

atom recombination arises, in part, from the redissociation of highly excited X_2 , an effect that increases with increasing temperature (Figure 4).

A complete theory of the dissociation of diatomic molecules should explicitly consider rotational motions and excited electronic states of the diatomic molecules. This presentation, however, shows that nonequilibrium distributions of the vibrational states of the ground electronic states are sufficient to explain the low, observed, activation energies.

Summary

The observed activation energy for the dissociation of diatomic molecules is substantially less than the bond dissociation energy, and it decreases with increasing temperature. This effect cannot be explained by a ladder-climbing model of the reaction process with dissociation occurring only from the top vibrational level, even with allowance for a nonequilibrium

distribution over vibrational states. This effect is readily explained by several models that allow dissociation to occur from any and all vibrational states and with allowance for nonequilibrium distribution over vibrational states. Two such models were set up that permitted the calculation of dissociation rate constants from separately determined vibrational relaxation times, vibrational frequency, and hard-spheres collision cross section—with no adjustable parameters. The nonequilibrium versions of these models give satisfactory predictions of rate constants and a good account of the observed low activation energies. These calculations indicate that diatomic molecules dissociate from all vibrational states.

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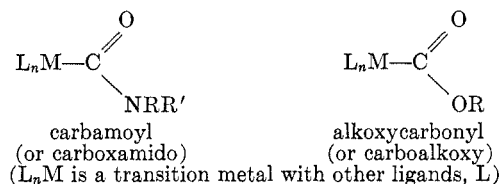
Carbamoyl and Alkoxy carbonyl Complexes of Transition Metals

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Although the carbamoyl and alkoxy carbonyl functional groups have been known in organic chemistry for over a century, only in the past 9 years have inorganic analogs been reported. It is the intent of

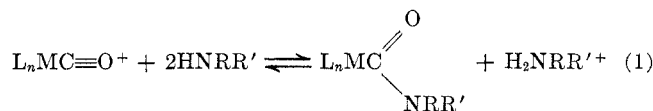


this Account to summarize the methods used in their preparation, their structural and spectral features, and their reactions, and to speculate about their role in synthetic organic and metal-catalyzed reactions.

Since these compounds sit directly on the borderline between inorganic and organic chemistry, it is hoped that chemists in both areas will see applications to their own research.

Preparative Methods

Metal Carbonyl Complexes with Amines or Alkoxides. The reaction



represents by far the most general method of preparing carbamoyl complexes. Usually the reactions are rapid and essentially quantitative at room temperature. Although NH_3 and primary and secondary alkylamines react smoothly, aniline and other aromatic amines have not yet been found to undergo a similar reaction with any metal carbonyl complex. In addition to those designated in Table I, complexes such as $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_4^+$,¹ $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_4^+$,¹ $(\text{C}_5\text{H}_5)\text{W}(\text{CO})_3(\text{NH}_3)^+$,² and $(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})_3(\text{NH}_3)^+$,² also yield carbamoyl complexes. A related reaction³ of the carbonyl-thiocarbonyl complex, $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{CS})^+$, with methylamine gives the thiocarbamoyl derivative $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CS-NHCH}_3$. Amine attack on a coordinated CO ligand is presumably also involved at an intermediate stage in the formation of $\text{Mn}(\text{CO})_4(\text{NH}_3)\text{CONH}_2$,² $\text{Re}(\text{CO})_4(\text{NH}_3)\text{CONH}_2$,⁴ $\text{Mn}(\text{CO})_3(\text{NH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]\text{CONH}_2$,² $\text{Co}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]\text{CONC}_5\text{H}_{10}$,⁵ and $\text{Hg}(\text{CONR}_2)_2$.⁶

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Robert J. Angelici was born in Minnesota, attended St. Olaf College, and received his Ph.D. from Northwestern University in 1962. He spent the following year working with E. O. Fischer at the University of Munich. He returned to this country and began his teaching career at Iowa State University where he is now Professor. In 1970-1972, he was an Alfred P. Sloan Foundation Fellow. His research interests are in two broad areas: (1) the synthesis of organometallic compounds and mechanistic studies of their reactions, and (2) transition metal complex catalysis of reactions of biological interest.

Table I
Correlation of C-O Force Constants with Metal
Carbonyl-Amine Reactions (Equation 1)

Compound	Force constant, mdyn/Å	Amine reaction
$\{[(C_6H_5)_3P]_2PtCl(CO)\}BF_4^a$	18.2	Yes ^b
$[(C_6H_5)_3Ru(CO)_3]PF_6$	17.6	Yes ^c
$[(C_6H_5)_3Fe(CO)_3]PF_6$	17.6	Yes ^d
$[(CH_3NH_2)Mn(CO)_5]PF_6$	17.5 (eq)	Yes ^e
	16.8 (ax)	
$[(CH_3NH_2)Re(CO)_5]PF_6$	17.5 (eq)	Yes ^f
	16.5 (ax)	
$Fe(CO)_5$	17.0 (ax)	Equil ^g
	16.4 (eq)	
$\{[(C_6H_5)_3P]_2Mn(CO)_4\}PF_6^a$	16.9	Equil ^h
$[(toluene)Mn(CO)_3]PF_6$	16.9	Equil ⁱ
$[C_6(CH_3)_6Mn(CO)_3]PF_6$	16.5	Equil ⁱ
$\{(C_6H_{11}NH_2)_3Mn(CO)_3\}PF_6$	15.7	No ⁱ
$(C_5H_5)Mn(CO)_3$	15.6	No ⁱ
$\{[(CH_3)_2CHNH_2]_3Mn(CO)_3\}PF_6$	15.5	No ⁱ
$\{[(CH_3)_2CHNH_2]_3Re(CO)_3\}PF_6$	15.5	No ⁱ
$[(dien)Mn(CO)_3]I$	15.3	No ⁱ
$[(NH_3)_3Re(CO)_3]B(C_6H_5)_4$	15.2	No ⁱ

^a Trans geometry. ^b C. R. Green and R. J. Angelici, *Inorg. Chem.*, submitted for publication. ^c A. E. Kruse and R. J. Angelici, *J. Organometal. Chem.*, **24**, 231 (1970). ^d L. Busetto and R. J. Angelici, *Inorg. Chim. Acta*, **2**, 391 (1968). ^e R. J. Angelici and D. L. Denton, *ibid.*, **2**, 3 (1968). ^f R. J. Angelici and A. E. Kruse, *J. Organometal. Chem.*, **22**, 461 (1970). ^g Reference 9. ^h R. Brink and R. J. Angelici, to be published. ⁱ Reference 7.

It should be emphasized that not all metal carbonyl complexes react according to eq 1. In Table I,⁷ the complexes are divided into three groups which reflect their tendency to react with amines: *yes*, which means a carbamoyl complex was isolated and there was no evidence for the reverse reaction; *equil*, which means that the carbonyl compound was not completely converted to the carbamoyl derivative or that it could readily be regenerated from the carbamoyl complex (*e.g.*, a CH_2Cl_2 solution of (mesitylene) $Mn(CO)_3^+$ and excess cyclohexylamine contains (mesitylene) $Mn(CO)_2CONHC_6H_{11}$; yet on evaporation (mesitylene) $Mn(CO)_3^+$ is recovered quantitatively);⁷ or *no*, which means that there was no evidence for reaction even when the carbonyl complex was dissolved in pure alkylamine.

In an attempt to understand this wide range of reactivity we have correlated the tendency to react with the C-O stretching force constant of the coordinated CO group. Darensbourg and Darensbourg⁸ pointed out that these force constants are a measure of the positive charge on the carbon of the CO group—*e.g.*, the higher the force constant, the higher the positive charge on the carbon. A high positive charge would favor, both kinetically and thermodynamically, the formation of a carbamoyl complex. However,

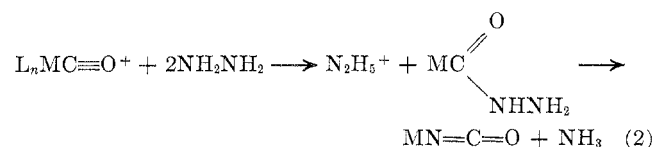
since these reactions are so rapid, it appears that the observed reactivity is controlled by thermodynamics.

Indeed, there does appear to be a rather good correlation between force constants and reactivity which may be summarized as follows: *CO ligands with force constants greater than 17.2 mdyn/Å readily form carbamoyl complexes; those with force constants between 16.0 and 17.0 give reversible equilibrium mixtures; and those with constants below 16.0 show no evidence for carbamoyl formation.*⁷ In terms of C-O stretching frequencies, it appears that carbonyl complexes with C-O stretching absorptions below approximately 2000 cm^{-1} do not yield carbamoyl complexes.⁷

The force constant correlation not only aids in predicting what metal carbonyl complexes will form carbamoyl derivatives but also in complexes where there are two chemically different kinds of CO groups, as in $Fe(CO)_5$, $(CH_3NH_2)Mn(CO)_5^+$, or $(CH_3NH_2)Re(CO)_5^+$, it correctly predicts that the CO group with the highest C-O force constant is that which is converted to the carbamoyl ligand.

With the exception of $Fe(CO)_5$,⁹ neutral metal carbonyl complexes have not been treated with amines for purposes of generating carbamoyl complexes. Fischer and coworkers, however, have isolated $Cr(CO)_5CON(C_2H_5)_2^-$ from the reaction of $Cr(CO)_6$ and $(C_2H_5)_2N^-$. Also, spectroscopic evidence has been obtained for $Ni(CO)_5CON(CH_3)_2^-$ produced in the reaction of $Ni(CO)_4$ with $(CH_3)_2N^-$,¹⁰ while $Fe(CO)_4CON(C_2H_5)_2^-$ has been postulated as an intermediate in the reaction of $Fe(CO)_5$ with $(C_2H_5)_2N^-$.^{11,12}

Closely related to the amine reactions is that of hydrazine which proceeds as follows



The carbamoyl intermediates have not been isolated in pure form because of their tendency to decompose to the isocyanate complexes. The reaction is a useful method of converting a terminal CO group into an isocyanate ligand and has been used with $(C_5H_5)FeFe(CO)_3^+$,¹³ $(C_5H_5)Fe(CO)_2(CS)^+$ ³ (to give the isothiocyanate complex), $(C_5H_5)Ru(CO)_3^+$,¹⁴ $Re(CO)_6^+$,¹⁵ $(CH_3NH_2)Re(CO)_5^+$,¹⁶ $Re(CO)_4[P(C_6H_5)_3]Br$,¹⁷ $Mn(CO)_3[P(CH_3)_2(C_6H_5)]_2Br$,¹⁸ and (arene) $Mn(CO)_3^+$.⁷

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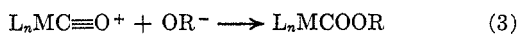
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Alkoxy carbonyl complexes may be prepared by the analogous reaction, eq 3. Some cationic complexes



which are known to react in this manner are $(C_6H_5)_3Fe(CO)_3^+$,¹⁹ $(C_6H_5)_3Ru(CO)_3^+$,¹⁴ $Os(CO)_3[P(C_6H_5)_3]_2^-Cl^+$,²⁰ $Mn(CO)_4[P(C_6H_5)_3]_2^+$,²¹ $(C_6H_5)_3Mn(CO)_2^-(NO)^+$,²² $Re(CO)_4[P(C_6H_5)_3]_2^+$,²¹ $Re(CO)_6^+$,²³ $Co(CO)_3[P(C_6H_5)_3]_2^+$,²⁴ $Ir(CO)_3[P(C_6H_5)_3]_2^+$,²⁵ $Ir(CO)_2[Sb(C_6H_5)_3]_3^+$,²⁶ $Rh(CO)_2[Sb(C_6H_5)_3]_3^+$,²⁶ and $Ir(CO)(H)[(CH_3)_2PCH_2CH_2P(CH_3)_2]_2^+$.²⁷ Complexes such as $Ir(CO)_2[P(C_6H_5)_3]_2I_2^+$ ²⁸ and $Pt(CO)Cl[P(C_6H_5)_3]_2^+$ ²⁹ react directly with alcohols to give alkoxy carbonyl derivatives. Although the reactions of $Pt[P(C_6H_5)_3]_2Cl_2$,³⁰ $Pd[P(C_6H_5)_3]_2Cl_2$,³⁰ and $Pt[P(C_6H_5)_3]_2(N_3)(NCO)$ ³¹ with CO and alkoxides (or alcohols) are slightly more complex, they presumably proceed through the cationic carbonyl intermediates, $[(C_6H_5)_3P]_2M(X)(CO)^+$. The alkoxy carbonyl complexes, $Rh_6(CO)_{16}CO_2CH_3^-$ ³² and $Ir(CO)[P(CH_3)_2(C_6H_5)]_3^-(HgCl)CO_2CH_3^+$,^{33a} result from still more complicated reactions. Methoxycarbonyl derivatives of corrinoids have been obtained from the reaction of CO and CH_3OH with the Co(III) corrinoids.^{33b}

In complexes containing both CO and CS ligands, such as $(C_6H_5)_3Fe(CO)_2(CS)^+$ and $Ir[P(C_6H_5)_3]_2(CO)_2(CS)^+$, methoxide attack occurs at both CO and CS of the former,³ depending on the conditions, whereas the iridium complex³⁴ yields only $Ir[P(C_6H_5)_3]_2(CO)(CS)CO_2CH_3$.

Like the alcohol reactions, water adds to a CO group in $IrCl_2[P(CH_3)_2(C_6H_5)]_2(CO)_2^+$ to give the carboxylic acid derivative $IrCl_2[P(CH_3)_2(C_6H_5)]_2(CO)CO_2H$.³⁵ Although CO_2H ligands have been postulated in a variety of reactions, this seems to be the only isolated member of this family.

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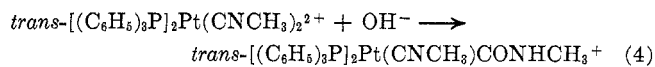
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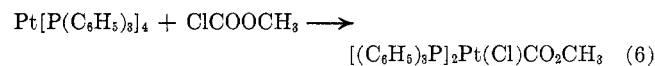
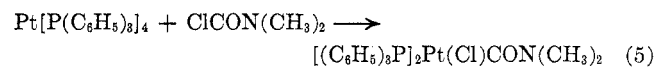
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Metal Isocyanide Complexes with Hydroxide. Although OH^- attack on a coordinated isocyanide ligand followed by proton migration to the nitrogen would appear to be a general method of carbamoyl synthesis, it has been reported for only one complex³⁶ (eq 4).



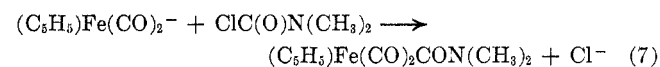
Reaction with SH^- yields the analogous thiocarbamoyl complex, $trans-[(C_6H_5)_3P]_2Pt(CNCH_3)CSN-HCH_3$.³⁶ The reaction of $[(C_6H_5)_3P]_2Rh(CNCH_3)Cl$ with water to give $[(C_6H_5)_3P]_2Rh(CO)Cl$ presumably proceeds *via* a carbamoyl intermediate.³⁷

Oxidative Addition of Carbamoyl Chlorides and Chloroformates. Metal complexes which are known to undergo oxidative addition reactions³⁸ also yield carbamoyl and alkoxy carbonyl derivatives by this route. For example^{30,38}



The analogous reactions of $Pd[P(C_6H_5)_3]_4$ have also been reported.^{39,40a} The thiocarbamoyl derivatives $[(C_6H_5)_3P]_2Pt(Cl)CSN(CH_3)_2$, $[(C_6H_5)_3P]_2Pd(Cl)CSN(CH_3)_2$,³⁹ and $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Ni(Cl)CSN(CH_3)_2$ ^{40b} and the dithioethoxycarbonyl complex $[(C_6H_5)_3P]_2Pt(Cl)CS_2C_2H_5$ ⁴¹ have been prepared similarly. Oxidative additions of $ClC(S)SC_2H_5$ to $RhCl[P(C_6H_5)_3]_3$ and $IrCl(CO)[P(C_6H_5)_3]_2$ also give dithioethoxycarbonyl complexes.⁴¹ The analogous reaction of $ClCSN(CH_3)_2$ with $RhCl[P(C_6H_5)_3]_3$ or $Rh(CO)Cl[P(C_6H_5)_3]_2$ gives the dimeric compound, $\{[(C_6H_5)_3P]_2Rh(Cl)_2CSN(CH_3)_2\}_2$ which presumably contains bridging Cl groups.^{40b} Chloroformates also react with $IrCl(CO)[P(CH_3)_2(C_6H_5)]_2$ to yield alkoxy carbonyl complexes, $IrCl_2(CO)[P(CH_3)_2(C_6H_5)]_2CO_2R$.³⁵

Nucleophilic Attack on Chloroformates and Carbamoyl Chlorides. The first known carbamoyl complex was prepared by King^{22,42} using this route



Since then transition metal nucleophiles also have been used to prepare $(C_6H_5)_3Fe(CO)_2CO_2R$,¹⁹ $(C_6H_5)_3Ru(CO)_2CO_2R$,¹⁴ $Mn(CO)_5CO_2R$,²¹ $Re(CO)_5CO_2R$,⁴³ and $Co(CO)_3[P(C_6H_5)_3]CO_2R$ ^{24,44} from the chloroformates, $ClC(O)OR$. Moreover, several derivatives

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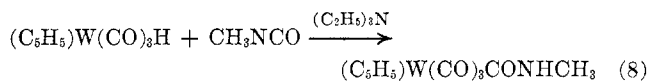
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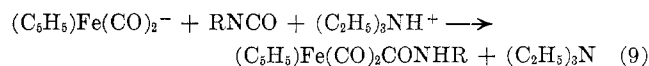
containing Co-CO₂R groups have been prepared from reduced forms of vitamin B₁₂,⁴⁵ bis(dimethylglyoximate)cobalt(II),⁴⁶ and bis(salicylaldehyde)ethylene-diiminatocobalt(II)⁴⁶ and chloroformates.

Alkyl Isocyanate Insertion into a Metal-Hydrogen Bond. The insertion reaction 8 in the presence of



catalytic amounts of triethylamine proceeds rapidly and in good yield to the carbamoyl product.¹ There is good evidence that the reaction proceeds by initial reaction of (C₅H₅)W(CO)₃H and (C₂H₅)₃N to give (C₂H₅)₃NH⁺ and (C₅H₅)W(CO)₃⁻, which attacks the isocyanate carbon. The resulting (C₅H₅)W(CO)₃CO-NCH₃⁻ then gains a proton to give the product. Reaction 8 is reversible¹ and will be discussed in detail later in this Account.

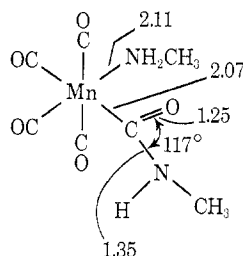
Although (C₅H₅)Fe(CO)₂H has been reported⁴⁷ to react with *tert*-butyl isocyanate to give a low yield of the insertion product (C₅H₅)Fe(CO)₂CONHC(CH₃)₃, the major products were (C₅H₅)Fe(CO)[CNC(CH₃)₃]-[CONHC(CH₃)₃] and (C₅H₅)₂Fe₂(CO)₃[CNC(CH₃)₃]. The simple insertion product probably results from the presence of catalytic amounts of (C₅H₅)Fe(CO)₂⁻. In fact, we have now found⁴⁸ that the carbamoyl complexes, (C₅H₅)Fe(CO)₂CONHR, may be prepared according to eq 9. Similarly Re(CO)₅⁻ reacts⁴⁹ with



CH₃NCO and (C₂H₅)₃NH⁺ to give Re(CO)₅CONHCH₃.

Structure and Bonding

X-Ray Studies. The compound *cis*-Mn(CO)₄(NH₂CH₃)CONHCH₃ crystallizes in both tetragonal and monoclinic forms, yet the molecular structure in both⁵⁰ is

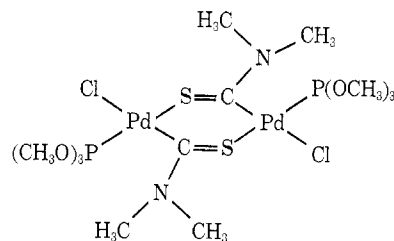


The Mn-C(O)NHCH₃ group is planar, and the bond distances and angles in the *N*-methylcarbamoyl group are essentially the same as in *N*-methylacetamide, acetamide, and acetanilide.⁵¹ The CH₃ group in the carbamoyl ligand is *cis* to the carbonyl oxygen; this contrasts with complexes³⁹ such as [(C₆H₅)₃P]₂Pt(Cl)-

CONHCH₃ where nmr results suggest that the CH₃ group is *trans* to the oxygen.

The Mn-C bond distance (2.07 Å) is considerably longer than the M-CO distances which range from 1.78 to 1.86 Å. This suggests that the Mn-C bond order is substantially lower for the carbamoyl group and may correspond to a simple σ bond. The Mn-C(sp²) σ-bond distance might be calculated from the known C(sp²) radius of 0.74 Å and a Mn radius. Although the latter value has been estimated⁵² as 1.46 and 1.39 Å, perhaps the best value in this instance may be calculated from the Mn-N distance (2.11 Å) in *cis*-Mn(CO)₄(NH₂CH₃)CONHCH₃ by subtracting the N(sp³) radius⁵³ of 0.70 Å. This gives an Mn radius of 1.41 Å and an expected Mn-C(sp²) bond distance of 2.15 Å. The shorter observed distance suggests there is some, although not much, double bond character in the Mn-carbamoyl bond.

A dimeric thiocarboxamido complex, {[(CH₃O)₃P]-Pd(Cl)CSN(CH₃)₂}₂, results from the oxidative-addition reaction (analogous to eq 5) of Pd[P(OCH₃)₃]₄ with ClC(S)N(CH₃)₂ which presumably proceeds initially *via* formation of [(CH₃O)₃P]₂Pd(Cl)CSN(CH₃)₂. On losing P(OCH₃)₃ from this intermediate, the bridged dimer is formed. Its novel structure⁵⁴



shows essentially square-planar coordination around each Pd with the plane of the thiocarboxamido ligand roughly (~67°) perpendicular to the coordination plane. The sulfur atom of each thiocarboxamido group is bound to the other Pd atom. As a result of the geometry of the bridging ligands, the square planes around the Pd atoms are oriented at an angle of 57° with respect to each other. The 2.00-Å Pd-C bond distance is that expected for σ bonding only, and the geometry of the thiocarboxamido ligands is essentially that which is found in organic thioamides. The analogous Ni complex {[(C₆H₅O)₃P]Ni(Cl)CSN(CH₃)₂}₂ has been postulated to have the same structure.^{40b} These structures indicate, as in organic thioamides, that the sulfur atom of thiocarboxamido complexes may be a donor atom in complexing with other metals. In general, the complexing ability of the oxygen or sulfur atom in carbamoyl and thiocarboxamido complexes has yet to be examined extensively.

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(46) G. Costa, G. Mestroni, and G. Pellizer, *J. Organometal. Chem.*, **11**, 333 (1968).

(47) W. Jetz and R. J. Angelici, *J. Organometal. Chem.*, **35**, C37 (1972).

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(50) D. M. Chipman and R. A. Jacobson, *Inorg. Chim. Acta*, **1**, 393 (1967); G. L. Breneman, D. M. Chipman, C. J. Galles, and R. A. Jacobson, *ibid.*, **3**, 447 (1969).

(51) "Interatomic Distances," *Chem. Soc., Spec. Publ., No. 11* (1958); M. B. Robin, F. A. Bovey, and H. Basch in "The Chemistry of Amides," J. Zabicky, Ed., Interscience, New York, N. Y., 1970, p 1.

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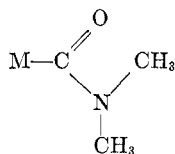
(53) F. A. Cotton and D. C. Richardson, *Inorg. Chem.*, **5**, 1851 (1966).

(54) J. Clardy, S. Porter, H. White, C. R. Green, and R. J. Angelici, to be published.

Infrared and Nmr Studies. Infrared spectra of the *N,N*-dimethylcarbamoyl ligands show a characteristic C=O stretching absorption in the range 1565 to 1615 cm^{-1} . Similar assignments for the secondary carbamoyl groups, CONHR, are more difficult because of the occurrence of the N-H bending mode in the same region; generally a broad absorption which presumably includes both modes is observed. Carbonyl (C=O) stretching frequencies for the alkoxy-carbonyl group are found in the 1610- to 1700- cm^{-1} range. Like their organic analogs, the carbonyl frequency range for the carbamoyl group is lower than that of the alkoxy-carbonyl group.

The frequency ranges for both the carbamoyl and alkoxy-carbonyl ligands are roughly 80 cm^{-1} lower than observed for their organic counterparts; this indicates that the C=O bond strength is decreased by metals as compared to organic groups and that metals in these complexes are better electron donors than are alkyl groups.

Some effort has been directed at studying the barrier to rotation around the C-N bond of *N,N*-dimethylcarbamoyl ligands. In proton nmr spectra of these



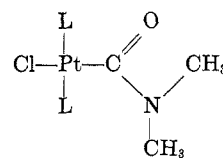
derivatives the CH_3 groups are observed in the region τ 7.1 to 8.5 and are nonequivalent. On warming, they broaden and coalesce into one resonance. The coalescence temperature (T_c) is a measure of the rate of rotation around the C-N bond. These values are recorded in Table II together with similar results for

Table II
Coalescence Temperatures of Inorganic and Organic Carbamoyl Derivatives, $\text{ZCON}(\text{CH}_3)_2$

Z	Solvent	T_c , $^{\circ}\text{C}$
OCH_3^a	CHCl_3	-13
$(\pi\text{-C}_6\text{H}_5)_2\text{Mo}(\text{CO})_2^b$	$(\text{CD}_3)_2\text{CO}$	~18
$(\pi\text{-C}_6\text{H}_5)_2\text{W}(\text{CO})_2^b$	$(\text{CD}_3)_2\text{CO}$	~18
CH_3^a	Neat	87
$[(\text{CH}_3)_2(\text{C}_6\text{H}_5)\text{P}]_2\text{PtCl}^b$	<i>c</i>	120-130
$[\text{CH}_3(\text{C}_6\text{H}_5)_2\text{P}]_2\text{PtCl}^b$	<i>c</i>	140-145
$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PdCl}^b$	<i>c</i>	155-165
$[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{PtCl}^b$	<i>c</i>	>200
2,4,6- $[(\text{CH}_3)_3\text{C}]_3\text{C}_6\text{H}_2^a$	<i>d</i>	>200

^a Reference 55. ^b Reference 39. ^c *o*-Dichlorobenzene. ^d Chloronaphthalene-benzotrichloride (1:1).

organic derivatives.⁵⁵ The coalescence temperatures have been interpreted in terms of the double bond character of the C-N bond and the bulkiness of groups near the rotating $\text{N}(\text{CH}_3)_2$ group. The high coalescence temperature of the platinum complexes appears to be related to the size of the phosphine (L) groups. This is supported by the decrease in T_c as phenyl groups are replaced by smaller CH_3 groups in these derivatives.



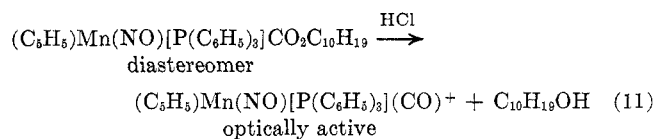
In the absence of steric effects, as in $(\text{C}_6\text{H}_5)_3\text{M}(\text{CO})_2\text{CON}(\text{CH}_3)_2$ (where $\text{M} = \text{Mo}$ or W), low coalescence temperatures are observed. Attempts to observe rotation in the monomethylcarbamoyl complex $(\text{C}_6\text{H}_5)_3\text{W}(\text{CO})_2\text{CONHCH}_3$ were unsuccessful,⁵⁶ the CH_3 resonance remains an unchanged sharp doublet over the temperature range -25 to 40° .

The methyl protons of methoxycarbonyl complexes noted in this Account have been reported to range from τ 6.3 to 7.6. There is no evidence relating to the possibility of restricted rotation around the C-O bond in these derivatives.

Optically Active Alkoxy-carbonyl Complexes. Brunner⁵⁷ and coworkers have prepared several optically active alkoxy-carbonyl complexes with four different groups around the metal atom. For example, the optically active mentholate anion ($\text{C}_{10}\text{H}_{19}\text{O}^-$) reacts with racemic $(\text{C}_6\text{H}_5)_3\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})^+$ (eq 10)

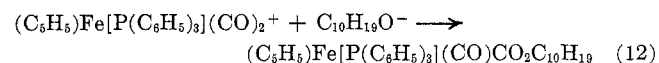
$$(\text{C}_6\text{H}_5)_3\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})^+ + \text{C}_{10}\text{H}_{19}\text{O}^- \longrightarrow (\text{C}_6\text{H}_5)_3\text{Mn}(\text{NO})[\text{P}(\text{C}_6\text{H}_5)_3]\text{CO}_2\text{C}_{10}\text{H}_{19} \quad (10)$$

to give the diastereomeric alkoxy-carbonyl complexes which can be readily resolved by crystallization. These derivatives in solution racemize slowly (2-3-hr half-lives at room temperature) at the asymmetric Mn atom by a mechanism which is postulated to involve rate-determining dissociation of $\text{P}(\text{C}_6\text{H}_5)_3$. On reaction with HCl, each diastereomer is converted to one enantiomer of the original cation (eq 11). The con-



figurational stability of these optically active cations is evidenced by the observation that specific rotations of their solutions at room temperature do not decrease on storage for several weeks. These enantiomers also react with CH_3O^- to give optically active alkoxy-carbonyl complexes whose kinetics of racemization have also been studied.⁵⁷

Similarly $(\text{C}_6\text{H}_5)_3\text{Fe}[\text{P}(\text{C}_6\text{H}_5)_3](\text{CO})_2^+$ reacts with mentholate ion to create a complex with four different groups (eq 12). The resulting diastereomeric mixture



can be resolved by crystallization. These diastereomers are much more stable to racemization than the alkoxy-carbonyl derivatives of manganese discussed above. This lack of racemization indicates not only that $\text{P}(\text{C}_6\text{H}_5)_3$ dissociation is slow but also that the

(56) C. G. Green, W. Jetz, and R. J. Angelici, unpublished results.

(57) H. Brunner, *Angew. Chem., Int. Ed. Engl.*, **10**, 249 (1971), and references therein.

mentholate group cannot readily migrate from one carbonyl group to the other in the complex since this migration would also result in racemization. This is the only available evidence which suggests that alkoxy groups remain fixed on one carbonyl carbon atom and do not rapidly migrate to other CO ligands in the complex.

Reactions of Carbamoyl and Alkoxy-carbonyl Ligands

Since these complexes have become available only recently, their chemistry has not been extensively investigated. Their potential utility in organic synthesis will almost certainly bring about more studies in this area. Those reactions which have been reported to date are summarized below.

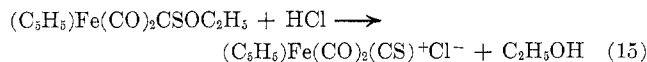
With Acids. Carbamoyl and alkoxy-carbonyl complexes react with acids to generate metal carbonyl complexes as shown in eq 13 and 14. With strong



acids such as HCl, there are no reported examples in which reactions 13 and 14 do not take place. The reliability of these reactions has in fact made them a useful chemical means of establishing the presence of these groups in complexes.

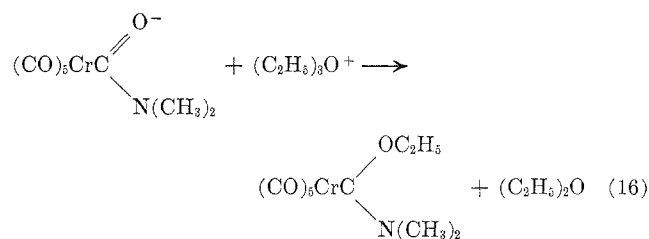
A qualitative study³⁹ of *trans*-[(C₆H₅)₃P]₂Pd(Cl)-CON(CH₃)₂ with several acids shows that HCl, Cl₃CCO₂H (pK_a = 0.70), and BrCH₂CO₂H (pK_a = 2.69) do react, whereas weaker acids such as *p*-NO₂C₆H₄CO₂H (pK_a = 3.41), C₆H₅CO₂H (pK_a = 4.19), and CH₃CO₂H do not. Although a systematic study has not been made, the strength of the acid required to carry out these reactions must be related to the reverse of reactions 13 and 14. That is, it must be related to the tendency of the metal carbonyl complex to add amines (or alcohols) according to eq 1 (or 3). In cases where the tendency is low (Table I), as for (arene)Mn(CO)₅⁺, the corresponding carbamoyl complex (arene)Mn(CO)₂CONRR' reacts⁷ with acids even as weak as H₂NRR'⁺. Where the tendency is high, as for [(C₆H₅)₃P]₂Pt(Cl)CO⁺, strong acids are required to remove the amine from the corresponding carbamoyl complex, [(C₆H₅)₃P]₂Pt(Cl)CONRR'.

A thiocarbonyl complex, (C₅H₅)Fe(CO)₂(CS)⁺, has been prepared⁵⁸ by making use of this general type of reaction (eq 15). A similar attempt⁵⁹ with the thio-



carbamoyl complexes, [(C₆H₅)₃P]₂M(Cl)CSN(CH₃)₂ (where M = Pd or Pt), gave no reaction.

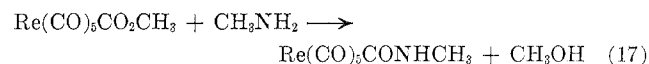
With R₃O⁺. In contrast to H⁺, the Lewis acid C₂H₅⁺ reacts with anionic carbamoyl complexes to give "carbene" complexes.¹¹ Similar reactions of W(CO)₆, Fe(CO)₅, and Ni(CO)₄ first with LiNR₂ (where R = CH₃ or C₂H₅) followed by (C₂H₅)₃O⁺ give analogous products, (CO)₅WC(OC₂H₅)NR₂, (CO)₄FeC-



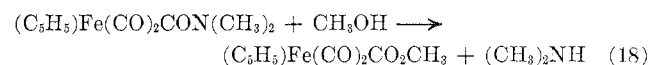
(OC₂H₅)NR₂, and (CO)₃NiC(OC₂H₅)NR₂.^{11,59} To date there have been no reports of (C₂H₅)₃O⁺ reactions with *uncharged* carbamoyl or alkoxy-carbonyl complexes.

Interconversion of Carbamoyl and Alkoxy-carbonyl Ligands.

Like the reaction of organic esters with amines, Re(CO)₅CO₂CH₃ reacts rapidly at room temperature with 1 equiv of methylamine as in eq 17.⁴⁹

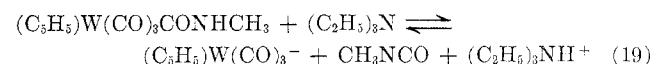


The reverse reaction, the conversion of a carbamoyl to an alkoxy-carbonyl group, has been accomplished by refluxing (C₅H₅)Fe(CO)₂CON(CH₃)₂ in CH₃OH for 1 hr²² (eq 18). In an ester interchange reaction, the

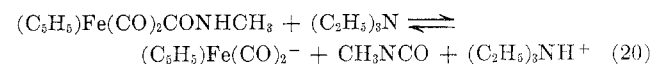


ethoxycarbonyl complex, [(C₆H₅)₃P]₂Pt(Cl)CO₂C₂H₅, reacts with methanol at 63° (12 hr) to give the corresponding methoxycarbonyl derivative.²⁹ In related reactions, it has been suggested⁶⁰ that the alkoxy-carbonyl complexes (C₅H₅)Fe(CO)₂CO₂CH₃ and Mn(CO)₅CO₂C₂H₅ react with H₂O to give carboxylic acid intermediates, (C₅H₅)Fe(CO)₂CO₂H and Mn(CO)₅CO₂H, which decompose with loss of CO₂ to the hydrides (C₅H₅)Fe(CO)₂H and Mn(CO)₅H.

With Bases. Triethylamine reacts rapidly at room temperature with the secondary carbamoyl complex (C₅H₅)W(CO)₃CONHCH₃ (eq 19¹). This is an equi-



librium reaction which can be displaced to the right or left (see eq 8) depending upon the reactant quantities present. Attempts to carry out the same reaction on (C₅H₅)Fe(CO)₂CONHCH₃ and [(C₆H₅)₃P]₂Pt(Cl)-CONHCH₃ showed no reaction. The lack of reaction in these cases is probably related to the stability of the products. For example, the reaction of (C₅H₅)Fe(CO)₂CONHCH₃ (eq 20) would yield the strongly



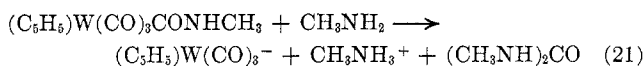
nucleophilic (C₅H₅)Fe(CO)₂⁻ which would favor the left side of eq 20. This is supported by the facility of the reverse reaction (eq 9).

If a primary amine such as CH₃NH₂ is used as the base in eq 19, the intermediate CH₃NCO reacts with excess amine to give the urea, and the overall reaction becomes¹

(58) L. Busetto and R. J. Angelici, *J. Amer. Chem. Soc.*, **90**, 3283 (1968); L. Busetto, U. Belluco, and R. J. Angelici, *J. Organometal. Chem.*, **18**, 213 (1968).

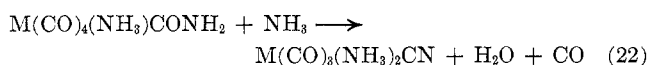
(59) E. Winkler, Ph.D. Dissertation, Technische Universität München, 1971.

(60) H. C. Clark and W. J. Jacobs, *Inorg. Chem.*, **9**, 1229 (1970).



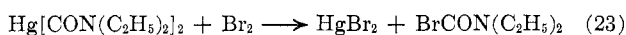
Although the analogous Mo complex also undergoes this reaction, $\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{CONHCH}_3$ does not, presumably for the same reasons that it does not react with $(\text{C}_2\text{H}_5)_3\text{N}$. The facile conversion of a carbamoyl group to an alkyl isocyanate or urea suggests that carbamoyl complexes may be intermediates in metal-catalyzed reactions of CO and alkylamines to form these organic compounds.

Dehydration to Cyano Complexes. Behrens and coworkers⁶¹ have observed the dehydration of the CONH_2 ligand under widely varying temperature conditions. For example, the reaction

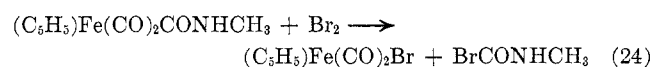


in liquid NH_3 proceeds at -45° for $\text{M} = \text{Mn}$, but 120° is required for the analogous Re complex. In addition to the main product, the manganese complex reaction also yields some $\text{Mn}(\text{CO})_3(\text{NH}_3)_2\text{NCO}$. The dehydration of $\text{Mn}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3](\text{NH}_3)\text{CONH}_2$ proceeds without the loss of CO to give $\text{Mn}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3](\text{NH}_3)\text{CN}$ in ether solution at -33° . Likewise $\text{Mn}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_5)_3]_2\text{CONH}_2$ is converted to $\text{Mn}(\text{CO})_3(\text{NH}_3)_2\text{CN}$ in liquid ammonia at 60° .

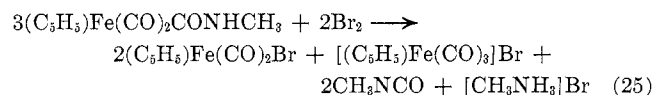
With Halogens. Cleavage of the Hg-C bond is reported⁶ in the reaction of $\text{Hg}[\text{CON}(\text{C}_2\text{H}_5)_2]_2$ with Br_2 (eq 23). The reaction of $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CONHCH}_3$



with Br_2 presumably also proceeds by initial bond cleavage⁶² (eq 24). The resulting carbamoyl bromide

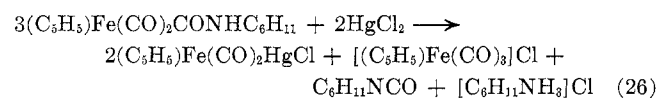


is known to decompose to HBr and CH_3NCO . This HBr would rapidly react (eq 13) with some of the starting carbamoyl complex to give $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_3^+$ and CH_3NH_3^+ . The overall reaction is



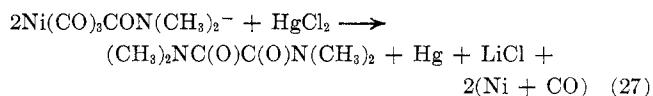
Thus the halogen reaction is another method (see eq 19) of converting carbamoyl complexes into alkyl isocyanates.

With Mercuric Chloride. Reaction of the cyclohexylcarbamoyl complex $(\text{C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{CONHC}_6\text{H}_{11}$ with HgCl_2 appears to proceed⁶² in much the same way as that with halogens. In this case, the Fe-C bond is cleaved with ClHg-Cl to give Fe-HgCl and Cl-C. Subsequent reaction of the carbamoyl chloride gives the overall reaction 26. In contrast, the reaction of



(61) H. Behrens, E. Lindner, D. Maertens, P. Wild, and R. Lampe, *J. Organometal. Chem.*, **34**, 367 (1972).

the anionic carbamoyl complex $\text{Ni}(\text{CO})_3\text{CON}(\text{CH}_3)_2^-$ with HgCl_2 proceeds quite differently¹⁰ (eq 27) to give



N,N,N',N'-tetramethyloxamide as the main organic product.

With Organic Halides. Both $\text{Hg}[\text{CON}(\text{C}_2\text{H}_5)_2]_2$ and $\text{Ni}(\text{CO})_3\text{CON}(\text{CH}_3)_2^-$ react with organic acid chlorides to give the simple amides $\text{RCON}(\text{CH}_3)_2$ resulting from removal of the $\text{N}(\text{CH}_3)_2$ group from the complex. With benzyl chloride the mercury complex⁶ gives only $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_2$, whereas benzyl bromide with the nickel complex⁶³ gives both $\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_3)_2$ and $\text{C}_6\text{H}_5\text{-CH}_2\text{CON}(\text{CH}_3)_2$. The nickel complex also reacts with *trans*- $\text{C}_6\text{H}_5\text{CH=CHBr}$, $\text{C}_6\text{H}_5\text{I}$, and 3-bromocyclohexene to give high yields of the product $(\text{RCON}(\text{CH}_3)_2)$ containing the $\text{CON}(\text{CH}_3)_2$ group in place of the halogen.

Other Reactions. In addition to the above reactions which have been definitely shown to involve carbamoyl or alkoxy-carbonyl complexes, there is a large number of metal-promoted reactions of carbon monoxide with amines or alcohols which very probably involve these types of complexes as intermediates. For example, Heck⁶⁴ has made extensive use of $\text{Hg-CO}_2\text{CH}_3$ complexes to generate very reactive $\text{Pd-CO}_2\text{CH}_3$ derivatives which on reaction with olefins yield methoxycarbonyl-substituted olefins $>\text{C}=\text{C}(\text{CO}_2\text{CH}_3)-$. Similar intermediates are presumably involved in the reaction⁶⁵ of organic halides (RX) with $\text{Ni}(\text{CO})_4$ and alkoxides (R'O^-) to give esters $\text{RCO}_2\text{R}'$.

There is an extensive literature of metal-catalyzed reactions of CO and amines to form organic isocyanates, formamides, and ureas.⁶⁶ For example, $\text{Mn}_2(\text{CO})_{10}$ catalyzes the reaction of primary alkylamines with CO to give dialkylureas and H_2 . Copper(II) catalyzes the reaction of amines and CO and oxygen to yield ureas and water.⁶⁷ The complex $(\text{RNH}_2)_2\text{PdCl}_2$ reacts with CO to give organic isocyanates (RNCO) and Pd metal.⁶⁸ The known existence of carbamoyl complexes of all of these metals suggests that carbamoyl complexes are probable intermediates in these reactions.

I am grateful to my coworkers for their major contributions to the ideas and results summarized here. I also very much appreciate the support of our research by the National Science Foundation, the Alfred P. Sloan Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

(62) W. Jetz and R. J. Angelici, *Inorg. Chem.*, **11**, 1960 (1972).

(63) S. Fukuoaka, M. Ryang, and S. Tsutsumi, *J. Org. Chem.*, **36**, 2721 (1971).

(64) R. F. Heck, *J. Amer. Chem. Soc.*, **93**, 6896 (1971), and references therein.

(65) E. J. Corey and L. S. Hegedus, *ibid.*, **91**, 1232 (1969).

(66) A. Rosenthal and I. Wender in "Organic Syntheses Via Metal Carbonyls," I. Wender and P. Pino, Ed., Interscience, New York, N. Y., 1968, p 405.

(67) W. Brackman, *Discuss. Faraday Soc.*, **46**, 122 (1968).

(68) E. W. Stern and M. L. Spector, *J. Org. Chem.*, **31**, 596 (1966).