonds with oxygen were introduced in order to help stabilize the final product.

The initial breakthrough came as a result of the reactions shown in eq 5. Addition of Mg and a metallocene dichloride, added because of its oxyphilicity, to $[Ta(CO)_2(dmpe)_2Cl]$, followed by addition of Me_3SiCl, resulted in reductive coupling of two CO

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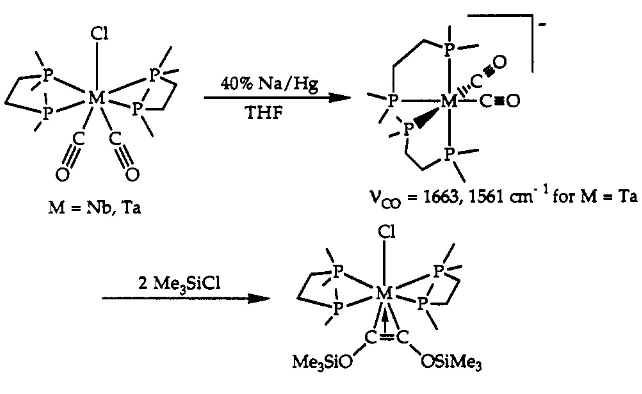
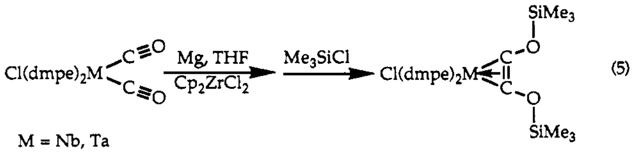
Scheme I. $Na[M(CO)_2(dmpe)_2]$ (M = Nb, Ta) Complexes Are Intermediates in the Reductive Coupling of Two CO Ligands in Seven-Coordinate $[M(CO)_2(dmpe)_2Cl]$ Complexes



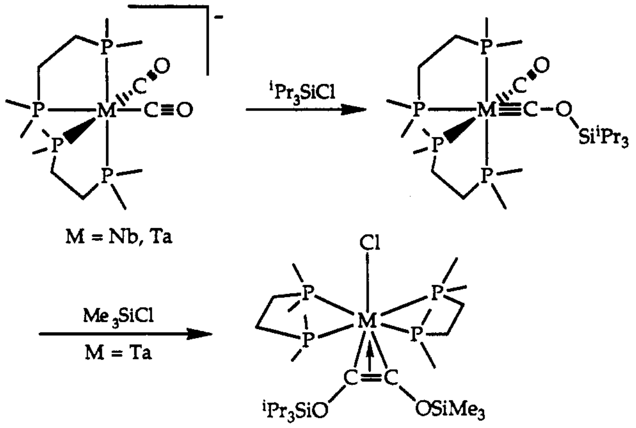
ligands to form a bis(trimethylsiloxy)acetylene complex (eq 5).[17,18] It soon became evident that the metallocene was unnecessary when a different reducing agent was employed (vide infra). The successful conversion of two carbonyl ligands into the unprecedented bis(trimethylsiloxy)acetylene ligand strengthened our belief that these unusual coupling reactions were promoted by high-coordinate transition metal complexes. Similar coupling reactions had not been observed for lower-coordinate species, and we carefully chose the capped trigonal prismatic precursor complex to fit our structural requirements. In order to examine the possible role of high coordination number on the reductive coupling reactions and to analyze the detailed steps in the reaction mechanism, it was first necessary to simplify the complex reaction mixtures.



(5)

Carbonyl Coupling as a Series of Discrete Reactions. Addition of Mg to $[M(CO)_2(dmpe)_2Cl]$ did not produce any observable reaction. The metallocene dihalide was thus serving a minimal function as an electron-transfer carrier. Substitution of 40% Na/Hg for the Mg/metallocene dihalide mixture, however, resulted in a two-electron reduction, with concomitant loss of the capping halide ligand, forming $Na[M(CO)_2(dmpe)_2]$ (Scheme I).[18] The low-frequency $C{\equiv}O$ modes in the infrared spectra of these metal(I–) complexes revealed them to carry significantly more electron density than traditional terminal carbonyl ligands, leading us to believe that the six-coordinate anions might be active participants in the CO coupling reaction. Indeed, addition of 2 equiv of Me_3SiCl to $Na[M(CO)_2(dmpe)_2]$ resulted in formation of the seven-coordinate coupled product (Scheme I).[17] Despite the similarity between the geometries of the coupling precursor and product complexes, we knew at this juncture that the reductive coupling reactions proceeded via six-coordinate intermediates!

Scheme II. Six-Coordinate Carbyne Complexes Are Intermediates in the Reductive Coupling of CO Ligands at $[M(CO)_2(dmpe)_2Cl]$ (M = Nb, Ta) Centers



Once it was established that $Na[M(CO)_2(dmpe)_2]$ could initiate the reductive coupling reaction, we began to investigate the details of how the CO ligands of this six-coordinate species were transformed into a bis(trimethylsiloxy)acetylene entity. Coupling reactions of a carbyne with a cis CO ligand were precedented.[19–22] Although the transformation of a terminal carbonyl ligand into a carbyne by electrophilic attack was unknown at the time, it proved to be the next step in the coupling mechanism. As shown in Scheme II, addition of $^iPr_3SiCl$ to $Na[M(CO)_2(dmpe)_2]$ resulted in formation of a (trialkylsiloxy)carbyne complex.[13] Furthermore, addition of Me_3SiCl to $[Ta(COSi^iPr_3)(CO)(dmpe)_2]$ yielded the asymmetric coupled product $[Ta(^iPr_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl]$ (Scheme II), proving that the six-coordinate carbyne species were on the pathway to reductive coupling.[23] In both the isocyanide and carbonyl reductive coupling reactions, the seven-coordinate precursor and coupled product complexes had similar geometries, differing only in the absence or presence of a bond between the two metal-bound carbon ligands. The reactions shown in Scheme II demonstrated, however, that the CO reductive coupling reaction was not a concerted process mediated by a seven-coordinate transition metal complex. Rather, it comprised a series of discrete steps, two of which involved six-coordinate, octahedral species. The implications of this discovery on the seven-coordinate hypothesis are discussed below. First, however, we need to consider whether analogous six-coordinate intermediates are involved in the isocyanide coupling reaction.

Parallel Studies of the Isocyanide Coupling Reaction. If the sequence of reaction steps for the isocyanide coupling reaction were analogous to those found for CO reductive coupling, several earlier observations could be explained. As already mentioned, attempts to extend the isocyanide coupling reaction to group VII metals resulted only in products corresponding to two-electron reduction of the starting materials (eq 3). We initially believed this reduction to be a competing reaction, but it now seemed likely that the reductive coupling pathway had been entered, but was

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(22) Mayr, A.; Bastos, C. M. *Prog. Inorg. Chem.* **1992**, *40*, 1.

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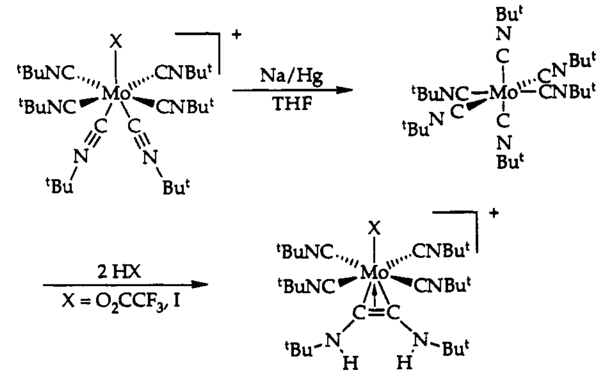
Scheme III. $[Mo(CNBu^t)_6]$ Is an Intermediate in the Reductive Coupling of Isocyanide in $[Mo(CNBu^t)_6X]X$ Complexes



terminated after the first step owing to the thermodynamic stability of the two-electron-reduced product. Presumably, sufficient electron density is not transferred to the nitrogen atoms of isocyanide ligands in $[M(CNBu^t)_6]^+$ (M = Tc, Re) for protonation and formation of the aminocarbyne. Replacement of two isocyanide ligands by electron-donating phosphine ligands would result in increased delocalization of electron density onto the isocyanide ligands, and therefore heightened reactivity with H^+. The isolation of an aminocarbyne complex following treatment of $[ReCl_2(PMePh_2)_2(CNBu^t)_3]^+$ with Zn in refluxing THF supported this view.[13]

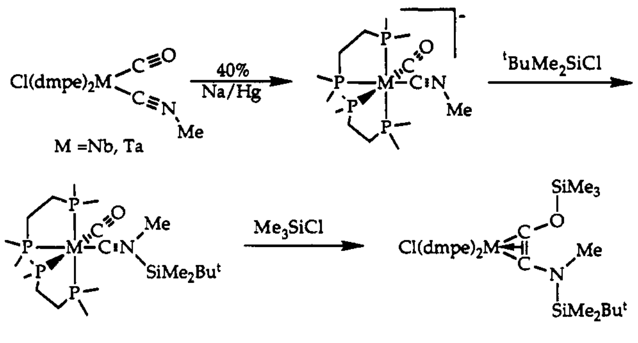
Subsequently, the reductive coupling of isocyanides in $[Mo(CNBu^t)_6I]I$ was indeed found to proceed by a series of discrete reaction steps. Addition of 1% Na/Hg to $[Mo(CNBu^t)_6I]I$ resulted in two-electron reduction to form $[Mo(CNBu^t)_6]$ (Scheme III).[24] Addition of acid to this six-coordinate, electron rich species resulted in the coupling of two isocyanide ligands, forming $[Mo(^tBuHNC{\equiv}CNHBu^t)(CNBu^t)_4X]X$. These results demonstrated that $[Mo(CNBu^t)_6]$, which is isoelectronic with $Na[Nb(CO)_2(dmpe)_2]$, is an intermediate in the isocyanide reductive coupling reaction.

Reaction of low-valent isocyanide complexes with acid to form aminocarbyne species was by this time well precedented.[25,26] We found no evidence of carbyne formation upon addition of acid to $[Mo(CNBu^t)_6]$, however. At low temperature, a complex protonated at both the carbon and nitrogen of one isocyanide ligand was identified.[24] Although this complex isomerized to the coupled product upon warming, we speculated that it was probably the result of a side reaction and that protiocarbyne complexes were too reactive to be isolated in this system. Addition of trialkylsilyl reagents did result in carbyne formation (eq 6), however, consistent

$$[Mo(CNBu^t)_6] + R_3SiOTf \rightarrow [Mo\{{\equiv}CN(Bu^t)(SiR_3)\}(CNBu^t)_5]OTf \quad (6)$$
$$R_3 = Me_3, {}^tBuMe_2$$

with our observations about the carbonyl coupling reaction. In complementary and independent work it was recently shown that addition of acid to (dialkylamino)carbyne complexes results in ligand coupling (eq 7),[27,28] providing additional evidence that aminocarbyne complexes are intermediates in these isocyanide reductive coupling reactions.

Scheme IV. Reductive Coupling of CO with CNR as a Series of Discrete Reactions



$$[Mo({\equiv}CNEt_2)(CNEt)_5]^+ + HI \rightarrow [Mo(Et_2NC{\equiv}CNHEt)(CNEt)_4I]^+ \quad (7)$$

Cross Coupling. Once the sequence of steps that resulted in reductive coupling of CO and CNR ligands was understood, we wished to extend this type of reaction to new ligand combinations. Our first goal was to accomplish the cross coupling of CO with CNR. Such a reaction would construct the unusual ($ROC{\equiv}CNRR'$) acetylene ligand, a framework found in that of amino acids. In addition, development of a successful cross coupling reaction would allow for study of new highly-reduced and carbyne intermediate species, as well as new carbyne coupling reactions. Finally, cross coupling of CO and CNR would intimately link the mechanisms for the two individual CO and CNR coupling reactions.

Cross coupling precursor complexes were prepared by photochemical substitution of CNR for one CO ligand in $[M(CO)_2(dmpe)_2Cl]$ (M = Nb, Ta).[29] When $[M(CNMe)(CO)(dmpe)_2Cl]$ was subjected to our reductive coupling conditions, a new asymmetrically substituted acetylene complex was isolated, as outlined in eq 8.[30] This product was predicted by our coupling

$$\underset{M\,=\,Nb,\,Ta}{[M(CNMe)(CO)(dmpe)_2Cl]} \xrightarrow[Na/Hg]{40\%} \xrightarrow{2Me_3SiCl} [M\{(Me_3Si)(Me)NC{\equiv}COSiMe_3\}(dmpe)_2Cl] \quad (8)$$

reaction sequence, demonstrating the ability to construct doubly functionalized acetylene ligands by this route. Investigation of the reaction mechanism revealed the now familiar series of steps. Reduction of $[Nb(CNMe)(CO)(dmpe)_2Cl]$ formed the six-coordinate Nb(I–) product (Scheme IV).[31] Addition of a trialkylsilyl reagent to this reactive species led to the formation of an aminocarbyne complex, which, upon addition of

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a second equivalent of trialkylsilyl halide, generated the coupled product (Scheme IV).

Hydrocarbons from CO: Reversing the Combustion Process. The above examples detail how CO and CNR ligands can be selectively transformed into functionalized acetylene ligands, one of the principle motivations for studying reductive coupling reactions. Because these reactions proceed in a stepwise manner, the precursor complexes and electrophiles can be chosen to construct other new acetylene ligands. Moreover, unlike reductive coupling reactions mediated by high-valent, early transition metals,[32-34] the heteroatoms of the coupled ligands are not irreversibly bound to a metal. For this reason, chemical modification of the acetylene ligand is possible, as is facile release of the new ligand from the metal with the C–C bond intact. This chemistry is outlined below.

Other New Functionalized Acetylenes. One of our early goals was to achieve the conversion of two CO molecules into a dihydroxyacetylene ligand by a reaction analogous to that which forms the bis(alkylamino)acetylene ligand (eq 1). Although we were unable to achieve this transformation directly, addition of HCl (aqueous) to the bis(trimethylsiloxy)acetylene complex formed by reductive coupling of CO molecules (eq 5) provided us with the first example of a stabilized dihydroxyacetylene complex (eq 9). Note that concomitant oxidation of the tantalum center to form the hydride also occurs in this reaction.

$$[\mathrm{Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl}] + \mathrm{HCl_{aq}} \xrightarrow{\mathrm{THF}} [\mathrm{Ta(H)(HOC{\equiv}COH)(dmpe)_2Cl}]\mathrm{Cl} \quad (9)$$

When 1 equiv of $HBF_4{\cdot}Et_2O$ was added to the carbonyl-coupled product, one of the trialkylsilyl groups was replaced with a BF_3 unit, again accompanied by formation of the metal hydride, eq 10.[35] A complex

$$[\mathrm{Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl}] + \mathrm{HBF_4{\cdot}Et_2O} \xrightarrow{\mathrm{THF}} [\mathrm{Ta(H)(Me_3SiOC{\equiv}COBF_3)(dmpe)_2Cl}] \quad (10)$$

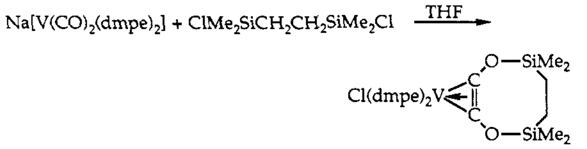
containing the hydroxy(methylamino)acetylene ligand was prepared in an analogous manner by starting with the mixed CO/CNR-coupled product (eq 11).[31] Re-

$$[\mathrm{Ta\{(Me_3Si)(Me)NC{\equiv}COSiMe_3\}(dmpe)_2Cl}] + \mathrm{HCl_{aq}} \xrightarrow{\mathrm{THF}} [\mathrm{Ta(H)(MeHNC{\equiv}COH)(dmpe)_2Cl}]\mathrm{Cl} \quad (11)$$

ductive coupling of two methyl isocyanide ligands using Me_3SiCl as the Lewis acid allowed for isolation of a bis{(trimethylsilyl)methylamino}acetylene complex (eq 12).[31] Finally, a fascinating compound containing an

$$[\mathrm{Ta(CNMe)_2(dmpe)_2Cl}] \xrightarrow{40\%\ \mathrm{Na/Hg}} \xrightarrow{2\mathrm{Me_3SiCl}} [\mathrm{Ta\{(Me_3Si)(Me)NC{\equiv}CN(Me)(SiMe_3)\}(dmpe)_2Cl}] \quad (12)$$

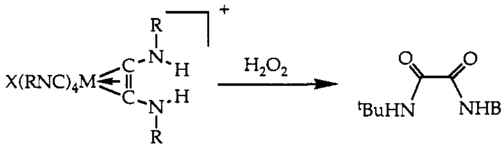
eight-membered acetylene ring as a ligand was prepared by reductive coupling of two CO ligands with the use of the chelating $[ClMe_2SiCH_2CH_2SiMe_2Cl]$ reagent (eq 13).[36] The use of a vanadium analogue in eq 13 is further discussed below. In principle, a variety of other, novel acetylene complexes could be prepared through reductive coupling of C_1 ligands.



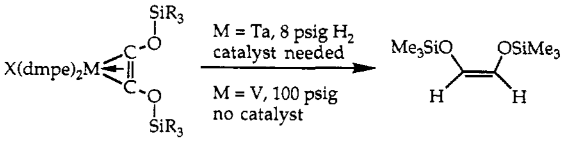
(13)

Removal of the Coupled Ligand. The reductive coupling reactions described above demonstrate that two CO or CNR ligands can be selectively linked to form new C_2 products. In order for these reactions to be of practical value, however, it is necessary to remove the coupled products from the metal with the newly-formed C–C bond intact. Moreover, if removal of the ligands occurred with concomitant regeneration of a precursor in the coupling reaction, the prospects would be good for selective, catalytic reductive coupling of carbon monoxide. Although this goal has not yet been achieved, there are some promising signs.

The organic product resulting from the coupling of two isocyanide ligands has been removed oxidatively, as shown in eq 14.[5] This reaction unfortunately proceeds with concomitant decomposition of the metal species. It was recently discovered, however, that some carbonyl-coupled products can be removed reductively. As shown in eq 15, hydrogenation of disiloxyacetylene complexes formed by reductive coupling of two bound carbonyl ligands liberates the acetylene as a *cis*-disiloxyethylene. Use of synthesis gas (H_2/CO) generated the olefin and a mixture of metal–carbonyl complexes. Although the mechanisms of these reactions are not yet fully understood, regeneration of metal–carbonyl species on release of the coupled ligand offers some encouragement that a catalytic CO coupling system may eventually emerge.



(14)



(15)

Mechanism of the C–C Bond-Forming Step. At this point we had demonstrated the ability to couple two CO or CNR ligands in any combination using seven-coordinate transition metal species. Although the reactions proceeded through six-coordinate intermediates, the final acetylene complexes were all seven-coordinate, and we still knew little about the critical C–C bond-forming step. One fundamental question remained unanswered: is seven coordination necessary to promote the coupling of the two ligands?

The C–C bond-forming step for carbyne–CO (or CNR) coupling reactions can be initiated in one of two

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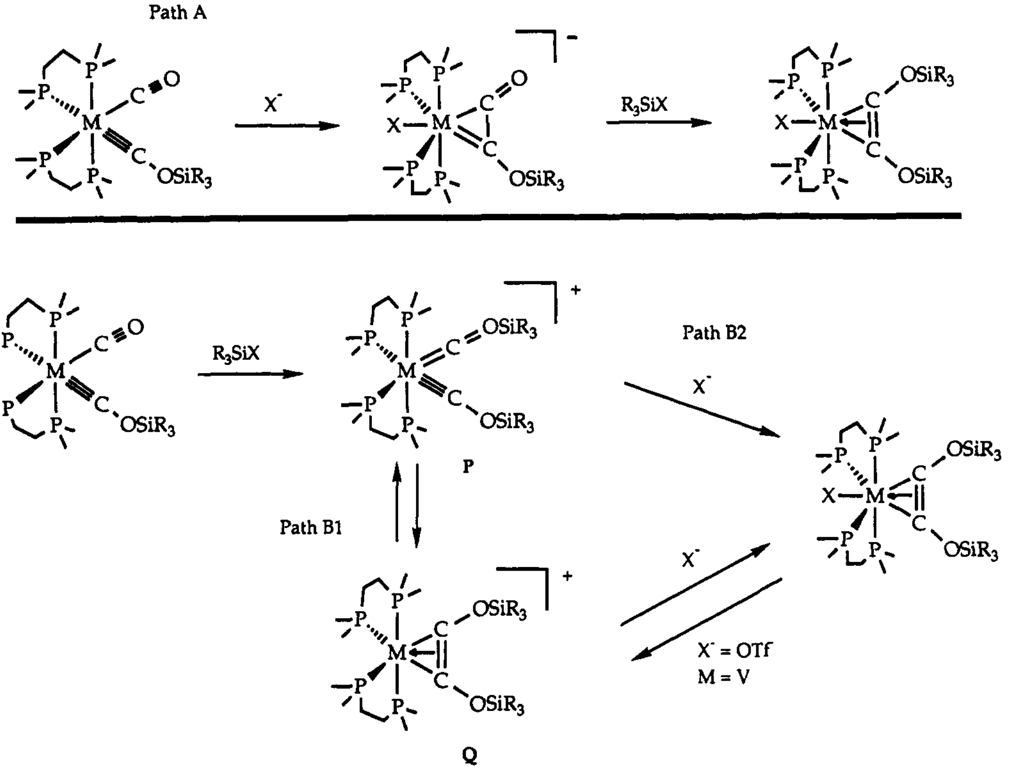
Scheme V. Possible Mechanistic Pathways for Reductive Coupling



ways, as outlined in Scheme V. Nucleophilic addition of a base to the carbyne complex could induce carbyne–CO coupling to form an η^2-ketenyl complex (path A), a reaction with much precedent.[19,22] Expansion of the coordination sphere upon addition of the base illustrates one way that increasing the coordination number at the metal center can promote the coupling of the carbyne and CO ligands. Alternatively, electrophilic attack of a trialkylsilyl group directly on the oxygen of the terminal CO ligand would lead to a carbene–carbyne complex (species P, Scheme V).[37,38] Coupling of the carbene–carbyne fragments might occur in concert with the electrophilic attack of the trialkylsilyl group or in a later step to give a lower-coordinate acetylene complex (path B1), which might subsequently be trapped by halide ion to give the observed product. On the other hand, carbene–carbyne coupling might *require* addition of halide in the C–C bond-forming step (path B2). Only the latter of these electrophile-induced C–C bond-forming pathways (B2) supports the idea that high coordination promotes ligand coupling.

Neither η^2-ketenyl nor carbene–carbyne complexes had been observed in our earlier mechanistic studies. During studies that extended the CO coupling reaction to the first-row transition metal vanadium, however, the complex $[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf$ was isolated (eq 16).[39] This complex was the first in which the final acetylene complex was not formally seven coordinate, lending some credibility to the postulate of a lower-coordinate coupled product (Q, Scheme V) and casting doubt on the viability of the η^2-ketenyl intermediate shown in path A. We soon discovered, however, that $[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf$ readily added bromide to form $[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Br]$, so that reversible triflate binding in the C–C bond-forming step could not be ruled out (path B2). Moreover, the analogous tantalum species, $[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2OTf]$, was seven-coordinate, further complicating the mechanistic picture.[18]

$$Na[V(CO)_2(dmpe)_2] + 2Me_3SiOTf \rightarrow [V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf \quad (16)$$

In order to differentiate among the possible mechanistic pathways of Scheme V, the kinetics of the reaction of $[Ta(COSi^iPr_3)(CO)(dmpe)_2]$ with Me_3SiCl (Scheme II) were explored by stopped-flow absorption spectroscopy, in which changes in the visible spectrum were monitored.[40] The measured reaction rate was first order in both $[Ta(COSi^iPr_3)(CO)(dmpe)_2]$ and $[Me_3SiCl]$, and at constant ionic strength, no dependence on halide concentration was observed.[41] These results definitively ruled out the mechanism involving the η^2-ketenyl intermediate (Scheme V, path A). Interaction of $[Ta(COSi^iPr_3)(CO)(dmpe)_2]$ with Me_3SiCl proceeds by initial silylation of the terminal CO ligand to form a cationic carbene–carbyne intermediate or transition state (P, Scheme V). Coupling of the carbene and carbyne ligands may occur spontaneously to give a cationic acetylene complex (Q, path B1) or require base

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(37) We and other groups occasionally refer to this pathway as the "bis carbyne" mechanism. Of course, such complexes could not exist for d-block transition metal complexes, for these species do not have enough d orbitals to form two independent metal carbon triple bonds. These complexes are therefore better described as bis carbene or carbene–carbyne complexes. See also: (a) Brower, D. C.; Templeton, J. L.; Mingos, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5203. (b) Wilker, C. N.; Hoffmann, R.; Eisenstein, O. *Nouv. J. Chem.* **1983**, *7*, 535. (c) See also ref 38.

(38) McDermott, G. A.; Mayr, A. *J. Am. Chem. Soc.* **1987**, *109*, 580.

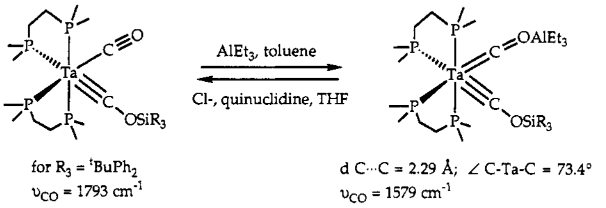
(39) Protasiewicz, J. D.; Lippard, S. J. *J. Am. Chem. Soc.* **1991**, *113*, 6564.

(40) Protasiewicz, J. D.; Masschelein, A.; Lippard, S. J. *J. Am. Chem. Soc.* **1993**, *115*, 808.

(41) The actual situation is more complicated. In the presence of chloride, $[Ta(COSi^iPr_3)(CO)(dmpe)_2]$ reacts with Me_3SiCl to yield $[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl]$, i.e., complete scrambling of the silyl groups from the starting carbyne complex is catalyzed by free halide. Full details will be presented elsewhere.

addition to the metal center to accomplish acetylene formation (path B2). We have not been able to distinguish these two possibilities by kinetic measurements, because the C–C bond-forming step may occur after the rate-determining step.

To address further the question of whether carbyne–CO coupling can occur solely upon addition of a Lewis acid, the interaction of $[Ta(COSiR_3)(CO)(dmpe)_2]$ with trialkylaluminum reagents was explored.[40] There are many reports of adducts formed by addition of aluminum reagents to electron rich metal carbonyl complexes,[42] and carbyne–CO coupling occurs when $[W(\equiv CH)(PMe_3)_4Cl]$ is exposed to CO and either $AlMe_3$ or $AlCl_3$ to form $[W(HC\equiv COAlR_3)(CO)(PMe_3)_3Cl]$.[43] Addition of $AlEt_3$ to solutions of $[Ta(COSiR_3)(CO)(dmpe)_2]$ (R_3 = $^iPr_3$, Ph_3, $^tBuPh_2$) resulted in adduct formation without concurrent coupling of the resulting carbene and carbyne ligands, as shown in eq 17. The $[Ta(COSiR_3)(COAlEt_3)(dmpe)_2]$ complexes are not completely analogous to the carbene–carbyne intermediates in the coupling reaction, however, because binding of $AlEt_3$ to the CO ligand of the carbyne species will not produce the same degree of charge withdrawal from the metal center as would R_3Si^+. Furthermore, addition of bases (Cl^-, THF, or quinuclidine) resulted only in removal of $AlEt_3$ and regeneration of the starting carbyne complexes. Further studies of these interesting adducts are in progress, and attempts to achieve coupling of the cis carbene and carbyne ligands continue.



(17)

Seven Coordination and Other Factors That Promote Reductive Coupling. With one exception, all examples of CO and CNR reductive coupling reactions to form bound acetylene complexes result in seven-coordinate (or higher) products.[44] This information, however, does not address the key issue of whether or not the coupling step is driven by coordination of the seventh ligand. Work from other laboratories is ambiguous on this issue. Mayr and coworkers have reported the spontaneous coupling of tungsten "bis carbyne" complexes.[38] On the other hand, bis carbyne complexes of the form *trans*-$[M(CNHMe)_2(dppe)]X_2$ (M = Mo or W) have been prepared by protonation of $[M(CNMe)_2(dppe)_2]$.[26] These complexes do not undergo ligand coupling, most likely because the ligands are in a trans configuration. More recently, spectroscopic characterization of formal tungsten cis bis carbyne complexes by Filippou and co-workers has been described.[45] These complexes do undergo ligand coupling, but only upon addition of a seventh ligand.

As shown in the diagram at the beginning of this Account, addition of the seventh ligand drives the two carbon atoms being coupled closer to one another. This stereochemical factor diminishes the nonbonded C···C distance from about 2.8 Å in six-coordinate complexes to about 2.28 Å in seven-coordinate ones. It was therefore of great interest when, as indicated in eq 17, the C···C distance in $[Ta(COSiR_3)(COAlR_3)(dmpe)_2]$ was measured to be 2.29 Å![36] Remarkably, the C···C nonbonded distance in this product is the same as found in the seven-coordinate, uncoupled dicarbonyl $[Ta(CO)_2(dmpe)_2X]$ complexes, revealing that incipient bond formation promoted by close nonbonded contacts with the coordination sphere does not require high coordination. Of course, addition of a seventh ligand to the $[Ta(COSiR_3)(COAlEt_3)(dmpe)_2]$ carbene–carbyne complex could diminish the distance even further.

Although an unequivocal answer to the question of whether or not seven coordination facilitates reductive coupling in these systems is not yet in hand, it seems clear that stereoelectronic factors have been optimized in the cases where such coupling reactions have been observed. These factors recall the empirical guidelines set forth in our early investigations of reductive coupling in isocyanide complexes. Firstly, increasing the number of good σ-donating ancillary ligands results in a more electron rich metal center. The formation of carbyne and carbene–carbyne species, key steps in the reductive coupling process, is clearly promoted by such an increase in electron density at the metal. Secondly, the higher the coordination number at the metal center, the more sterically crowded it becomes, reducing the chance of electrophilic attack at the metal or the metal-bound carbon atoms of the unsaturated ligands, two reactions that divert the system from the coupling pathway. Cooper and co-workers have recently reported the synthesis and characterization of highly reduced anionic isocyanide complexes, $K[Co(CNAr)_4]$ (Ar = 2,6 dimethylphenyl, $\nu_{C\equiv NR}$ = 1815 (s, br) cm^{-1})[46] and $Na_2[Ru(CN^tBu)_4]$ ($\nu_{C\equiv NR}$ = 2140, 1670, and 1580 cm^{-1}).[47] The isocyanide ligands in these species are more reduced than those in $[Mo(CN^tBu)_6]$, judging by their infrared properties ($\nu_{C\equiv NR}$ = 1957 (s, sh), 1837 (s) cm^{-1}); their reactivity with electrophiles, however, is quite different. The cobaltate complex reacts with Ph_3SnCl to form $[Co(CNAr)_4SnPh_3]$, whereas the dianionic ruthenate complex reacts with 2 equiv of Ph_3SnCl, Me_2SiCl_2, or $PhCH_2Cl$ to form six-coordinate complexes of the type $[Ru(CN^tBu)_4(ER_3)_2]$. Finally, the nature of the electrophile is also an important factor, as illustrated in the reaction of R^+ with $Na[M(CO)_2(dmpe)_2]$ (M = V, Nb, or Ta). When R = Me or H, oxidation of the metal occurs to form $[M(CO)_2(dmpe)_2R]$. Addition of Et^+ to $Na[M(CO)_2(dmpe)_2]$ yields $[M(CO)_2(dmpe)_2Et]$ for M = Ta and $[M(\eta^2\text{-}C(O)Et)(CO)(dmpe)_2]$ for M = V.[16,36,48] When the sterically more demanding R_3SiX reagents are added, however, only O-silylated species are isolated. One must also consider that the silyl reagents are expected to form more stable bonds to the oxygen atoms of the CO ligands than the corresponding carbon electrophiles. A similar analysis of the reactions of

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(44) We consider the acetylene ligand to occupy two coordination sites, although it is also considered as occupying a single site. See: Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

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$[M(CNR)_6]$ (M = Mo or W) complexes is not so straightforward. Addition of Me^+ reagents yields η^2-iminoacyl complexes, whereas Et^+ and R_3Si^+ sources will generate carbyne complexes.[24,27,28] Proton sources, such as employed in the original discovery, have not yielded observable carbyne complexes (see above), yet are able to couple two isocyanide ligands to form a bis(alkylamino)acetylene.[24]

Reversing the Coupling Process. Up to this point, we have only discussed the reductive coupling of CO and CNR ligands. Not long after the initial discovery, however, it was noted that the reverse reaction, uncoupling of the bis(alkylamino)acetylene ligand in $[Mo(CN^tBu)_4(^tBuHNC{\equiv}CNHBu^t)I]^+$, occurred to form the starting material, $[Mo(CN^tBu)_6I]^+$. Addition of 2 equiv of *n*-butyllithium to the isocyanide-coupled product (eq 18) followed by addition of dibromoethane

$$[Mo(CN^tBu)_4(^tBuHNC{\equiv}CNHBu^t)I]BF_4 \xrightarrow[-78\ ^\circ C]{2\ ^nBuLi} \xrightarrow{BrCH_2CH_2Br} 0.5[Mo(CN^tBu)_4(^tBuHNC{\equiv}CNHBu^t)I]BF_4 + 0.5[Mo(CN^tBu)_6I]BF_4 \quad (18)$$

led to formation of $[Mo(CN^tBu)_6I]^+$.[49] Similarly, attempts to purify the CO-coupled product shown in eq 19 by column chromatography on alumina yielded

$$[Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl] \xrightarrow[THF]{alumina} [Ta(CO)_2(dmpe)_2Cl] \quad (19)$$

the starting dicarbonyl complex.[50] More recently, uncoupling of the acetylene ligand in $[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf$ was observed (eq 20) during

$$[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf \xrightarrow[or\ 3CF_3COOH]{3HCl_{aq}} [V(CO)_2(dmpe)_2X] \quad (20)$$
$$X = Cl \text{ or } CF_3CO_2$$

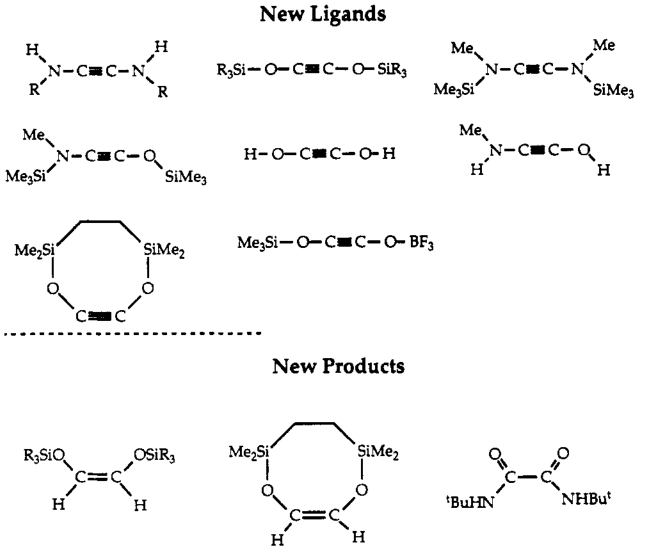
attempts to generate a vanadium analogue of the dihydroxyacetylene complex by analogy to the chemistry illustrated in eq 9.[36] These three examples all involve loss of 2 equiv of electrophile and two electrons during the uncoupling process. Uncoupling to form the carbyne complex occurred when $[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf$ was treated with $LiC{\equiv}CPh$, eq 21. Finally, the reverse of the reaction to form

$$[V(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2]OTf + LiC{\equiv}CPh \rightarrow [V{\equiv}COSiMe_3(CO)(dmpe)_2] + Me_3SiC{\equiv}CPh \quad (21)$$

the siloxycarbyne species has been observed (eq 22). Study of these reactions that reverse the coupling process may ultimately afford further insights into its mechanism.

$$[Ta{\equiv}COSi^iPr_3(CO)(dmpe)_2] + KO^tBu \rightarrow K[Ta(CO)_2(dmpe)_2] + {}^tBuOSi^iPr_3 \quad (22)$$

Scheme VI. New Ligands and Products Formed by Reductive Coupling Reactions Discovered in this Research



Conclusions. The studies described here have, over the past 15 years, led to a general class of CO and CNR reductive coupling reactions which proceed by a series of clearly defined reaction steps. A highly reduced six-coordinate metal species with cis CO or CNR ligands is first generated (Schemes I, III, IV). The delocalization of metal π-electron density out onto the unsaturated ligands in these complexes makes them susceptible to electrophilic attack at the heteroatom. Addition of a Lewis acid can transform one CO or CNR ligand into a heterocarbyne moiety (Schemes II, IV). If the resulting carbyne complex is sufficiently electron rich, a second equivalent of a Lewis acid can activate another unsaturated ligand (Scheme V). The resulting carbene–carbyne complexes may undergo a spontaneous coupling reaction, or may prefer instead to interact with an external base. The former possibility suggests that a high coordination number plays no real role in these coupling reactions, but rather that the seventh ligand is necessary only to allow the product to achieve an 18-electron configuration. Work continues in an effort to find a definitive experiment that would distinguish these possibilities.

From a synthetic standpoint, our study of reductive coupling reactions of CO and CNR ligands has been very fruitful. The highly-reduced intermediate species, as well as the hetero-substituted carbyne complexes, have considerably extended the current knowledge of the reactivity of electrophiles with such transition metal complexes, especially those with CO and CNR ligands. As shown in Scheme VI, this reaction chemistry has afforded many new, high-functionalized acetylene ligands as well as isolated alkenes in which the carbon atoms derive from carbon monoxide or alkyl isocyanide, which further testify to its success.

The work described in this Account was supported continuously over the 15-year period by grants from the National Science Foundation, for which we are very grateful. We also acknowledge the experimental and intellectual contributions of our talented colleagues who have worked on this project.

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(50) Bianconi, P. A. Ph.D. Thesis, Massachusetts Institute of Technology, 1986.