(3) (a) G. Chandra and M. F. Lappert, *J. Chem. Soc. A*, 1940 (1968); (b) G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *ibid.*, 2550 (1970).
(4) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 1152 (1969).
(5) M. E. Volpin and I. S. Kolomnikov, *Organomet. React.*, **5**, 313 (1975).
(6) C. W. Newing, Ph.D. Thesis, University of London, 1971.
(7) M. H. Chisholm and M. Extine, *J. Am. Chem. Soc.*, **96**, 6214 (1974).
(8) M. H. Chisholm and M. Extine, *J. Chem. Soc., Chem. Commun.*, 438 (1975).
(9) J. Weidlein, U. Mueller, and K. Dehnicke, *Spectrochim. Acta, Part A*, **24**, 253 (1968).
(10) J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).
(11) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley-Interscience, New York, N.Y., 1970.
(12) C. G. Barraclough, D. C. Bradley, J. Lewis, and I. M. Thomas, *J. Chem. Soc.*, 2601 (1961); D. C. Bradley and A. H. Westlake, Proceedings of the Symposium on Coordination Chemistry, Tihany, Hungary, 1964.
(13) M. H. Chisholm, Ph.D. Thesis, University of London, 1969.
(14) M. Colapietro, A. Vaciago, D. C. Bradley, M. B. Hursthouse, and I. F. Rendall, *J. Chem. Soc., Dalton Trans.*, 1052 (1972).
(15) S. J. Lippard, *Prog. Inorg. Chem.*, **8**, 109 (1967).
(16) E. L. Muetterties, *Inorg. Chem.*, **12**, 1963 (1973); **13**, 1011 (1974).
(17) A. N. Bhat, R. C. Fay, D. F. Lewis, A. F. Lindmark, and S. H. Strauss, *Inorg. Chem.*, **13**, 886 (1974).
(18) R. C. Fay, D. F. Lewis, and J. R. Weir, *J. Am. Chem. Soc.*, **97**, 7179 (1975).
(19) E. L. Muetterties and C. M. Wright, *Q. Rev., Chem. Soc.*, **21**, 109 (1967).
(20) G. A. Barclay, T. M. Sabine, and J. C. Taylor, *Acta Crystallogr.*, **19**, 205 (1965).
(21) E. Lustig, W. R. Benson, and N. Duy, *J. Org. Chem.*, **32**, 851 (1967).
(22) F. A. Cotton and J. G. Norman, Jr., *J. Am. Chem. Soc.*, **94**, 5697 (1972).
(23) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4683 (1976).
(24) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4477 (1976).
(25) D. C. Bradley, M. H. Chisholm, C. E. Heath, and M. B. Hursthouse, *Chem. Commun.*, 1261 (1969).
(26) M. H. Chisholm and M. W. Extine, unpublished results.
(27) M. Boudart, "Kinetics of Chemical Processes", Prentice-Hall, Englewood Cliffs, N.J., 1968, p 89.
(28) (a) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **5**, 233 (1966); (b) A. C. Adams and E. M. Larsen, *ibid.*, **5**, 228 (1966).
(29) C. D. Garner and S. C. Wallwork, *J. Chem. Soc. A*, 1496 (1966).
(30) D. C. Bradley and I. M. Thomas, *J. Chem. Soc.*, 3857 (1960).
(31) D. C. Bradley and M. H. Gitlitz, *J. Chem. Soc. A*, 980 (1969).
(32) D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, **40**, 449 (1962).
(33) D. C. Bradley and I. M. Thomas, *Can. J. Chem.*, **40**, 1355 (1962).
(34) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.

Reactions of Transition Metal–Nitrogen σ Bonds. 4.[1] Mechanistic Studies of Carbon Dioxide Insertion and Carbon Dioxide Exchange Reactions Involving Early Transition Metal Dimethylamido and *N,N*-Dimethylcarbamato Compounds

Malcolm H. Chisholm* and Michael W. Extine

Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received May 28, 1976*

Abstract: The reactions between $M(NMe_2)_n$ (where M = Ti, Zr, V and n = 4, Nb, Ta and n = 5, and W, n = 6) and CO_2 ($\leq n$ equiv) have been studied. The mixed dimethylamido-dimethylcarbamato compounds TiN_2L_2, $TiNL_3$, VNL_3, TaN_2L_3, and WN_3L_3 (N = NMe_2, L = O_2CNMe_2) have been isolated and characterized by a number of physicochemical techniques. The reaction between $Ti(NMe_2)_4$ and CO_2 leads to rapid attainment of the thermodynamically favored distribution of products $TiN_{4-n}L_n$. By appropriate labeling experiments the compounds $TiN_{4-n}L_n$ (n = 0–4) are shown to be labile toward ligand (both N and L) exchange reactions. $MN_{5-n}L_n$, where M = Nb or Ta and n = 0–5, are notably less labile toward ligand exchange reactions. Carbon dioxide exchange reactions, $ML^* + {}^{12}CO_2 \rightleftarrows ML + {}^{13}CO_2$, where $L^* = O_2{}^{13}CNMe_2$, proceed via a catalyzed reaction sequence involving fortuitous amine which is present in solutions of ML_n compounds: (i) ${}^{12}CO_2 + HNMe_2 \rightleftarrows HO_2{}^{12}CNMe_2$ (ii) $ML^* + HO_2{}^{12}CNMe_2 \rightleftarrows ML + HO_2{}^{13}CNMe_2$. Carbon dioxide exchange reactions, $MO_2{}^{13}CNMe_2 + MO_2{}^{12}CNR_2 \rightleftarrows MO_2{}^{12}CNMe_2 + MO_2{}^{13}CNR_2$, occur via the same mechanism due to the presence of both fortuitous CO_2 and amine. The insertion reactions between $W(NMe_2)_6$ and $W_2(NEt_2)_4Me_2$ and carbon dioxide, which give $W(NMe_2)_3(O_2CNMe_2)_3$ and $W_2(O_2CNEt_2)_4Me_2$, respectively, have been shown to occur via an amine catalyzed mechanism: (i) $CO_2 + HNR_2 \rightleftarrows HO_2CNR_2$ (ii) $MNR_2 + HO_2CNR_2 \rightarrow MO_2CNR_2 + HNR_2$.

A fundamental reaction in coordination chemistry is the so-called insertion reaction.[2–5] This may be represented by the generalized equation 1 in which an unsaturated molecule, un, is inserted into a metal-ligand bond,

$$M\text{-}L + un \rightleftarrows M\text{-}un\text{-}L \qquad (1)$$

Such reactions involving unsaturated hydrocarbons, carbon monoxide, metal-hydrogen, and metal-carbon (alkyl) bonds are involved in a multitude of catalytic processes including Zeigler-Natta polymerizations, hydrogenations, and hydroformylations. Studies of metal-carbon (alkyl) insertion reactions suggest that they may be described as ligand migration reactions: both the unsaturated ligand (CO, C=C, C≡C) and the alkyl ligand are coordinated to, or at least have some affinity for, the metal in the transition state. Insertion of CO and RC≡CR into M—*C bonds has been found[6] to occur with retention of stereochemistry at *C.

As part of a general study of the reactions of transition metal-nitrogen σ bonds we have examined the reactions between early transition metal dimethylamides $M(NMe_2)_n$ and carbon dioxide ($\geq n$ equiv). For titanium, zirconium, and vanadium (n = 4) and niobium and tantalum (n = 5) the *N,N*-dimethylcarbamato compounds $M(O_2CNMe_2)_n$ are formed according to eq 2.

$$M(NMe_2)_n + nCO_2 \rightarrow M(O_2CNMe_2)_n \qquad (2)$$

Similarly the dinuclear compound $W_2(NMe_2)_6$ reacted with CO_2 to give $W_2(O_2CNMe_2)_6$, retaining the W-W triple bond. An exception to this apparently general reaction 2 was found in the reaction of $W(NMe_2)_6$ which gave $W(NMe_2)_3$-

$(O_2CNMe_2)_3$, even in the presence of excess CO_2. Characterization of these carbamato compounds ML_n (L = O_2CNMe_2) was given in the previous paper in which we also reported their liability towards CO_2 exchange reactions which may be represented by eq 3 and 4

$$ML^* + {}^{12}CO_2 \rightleftarrows ML + {}^{13}CO_2 \quad (3)$$

$$ML^* + ML' \rightleftarrows ML'^* + ML \quad (4)$$

where L = $O_2{}^{12}CNMe_2$, L* = $O_2{}^{13}CNMe_2$, L′ = $O_2{}^{12}CN(CD_3)_2$ and L′* = $O_2{}^{13}CN(CD_3)_2$.

In addition to the CO_2 exchange reactions 3 and 4 we also observed ligand exchange reactions 5.

$$ML + M'L' \rightleftarrows ML' + M'L \quad (5)$$

where M ≠ M′ and L = O_2CNMe_2 and L′ = $O_2CN(CD_3)_2$.

Insertion reactions involving M-NR_2 bonds are well known[7,8] and have often been presumed to occur via attack of the unsaturated moiety (CO_2, CS_2, MeCN, etc) at the nucleophilic lone pair of the coordinated amide ligand.[7,9] The facility of reactions 3 and 4 led us to suggest[10,11] a mechanism for CO_2 exchange involving a reversible insertion reaction 6.

$$L_{n-1}MO_2CNMe_2 \rightleftarrows L_{n-1}MNMe_2 + CO_2 \quad (6)$$

Although eq 6 seemed eminently plausible and was analogous to known reversible insertion reactions involving metal-hydrogen and metal-carbon (alkyl) bonds, we could not rule out all alternate mechanisms.

Equation 6 poses certain questions. For example, can compounds of the type $L_{n-1}MNMe_2$ or in general $L_{n-m}M(NMe_2)_m$ be isolated and for the reaction between $M(NMe_2)_n$ and nCO_2 are there n readily reversible steps? In order to answer these questions we initiated a study of reactions of type 7.

$$M(NMe_2)_n + mCO_2 \rightarrow M(NMe_2)_{n-m}L_m \quad (7)$$

where $m = 1, 2, \ldots, n - 1$.

In this paper we report our studies of eq 7. We show that extrusion of CO_2 from a carbamate ligand, as indicated by the reversible insertion reaction 6, does not occur readily and is not responsible for the CO_2 exchange reactions 3 and 4. The insertion reactions 2 and the exchange reactions of type 3 are catalyzed by the presence of fortuitous free amine. Equation 4 occurs by the same mechanism as 3 due to the presence of fortuitous free CO_2.

Results and Discussion

Throughout this paper we use the following abbreviations: L = $O_2{}^{12}CNMe_2$, L* = $O_2{}^{13}CNMe_2$, L′ = $O_2{}^{12}CN(CD_3)_2$, L′* = $O_2{}^{13}CN(CD_3)_2$, N = NMe_2, N′ = $N(CD_3)_2$.

^{1}H NMR Studies of Reaction 7. Reactions 7 were easily carried out on a small scale (0.01-0.1 mmol) in benzene or toluene-d_8 in sealed NMR tubes and were followed via ^{1}H NMR spectroscopy. A general conclusion which can be drawn from this work is that the successive insertion of CO_2 into M-NMe_2 groups leads to increased deshielding of the remaining M-NMe_2 protons: $\delta[M(NMe_2)_{n-1}L_{m+1}] > \delta[M(NMe_2)_nL_m]$. This is most pronounced for the compound WN_3L_3 and may in general be attributed to increased N to M π-bonding which results from replacing a NMe_2 ligand by the weaker π-donating and more electronegative O_2CNMe_2 ligand. This reasoning is supported by the structural data on WN_3L_3 which reveals very short W-N bond distances: compare W-N 1.922 (7) Å in WN_3L_3 with W-N 2.032 (25) Å in $W(NMe_2)_6$.[9] Of course many factors influence ^{1}H chemical shifts. The correlation of δ(M-N*Me*$_2$) with successive CO_2 insertion is an empirical observation for MN_nL_m compounds. In addition to the chemical shift of the M-N*Me*$_2$ protons, a given compound MN_nL_m is identified by the N to L methyl integral ratio, n/m.

Table I. ^{1}H NMR Data[a] for $W(NMe_2)_{6-n}L_n$[b,c]

n	δ(N*Me*$_2$)[d]	δ(O_2CN*Me*$_2$)[d]
0	3.33	
1	3.85	2.86
2	4.21	2.86
3	4.75	2.82

[a] Spectra recorded at 40 °C, 60 MHz. [b] Observed during the reaction: $W(NMe_2)_6 + 2CO_2$, in benzene: t = 30 min. [c] L = O_2CNMe_2. [d] δ in ppm downfield from HMDS.

Table II. ^{1}H NMR Data[a] for $M(NMe_2)_{5-n}L_n$ (M = Nb, Ta)[b]

	M = Nb		M = Ta	
Compound[c]	δ(N*Me*$_2$)[d]	δ(O_2CN-Me_2)[d]	δ(N*Me*$_2$)[d]	δ(O_2CN-*Me*$_2$)[d]
$M(NMe_2)_5$	3.09		3.15	
$M(NMe_2)_4L$	3.22	2.62	3.35	2.54
$M(NMe_2)_3L_2$[e]				
$M(NMe_2)_2L_3$	3.59	2.63	3.75	2.56
$M(NMe_2)L_4$	3.98	2.58	4.07	2.55
ML_5		2.63		2.57

[a] Spectra recorded at 40 °C, 60 MHz. [b] Observed during the reactions $M(NMe_2)_5 + nCO_2$ (n = 1-5), carried out in toluene-d_8, at 25 °C. [c] L = O_2CNMe_2. [d] δ in ppm downfield from HMDS. [e] $M(NMe_2)_3L_2$ not present in detectable concentrations.

Although MN_mL_n compounds may exist as isomers in solution and may contain inequivalent NMe_2 and O_2CNMe_2 methyl groups, none appears to do so on the *^{1}H NMR time scale* at 40 °C. While we have carried out variable temperature ^{1}H NMR studies on all isolable MN_mL_n compounds (discussed later), no attempt was made to do so for MN_mL_n compounds observed only in situ.

$W(NMe_2)_6 + nCO_2$. ^{1}H NMR spectra of the reaction between WN_6 and $2CO_2$ in benzene revealed after 30 min at 25 °C the presence of WN_6 and WN_3L_3 as well as other resonances (see Table I) which we assign to the compounds WN_5L and WN_4L_2 on the basis of the reasoning outlined above. The intermediate compounds were unstable and decomposed in solution at 25 °C. No attempts were made to isolate or further characterize these species.

$M(NMe_2)_5 + nCO_2$ (M = Nb, Ta). Reactions of $M(NMe_2)_5$ (M = Nb, Ta) with 1, 2, 3, or 4 equiv of CO_2 yielded solutions containing mixtures of $M(NMe_2)_{5-n}L_n$ (n = 1-5). See Table II. Of course, the distribution of products was dependent upon the amount of CO_2 used. See Table III. The product distributions obtained for the Nb and Ta compounds were similar. However, $TaN_{5-n}L_n$ are more stable (only slight decomposition observed after 72 h at 25 °C) than the corresponding $NbN_{n-5}L_n$ compounds (significant decomposition observed after 72 h at 25 °C). It is interesting that the compounds MN_3L_2 are not observed, even in solutions containing both MN_2L_3 and MN_4L. This indicates that eq 8 does not occur, which may be due either to kinetic or thermodynamic factors.

$$MN_2L_3 + MN_4L \rightarrow MN_3L_2 \quad (8)$$

We have observed that the reaction $TaN_5 + 4.2CO_2$ yields an initial mixture of TaN_2L_3, $TaNL_4$, and TaL_5 and that the

Table III. Product Distribution as a Function of Time for the Reaction $TaN_5^a + nCO_2^b$

		Product distribution (mol %)[c]					
n	Time, h	TaN_5	TaN_4L	TaN_3L_2	TaN_2L_3	$TaNL_4$	TaL_5
1.1	0.5	59	7	0	32	2	0
	72	56	11	0	33	0	0
2.1	0.5	28	12	0	58	3	0
	72	23	16	0	58	3	0
4.2	0.5	1	2	0	23	29	45
	72	0	0	0	11	63	27

[a] N = NMe_2; reaction carried out in toluene-d_8 at ca. 25 °C. [b] See experimental section for detailed description of procedure. [c] Product distribution determined via ^1H NMR.

concentration of $TaNL_4$ slowly increases, indicating that eq 9 occurs.

$$TaL_5 + TaN_2L_3 \rightarrow TaNL_4 \qquad (9)$$

The product distribution at short reaction times seems to be under kinetic control and at longer reaction times thermodynamic control begins to be seen. Unfortunately, the $MN_{5-n}L_n$ compounds were not all sufficiently stable in solution to verify that thermodynamic control was ever reached.

Inspection of Table III led us to conclude that no single $MN_{5-n}L_n$ compound was favored by kinetic and/or thermodynamic factors. Thus, we were pessimistic about ever isolating individual $TaN_{5-n}L_n$ compounds. However, we have isolated TaN_2L_3 from eq 10 and 11. The lower solubility in hexane of TaN_2L_3 relative to TaN_5, TaN_4L, and TaN_3L_2 allows its isolation from eq 10 and 11. The properties of TaN_2L_3 will be discussed subsequently.

$$TaN_5 + 3CO_2 \xrightarrow{\text{toluene}} TaN_2L_3 \qquad (10)$$

$$TaN_5 + 2CO_2 \xrightarrow{\text{hexane}} TaN_2L_3\downarrow \qquad (11)$$

In a previous paper we discussed evidence for eq 6 based on the observation of $NbNL_4$ in solutions of NbL_5. At that time we felt that $NbNL_4$ arose from NbL_5 via eq 6. This is not the case. During the preparation of NbL_5, small amounts (<1%) of $NbNL_4$ often coprecipitate with the NbL_5. This product, when redissolved in benzene, yields a very pale yellow solution (due to the $NbNL_4$) which turns colorless upon addition of CO_2. We also observed that repeated degassing of solutions of NbL_5 yielded peaks (in the carbamato region) in the ^1H NMR spectrum which we assigned to $NbNL_4$. However, we now know that solutions of NbL_5 are somewhat unstable and the repeated degassing enhanced the rate of decomposition.

$Ti(NMe_2)_4 + nCO_2$. The reactions $TiN_4 + nCO_2$ (n = 1, 2, and 3) have also been followed by ^1H NMR spectroscopy. See Tables IV and V. All compounds, $TiN_{4-n}L_n$, have been observed. Furthermore, the product distribution is under thermodynamic control. The reactions, $TiN_4 + 2CO_2$ and $TiN_4 + 3CO_2$, yield only TiN_2L_2 and $TiNL_3$, respectively. We have isolated and characterized these two compounds (see below). However, for the reaction, $TiN_4 + 1CO_2$, a mixture of TiN_4, TiN_3L, and TiN_2L_2 is observed (ca. 1:6:1 ratio). That these products are in equilibrium as indicated by eq 12, was demonstrated by the reaction between TiN_4 and TiN_2L_2,

$$TiN_2L_2 + TiN_4 \rightleftarrows 2TiN_3L \qquad K_{eq} = 35 \qquad (12)$$

which rapidly yielded the same product distribution as the $TiN_4 + 1CO_2$ reaction. Although it is possible to prepare TiN_3L in situ in ca. 70% yields it was not possible to isolate it as a pure compound because of the equilibrium, eq 12, and the fact that TiN_2L_2 preferentially crystallizes from such mixtures

Table IV. ^1H NMR Data[a] for $Ti(NMe_2)_nL_{4-n}$ and $Ti(NMe_2)_2(O_2CNEt_2)_2$

Compound	Solvent	$\delta(NMe_2)^b$	$\delta(O_2CNR_2)^b$
$Ti(NMe_2)_4$	C_6H_6	3.03	
$Ti(NMe_2)_3L$	C_6H_6	3.23	2.47
$Ti(NMe_2)_2L_2$	C_6H_6	3.46	2.45
$Ti(NMe_2)L_3$	C_6H_6	3.57	2.46
	CH_2Cl_2	3.41	2.90
TiL_4	C_6H_6[c]		2.33
	CH_2Cl_2		2.85
$Ti(NMe_2)_2(O_2CNEt_2)_2$	C_6H_6	3.44	3.03 (q), 0.80 (t)[d]

[a] Spectra recorded at 40 °C, 60 MHz, L = O_2CNMe_2. [b] δ in ppm downfield from HMDS. [c] Sparingly soluble. [d] $^3J_{H-H}$ = 7 Hz.

Table V. Product Distribution for the Reaction: $TiN_4 + nCO_2^a$

		mol % $TiN_{4-n}L_n$				
n	Time, h	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
1.0	20[b]	13	75	13	0	0
1.15	0.5	7	71	22	0	0
	40[b]	7	72	22	0	0
2.0[c]	[b]	0	0	100	0	0
3.0[c]	[b]	0	0	0	100	0
3.1	12[b]	0	0	0	93	8

[a] Carried out in benzene at 25 °C, monitored via ^1H NMR; N = NMe_2, L = O_2CNMe_2. [b] No changes in product distribution seen at longer times. [c] ^1H NMR spectrum of the pure compound, TiN_2L_2 or $TiNL_3$, respectively, dissolved in benzene.

(see Experimental Section). In fact, we have established that a number of reactions related to eq 12 are facile (complete in <5 min at 25 °C).

An example is shown in eq 13

$$2TiNL_3 + TiN_4 \rightarrow 3TiN_2L_2 \qquad (13)$$

In general, mixing any $TiN_{4-n}L_n$ ($n \leqslant 4$) and $TiN_{4-m}L_m$ ($m \leqslant 4$) in benzene will rapidly yield the expected thermodynamically controlled product distribution. Reactions of TiL_4 and $TiN_{4-n}L_n$ react similarly but are somewhat slower because of the limited solubility of TiL_4 in benzene.

These observations clearly define the free energy profile for the successive insertion reactions between CO_2 and TiN_4 and demonstrate that thermodynamic control is readily attained due to the kinetic lability of $TiN_{4-n}L_n$.

$MN_{n-m}L_m$ Compounds. Synthesis. TiN_2L_2, $TiNL_3$, VNL_3, and TaN_2L_3 were prepared similarly. An accurately (±1%) measured aliquot of CO_2 (m equiv) was slowly allowed to react

Table VI. Characterization of Some Mixed Dialkylaminato-Dialkylcarbamato Compounds

Compound[b]	Color	C Found (calcd)	H Found (calcd)	N Found (calcd)	Mol[a] wt Found (calcd)
$Ti(NMe_2)_2L_2$	Red	38.26 (38.47)	7.59 (7.75)	17.68 (17.95)	307 ± 10 (312)
$Ti(NMe_2)L_3$	Brown	36.98 (37.09)	6.94 (6.79)	15.53 (15.73)	346 ± 10 (356)
$Ti(NMe_2)_2(O_2CNEt_2)_2$	Red	45.41 (45.65)	8.66 (8.76)	15.07 (15.21)	
$V(NMe_2)L_3$	Red	36.55 (36.77)	6.95 (6.73)	15.69 (15.60)	322 ± 20 (359)
$Ta(NMe_2)_2L_3$	White	29.38 (29.27)	5.55 (5.67)	13.04 (13.13)	

[a] Determined cryoscopically in benzene. [b] L = O_2CNMe_2.

with a benzene or toluene solution of TiN_4, VN_4, or TaN_5. Too rapid addition of the CO_2 resulted in formation of some TiL_4, VL_4, or NbL_5 which precipitated. Usually a slight deficiency of CO_2 was used, because the solubility of $MN_{m-n}L_n$ decreases as n increases; the least soluble component may be isolated by crystallization. This is the reason that reaction 11 yielded TaN_2L_3. TaN_5 and TaN_4L are quite soluble in hexane, whereas TaN_2L_3 is not.

Characterization. Analytical data for TiN_2L_2, $TiNL_3$, $TiN_2(O_2CNEt_2)_2$, VNL_3, and TaN_2L_3 are shown in Table VI. ^1H NMR data are shown in Tables II and IV. These compounds are very sensitive towards moisture and oxygen (VNL_3) but appear to be stable indefinitely when stored in vacuo or under nitrogen. All compounds are soluble in benzene or toluene. TiN_2L_2 and $TiN_2(O_2CNEt_2)_2$ are also soluble in hexane; TaN_2L_3 is slightly soluble in hexane. Molecular weight determinations indicate that TiN_2L_2, TaN_2L_3 and VNL_3 are monomeric in benzene. The compounds TiN_2L_2 and $TiNL_3$ showed molecular ions M^+ and ions $(M - m)^+$ corresponding to the loss of 44 and 88 mass units in the mass spectrum. Mass spectra of TiN_2L_2* and $TiN_2(O_2CNEt_2)_2$ showed loss of NMe_2 and NEt_2, respectively, from the molecular ion. Apparently the NR_2 moiety is eliminated from the carbamato ligand in the mass spectrometer. For the compound VNL_3 a molecular ion was not observed, the parent ion corresponded to $(M - 44)^+$. This is not surprising since the compound $TiNL_3$ yielded only a weak molecular ion and an intense ion corresponding to $(M - 44)^+$.

Infrared Spectra. TiN_2L_2 and $TiNL_3$ exhibit strong bands at 1575 cm^{-1} which we assign to $\nu_{str}(O_2CN)$ of the bidentate O_2CNMe_2 moiety.[1] Bands at 433-453 cm^{-1} may be due to $\nu_{str}(M-O)$. We assign the bands at ca. 582 cm^{-1} to $\nu(M-N)$. TaN_2L_3 exhibits three bands between 1608 and 1645 cm^{-1} and may contain both bidentate and monodentate O_2CNMe_2 ligands. The asymetric band at 430 cm^{-1} and the band at 559 cm^{-1} can be assigned to $\nu(M-O)$ for bidentate and monodentate carbamate ligands, respectively. These assignments are based on the arguments presented for ML_4, ML_5, and WN_3L_3 in the preceding paper.[1]

$Ti(NMe_2)(O_2CNMe_2)_3$. $TiNL_3$ is a brown crystalline solid. Its infrared spectra ($\nu_{str}(O_2CN)$ 1576 cm^{-1}) suggest that the carbamate ligands are bidentate and that the titanium atom is seven-coordinated. ^1H NMR spectra show only two widely separated resonances in 1:3 integral ratio, assigned to NMe_2 and O_2CNMe_2 groups, respectively (see Table IV), even as low as −80 °C (^1H NMR at 60 MHz in toluene-d_8). From these observations, and from considerations of the stereochemical nonrigidity of other carbamato compounds, cf.[1] NbL_5, it is not possible to predict a geometry for the $TiN(O-O)_3$ moiety.[12] However, it could be similar to the $TiClS_6$ moiety of $TiCl(S_2CNMe_2)_3$.[13]

$Ti(NMe_2)_2(O_2CNMe_2)_2$. TiN_2L_2 is a red crystalline solid. Its infrared spectrum ($\nu_{str}(O_2CN)$ 1575 cm^{-1}) suggested the presence of bidentate ligands, which together with its monomeric nature (Table VI) indicated a TiN_2O_4 moiety. To verify this prediction we obtained a single-crystal x-ray structural determination.

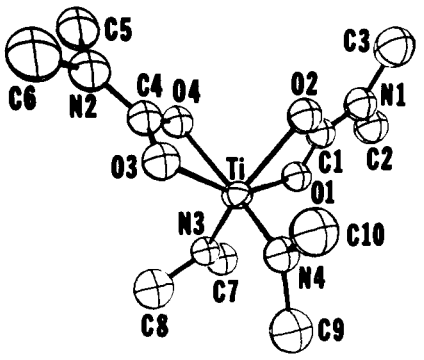


Figure 1. A view of the $Ti(NMe_2)_2(O_2CNMe_2)_2$ molecule showing 50% probability ellipsoids and the atomic numbering scheme.

Table VII. Bond Distances (Å) and Bond Angles (deg) for $Ti(NMe_2)_2(O_2CNMe_2)_2$[a]

Bond distances[b]		Bond angles[b]	
Ti-O1	2.086 (4)	O1-Ti-N4	107.6 (2)
Ti-O2	2.149 (4)	O2-Ti-O3	95.3 (2)
Ti-O3	2.030 (4)	O2-Ti-O4	82.6 (2)
Ti-O4	2.197 (4)	O2-Ti-N3	151.2 (2)
Ti-N3	1.878 (5)	O2-Ti-N4	93.2 (2)
Ti-N4	1.888 (5)	O3-Ti-O4	62.1 (2)
O1-C1	1.273 (7)	O3-Ti-N3	109.8 (2)
O2-C1	1.264 (7)	O3-Ti-N4	93.3 (2)
O3-C4	1.301 (7)	O4-Ti-N3	96.6 (2)
O4-C4	1.249 (7)	O4-Ti-N4	154.3 (2)
N1-C1	1.349 (8)	N3-Ti-N4	99.0 (2)
N1-C2	1.485 (9)	C1-N1-C2	119.4 (6)
N1-C3	1.477 (9)	C1-N1-C3	119.9 (6)
N2-C4	1.354 (8)	C2-N1-C3	120.6 (6)
N2-C5	1.489 (9)	C4-N2-C5	119.8 (6)
N2-C6	1.446 (9)	C4-N2-C6	122.1 (6)
N3-C7	1.466 (8)	C5-N2-C6	118.0 (6)
N3-C8	1.471 (9)	C7-N3-C8	112.4 (5)
N4-C9	1.500 (8)	C9-N4-C10	112.0 (5)
N4-C10	1.470 (8)	O1-C1-O2	118.1 (5)
		O1-C1-N1	119.7 (6)
Bond angles[b]		O2-C1-N1	122.2 (6)
O1-Ti-O2	61.8 (2)	O3-C4-O4	117.9 (6)
O1-Ti-O3	149.1 (2)	O3-C4-N2	118.6 (6)
O1-Ti-O4	92.8 (2)	O4-C4-N2	123.4 (6)
O1-Ti-N3	89.6 (2)		

[a] For complete details see supplementary data. [b] Numbers in parentheses are estimated standard deviations in the least significant digit.

An ORTEP view of the molecular structure is shown in Figure 1 and the pertinent bond distances and bond angles are given in Table VII. The C_2NCO_2Ti and C_2NTi moieties are essentially planar and the Ti-N bonds (av = 1.883 (5) Å) are ca. 0.24 Å shorter than the Ti-O bonds (av = 2.12 (6) Å). The TiN_2O_4 moiety is a severely distorted octahedron with cis ni-

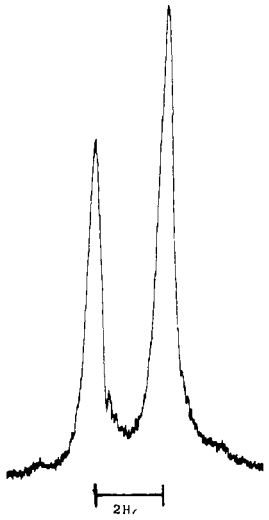


Figure 2. ^{1}H NMR spectrum in the O_2CNMe_2 region of the reaction between $Ti(NMe_2)(O_2CNMe_2)_3$ and $Ti(O_2{}^{13}CN(CD_3)_2)_4$ in CH_2Cl_2; t = 10 min, demonstrating ligand exchange in the absence of $^{13}CO_2$ scrambling; no further change occurs with time. The high field resonance is due to $TiL_nL'_{4-n}$.

trogens (N-Ti-N = 99.0 (2)°) and has approximate C_2 symmetry. Furthermore, the Ti-O2 and Ti-O4 bonds (av = 2.17 (2) Å), which are "trans" to nitrogen, are significantly longer than the Ti-O1 and Ti-O3 bonds (av = 2.06 (3) Å), which are "trans" to oxygen. A similar trans influence has been observed for $W(NMe_2)_3(O_2CNMe_2)_3$.[9]

The dynamical behavior of some stereochemically similar compounds, $Ti(acac)_2X_2$ (X = OR, $\frac{1}{2}[OCH_2CMe_2CH_2O]$, and Cl), has been studied by ^{1}H NMR spectroscopy.[14] These molecules apparently adopt a cis configuration with C_2 symmetry in solution. The acac methyl groups are inequivalent on the ^{1}H NMR time scale below ca. 30 °C. The barrier to their interconversion is ca. 16 kcal/mol. These molecules can be viewed as twin bladed propellors and "compelling evidence" [15] indicates that reversal of helicity is the mechanism for stereoisomerization. This may be achieved by rotations about the metal-acac centroids.

Based on its solid state structure, TiN_2L_2 should exhibit similar behavior. However, the NMe_2 and O_2CNMe_2 resonances remain singlets as low as −100 °C (at 100 MHz in toluene-d_8). There are several possible explanations for this observation (1) the two types of methyl groups are accidentally magnetically degenerate, (2) the "reversal of helicity" is much more facile because the Me_2NCO_2 ligand is much smaller than the acac ligand, or (3) the molecule adopts a different configuration in solution, *trans*-$TiN_2(O\text{-}O)_2$, which has equivalent methyl groups. Either of the first two possibilities seems eminently reasonable, but we cannot eliminate the third possibility.

Finally, we note that the $Ti(NMe_2)_2$ group is also a twin bladed propellor and thus, in the dynamical solution behavior of TiN_2L_2, rotations about the Ti-N bonds should also be considered. Rotation about M-NR_2 bonds is generally facile but has been frozen out on the NMR time scale for $M_2(NR_2)_6$[16] (M = Mo and W) and $Ti(NSi_2Me_6)_3Cl$.[17]

$Ta(NMe_2)_2(O_2CNMe_2)_3$. Variable temperature ^{1}H NMR studies of TaN_2L_3 in toluene-d_8 indicate an interesting dynamical solution behavior. The high temperature spectrum consists of single resonances for the N and L methyl groups. At low temperatures (ca. −70 °C) we observed two N and three L methyl resonances, all of equal intensity. An interpretation of these results awaits an x-ray structural determination of this compound.[12]

$V(NMe_2)(O_2CNMe_2)_3$. The only experimental data we have concerning this compound, beyond those already discussed, is its room temperature ESR spectrum. Room temperature ESR spectra of VNL_3 in pentane or toluene show eight lines of near equal intensity due to coupling to ^{51}V (I = $\frac{7}{2}$ 100% abundance), g_{av} = 1.976 and A_{av} = 74 G (at 9.526 GHz).

The Question of CO_2 Deinsertion. If the mechanism of CO_2 exchange involves the deinsertion of CO_2 as shown in eq 6, then any MNL_{n-1} compound *must* undergo a facile CO_2 exchange reaction as depicted by eq 14.

$$L_{n-1}MN + ML'^*_n \rightleftarrows L_{n-1}ML^* + MN'L'^*_{n-1} \quad (14)$$

Having isolated $TiNL_3$ we were in a position to test for the existence of eq 6. We carried out reaction 15 as an NMR tube experiment.

$$TiNL_3 + TiL'^*_4 \quad (15)$$

To our surprise, CO_2 exchange did *not* occur, only facile ligand exchange was observed. This result is shown in Figure 2. This observation clearly precludes a mechanism for eq 3 or 4 based on eq 6. Furthermore, it indicates that eq 4 must occur either (i) by the same mechanism as eq 3, due to the presence of fortuitous CO_2, or (ii) by an entirely different mechanism. In an attempt to clarify this issue, we carried out reaction 16 in the presence and absence of the CO_2 scavenger, $TiNL_3$.

$$TiL_4 + TiL'^*_4 \quad (16)$$

Trace amounts (ca. 1 mol %) of $TiNL_3$ were sufficient to inhibit CO_2 exchange for eq 16. See Figure 3. After an induction period of ca. 10 h, during which time the scavenger was apparently consumed, CO_2 exchange occurred. Reaction 4 must occur by the same mechanism as 3, due to the presence of fortuitous CO_2. Presumably the latter arises from trace decomposition of ML_n.

Although eq 6 is clearly not responsible for eq 3 and 4, deinsertion must occur as the microscopic reverse of insertion. However, it could occur at an insignificant rate. Additional reactions 17 through 21 were carried out at 25 °C and monitored (via ^{1}H NMR spectroscopy) for as long as 6 days.

$$TiN_4 + TiN'_2L'^*_2 \quad (17)$$

$$TiN_2L_2 + TiN'_2L'^*_2 \quad (18)$$

$$TiNL_3 + TiN'_2L'^*_2 \quad (19)$$

$$TaN'_5 + NbL_5 \quad (20)$$

$$TaN_2L_3 + TaL'^*_5 \quad (21)$$

CO_2 exchange, as predicted by deinsertion 6, was *never* observed. Ligand exchange was facile for 17 and 19 and slow for 20 and 21. For reaction 18 ligand exchange is not observable by ^{1}H NMR spectroscopy.

The Mechanism of CO_2 Exchange. Equilibrium 6 had been proposed mainly on the basis of the facility of eq 4 and the fact that CO_2 exchange for WN_3L_3 was approximately zeroth order in CO_2. Having demonstrated that eq 4 does not occur via eq 6, we felt it necessary to reexamine the CO_2 exchange reaction for WN_3L_3. Reaction 22 was carried out (preparation of $W(N(CD_3)_2)_3(O_2CNMe_2)_3$ is given in the experimental section) and monitored via ^{1}H NMR spectroscopy. See Figure 4.

$$WN'_3L_3 + \text{excess}\,{}^{13}CO_2 \rightarrow WN'_3L^*_3 + {}^{12}CO_2 \quad (22)$$

We observed that CO_2 exchange occurred *without* interchanging $N(CD_3)_2$ and NMe_2 groups. This result clearly eliminates CO_2 deinsertion 23 as well as CO_2 insertion 24 as the mechanism of CO_2 exchange for WN_3L_3. Equation 23 and 24 would scramble the dimethylamide groups.

$$WN'_3L_3 \rightleftarrows WN'_3NL_2 + CO_2 \quad (23)$$

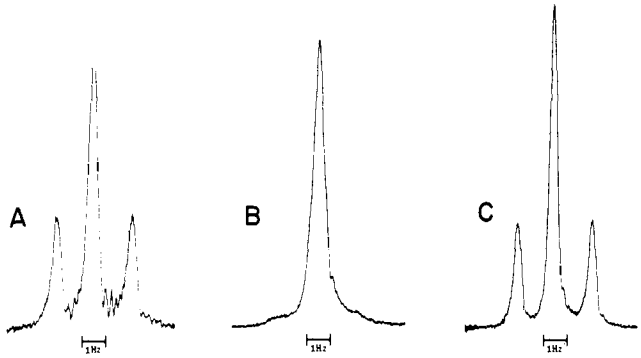
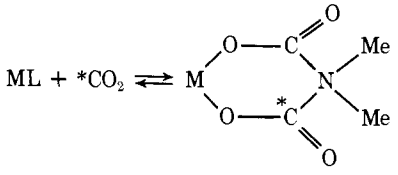


Figure 3. ^{1}H NMR spectra of the O_2CNMe_2 region: (A) $Ti(O_2CNMe_2)_4$ + $Ti(O_2{}^{13}CN(CD_3)_2)_4$ in CH_2Cl_2, t = 5 min; (B) $Ti(O_2CNMe_2)_4$ + $Ti(O_2{}^{13}CN(CD_3)_2)_4$ + ca. 1% $Ti(NMe_2)(O_2CNMe_2)_3$, in CH_2Cl_2, t = 20 min; (C) same as B; t = 12 h. For $O_2{}^{13}CNMe_2$ $^3J_{^{13}C-H}$ = 3 Hz.

$$WN'_3L_3 + CO_2 \rightleftarrows WN'_2L_3L' \quad (24)$$

Thus, CO_2 exchange must involve attack at the carbamato ligand. We felt that exchange could occur by eq 25 involving a bimolecular reaction of CO_2 and a coordinated (25a) or free (25b) carbamate ligand.



(25a)

$$ML \rightleftarrows M^+L^- \quad (25b)$$

$$^-O_2CNMe_2 + {}^*CO_2 \rightleftarrows {}^-O_2{}^*CNMe_2 + CO_2$$

$$M^+ + L^{*-} \rightleftarrows ML^*$$

Alternatively, CO_2 exchange could be catalyzed by trace amounts of amine due to the equilibria 26 and 27. Since fortuitous CO_2 is present in solutions of ML_n it seemed likely that $HNMe_2$ would also be present: both would be formed by trace hydrolysis of ML_n.

$$HNMe_2 + CO_2 \rightleftarrows HO_2CNMe_2 \quad (26a)$$

$$Me_2NH + HO_2CNMe_2 \rightleftarrows Me_2NH_2{}^+O_2CNMe_2{}^- \quad (26b)$$

$$ML^* + LH \rightleftarrows ML + L^*H \quad (27a)$$

$$ML^* + L^- \rightleftarrows ML + L^{*-} \quad (27b)$$

Equilibria of type 26 have been studied and salts $R_2NH_2{}^+O_2CNR_2{}^-$ isolated.[18] Reaction 27a is comparable to alcoholysis of metal alkoxides[8] and 27b has many precedents in coordination chemistry.

The positions of equilibria in 26 are dependent on the relative concentrations of CO_2 and amine. When $[CO_2]/[HNMe_2]$ is very large, as is certainly the case during CO_2 exchange reactions of type 3, amine is present as HO_2CNMe_2. When $[CO_2]/[HNMe_2]$ is small, the CO_2 would be in the form of $O_2CNMe_2{}^-$.

In an attempt to differentiate between mechanisms 25 and 27, we studied amine exchange reactions of WN_3L_3 and NbL_5. Amine exchange was not observed for reactions 28 and 29 which were carried out in benzene at 25 °C.

$$WN_3L_3 + HN(CD_3)_2 \rightarrow \text{no exchange} \quad (28)$$

$$NbL_5 + HN(CD_3)_2 \rightarrow \text{no exchange} \quad (29)$$

This observation rules out an exchange process such as eq 27b, since 27b would lead to amine exchange via reaction 30.

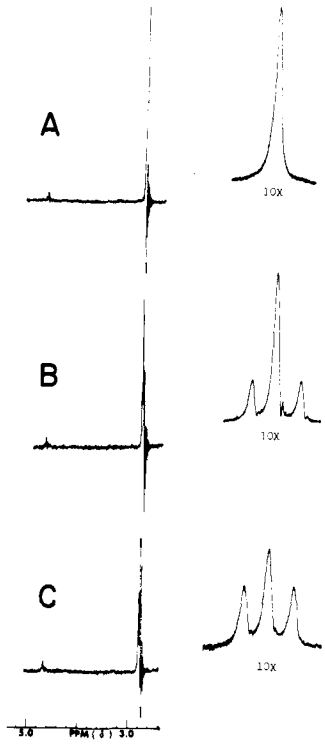


Figure 4. ^{1}H NMR spectra taken during the reaction, $W(N(CD_3)_2)_3(O_2{}^{12}CNMe_2)_3$ + $^{13}CO_2$, in toluene-d_8 at 40 °C. The carbamato region is expanded 10× and exhibits $^3J(^{13}C-H)$ = 3 Hz. The small peak at δ 4.8 ppm is due to protic impurities in the $W-N(CD_3)_2$ groups and did not increase in intensity with time: (A) t = 0, (B) t = 15 h, (C) t = 37 h.

$$^-O_2CNMe_2 + HN(CD_3)_2 \rightleftarrows {}^-O_2CN(CD_3)_2 + HNMe_2 \quad (30)$$

However, CO_2 exchange and amine exchange were facile for reactions 31 and 32. Reactions 31 and 32, which were carried out in benzene at 25 °C, were complete within ca. 24 h and 3 min, respectively. These amine exchange reactions could only have occurred via eq 27a.

$$WN_3L^*_3 + 14\,{}^{12}CO_2 + 16HN(CD_3)_2 \rightarrow \text{exchange} \quad (31)$$

$$NbL_5 + 18\,{}^{13}CO_2 + 18(\text{or } 40)\ HN(CD_3)_2 \rightarrow \text{exchange} \quad (32)$$

It is important to note that for eq 31 amine exchange occurred only at the $W-O_2CNMe_2$ groups and *not* at the $W-NMe_2$ groups.

The facility of eq 32 was further demonstrated by variable temperature ^{1}H NMR studies of reaction 33. See Figure 5.

$$NbL_5 + 14\,{}^{13}CO_2 + 6HNMe_2 \quad (33)$$

The spectra shown in Figure 5 demonstrate certain important points. Firstly, observation of $^3J(^{13}C-H)$ = 3 Hz for $[^{13}CO_2 + HNMe_2]$ at −25 °C indicates that a substantial concentration of $HO_2{}^{13}CNMe_2$ is present. Secondly, the significant line broadening observed at 80 °C is evidence for the facility of eq 27a for NbL_5. Spectra at higher temperatures were not obtained due to significant decomposition of NbL_5 at 100 °C.

A distinction between the mechanisms implied by eq 27a and 27b was also found in studies of reaction 34.

$$WN_3L^*_3 + 18\,{}^{12}CO_2 + xHN(CD_3)_2 \quad (34)$$

a, x = 0

b, x = 3.6

c, x = 90

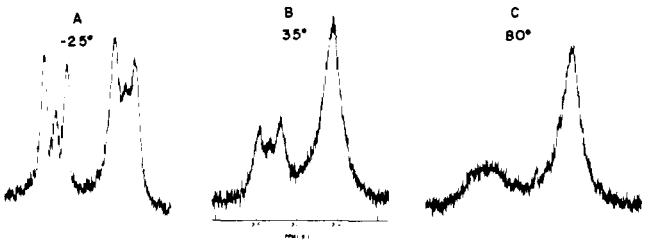


Figure 5. Variable temperature ^{1}H NMR spectra (60 MHz) taken of the reaction: $Nb(O_2{}^{12}CNMe_2)_5 + 18{}^{13}CO_2 + 6HNMe_2$. The $Nb(O_2CNMe_2)_5$ resonance is downfield from the $[CO_2 + HNMe_2]$ resonance.

Reaction 34a proceeded as expected; CO_2 exchange occurred slowly at 25 °C. Reaction 34b proceeded as indicated for eq 31, amine exchange at the carbamato ligand occurred as well as CO_2 exchange. See Figure 6. For reaction 34c, no amine exchange or CO_2 exchange was observed; some white precipitate formed, probably $(Me_2NH_2)(O_2CNMe_2)$. The absence of exchange in eq 34c indicates that CO_2 exchange does not occur via eq 27b.

^{1}H NMR spectra recorded during reaction 34b are shown in Figure 6 and warrant specific comment. In this experiment involving ^{1}H, ^{2}H, ^{12}C, and ^{13}C labeled compounds several net reactions occur as indicated by reactions 35a through h.

$$HN' + {}^{12}CO_2 \rightleftarrows HL' \quad (35a)$$

$$HN + {}^{12}CO_2 \rightleftarrows HL \quad (35b)$$

$$HN' + {}^{13}CO_2 \rightleftarrows HL'^* \quad (35c)$$

$$HN + {}^{13}CO_2 \rightleftarrows HL^* \quad (35d)$$

$$WL^* + HL' \rightleftarrows WL' + HL^* \quad (35e)$$

$$WL^* + HL \rightleftarrows WL + HL^* \quad (35f)$$

$$WL + HL' \rightleftarrows WL' + HL \quad (35g)$$

$$WL + HL'^* \rightleftarrows WL'^* + HL \quad (35h)$$

However, by ^{1}H NMR spectroscopy only certain of these reactions can be observed. As is seen in Figure 6, L and L* are readily monitored and HN + HL + HL* yield a single resonance. Initially, when $[HN'] \gg [HN]$ and $[{}^{12}CO_2] \gg [{}^{13}CO_2]$ reactions 35a and 35e predominate. Thus, at short reaction times we observe formation of HN (actually HL* + HN) with concomitant disappearance of WL* (which may be measured relative to the W–N methyl protons) with no observable ^{13}C exchange (L*/L). *Observable* ^{13}C exchange occurs only by eq 35f, and is not apparent until [HL] becomes significant; i.e., it is only observed after aminolysis affected by eq 35e has occurred.

The observations that CO_2 exchange is ca. zeroth order in CO_2 for WN_3L_3 and ca. first order in CO_2 for ZrL_4 and NbL_5 can also be explained by the overall exchange process eq 26a + 27a. For WN_3L_3, if eq 27a is the rate limiting step then it should be first order in $[Me_2NCO_2H]$. Since $[CO_2] \gg$ [fortuitous $HNMe_2$], the concentration of Me_2NCOOH is independent of $[CO_2]$. Therefore, the rate of CO_2 exchange should be zeroth order in CO_2. Actually, under the conditions of eq 3 ($[CO_2] \gg$ [fortuitous amine]), CO_2 exchange should be first order in fortuitous amine. This has been qualitatively confirmed by a comparison of the rates of eq 34a and 34b.

Carbon dioxide exchange for NbL_5 and ZrL_4 is extremely facile. The observed rate dependence on $[CO_2]$ can be explained by assuming that eq 27a is no longer the rate limiting step. Equilibrium 36, which presumably occurs via 26a must be of comparable or slower rate.

$$Me_2N{}^{12}CO_2H + {}^{13}CO_2 \rightleftarrows Me_2N{}^{13}CO_2H + {}^{12}CO_2 \quad (36)$$

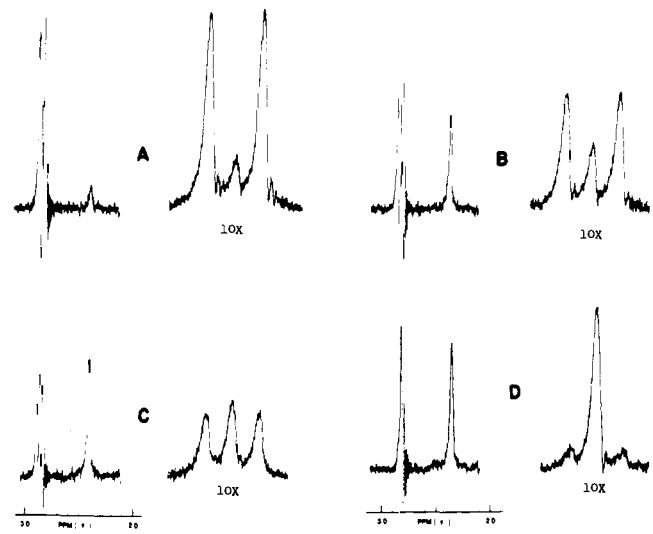


Figure 6. ^{1}H NMR (60 MHz) spectra of the O_2CNMe_2 (δ 2.9 ppm) and $[HNMe_2 + CO_2]$ (δ 2.4 ppm) region taken during the reaction: $W(NMe_2)_3(O_2{}^{13}CNMe_2)_3 + 18{}^{12}CO_2 + 3.6HN(CD_3)_2$ in benzene at 25 °C. The O_2CNMe_2 resonances are expanded 10× and $O_2{}^{13}CNMe_2$ shows $^3J(^{13}C\text{–}H) = 3$ Hz. No changes were observed in the $WNMe_2$ region which is not shown: (A) $t = 0.2$ h, (B) $t = 33$ h, (C) $t = 50$ h, (D) $t = 226$ h.

It is interesting to note that although fortuitous amine catalyzes eq 3, we were able to obtain reasonable kinetic results for WN_3L_3, ZrL_4, and NbL_5 exchange reactions (especially for WN_3L_3). This may be due to our use of stock solutions of these compounds for kinetic runs.

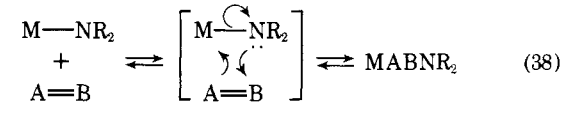
Thus, we have clearly demonstrated that reaction 27a occurs and have presented compelling evidence that CO_2 exchange reactions 3 also occur via 27a, catalyzed by fortuitous amine. This we have demonstrated for NbL_5 and WN_3L_3. There is no reason to believe that reaction 3 occurs differently for any other ML_n compound than via eq 27a.

The Mechanism of CO_2 Insertion. Having demonstrated that reaction 27a was facile, we felt compelled to consider a mechanism for CO_2 insertion catalyzed by fortuitous amine, eq 37.

$$Me_2NH + CO_2 \rightleftarrows L\text{-}H \quad (37a)$$

$$M\text{-}NMe_2 + L\text{-}H \rightleftarrows M\text{-}L + HNMe_2 \quad (37b)$$

Breederveld[19] found that the reaction between Me_3SiNMe_2 and CO_2, which yields Me_3SiL, occurs via eq 37. Other examples of amine catalyzed insertion reactions into $M\text{-}NR_2$ bonds have been discussed by Lappert.[5] The only evidence concerning insertion of CO_2, COS, or CS_2 into $M\text{-}NR_2$ bonds that suggests an alternate mechanism is an experiment carried out by Lappert and co-workers.[20] They found that the reaction between CS_2 and Me_3SnNMe_2 was not inhibited by an amine trap (Me_3SnCl). Based upon this they suggested a mechanism for this reaction and other insertion reactions of Me_3SnNMe_2 that involved electrophilic attack at the nitrogen lone pair. This reaction mechanism, eq 38, has also been suggested for the insertion reactions of $Ti(NMe_2)_4$ with A=B dipoles (e.g., CO_2, CS_2, RCN, RCNO, RCNS, etc.).[7] We have also suggested this mechanism for the reaction of $W(NMe_2)_6$ with CO_2.[9]



(38)

Amine catalysis of insertion may be proven by demonstrating that the insertion reaction does *not* occur either (i) in the presence of an amine trap or (ii) without the addition of amine. If the reaction proceeds in the presence of an amine

"trap", it is inconclusive: either the insertion reaction is not catalyzed *or* the trap was not sufficiently reactive towards amine.

All dialkylamides, MN_n, for which we have studied eq 2, MN_4 (M = Ti, Zr, V), MN_5 (M = Nb, Ta) W_2N_6, and WN_6, are easily hydrolyzed. There can be little doubt that solutions of MN_n contain fortuitous $HNMe_2$ caused by trace decomposition.

Therefore, in order to differentiate between mechanisms 37 and 38, it is necessary to test for CO_2 insertion into M-NMe_2 bonds in solutions of MN_n from which all free amine has been removed by a suitable trap. We experienced considerable difficulties in finding a trap which did not react with the substrates.

Alkyl-lithium compounds should be suitable traps for amines since reaction 39 proceeds irreversibly.

$$LiR + HNMe_2 \rightarrow LiNMe_2 + RH \quad (39)$$

We attempted to inhibit CO_2 insertion as indicated in eq 40.

$$MN_n + RLi \rightarrow \text{amine free solution} \xrightarrow{\text{excess}CO_2} ?? \quad (40)$$

This scheme has several drawbacks: (1) RLi may react with MN_n. (2) RLi may not react with fortuitous amine, particularly if the amine is coordinated to MN_n. (3) CO_2 reacts with LiR to form RCO_2Li; thus, addition of CO_2 deactivates the amine trap. Subsequent decomposition of MN_n could catalyze the insertion. (4) LiO_2CR could react with MN_n or ML_n yielding misleading results.

We were unable to inhibit a reaction between TiN_4 and CO_2 with BuLi. However, the product isolated was not TiL_4 (via ^1H NMR spectra). At this point we decided that this approach probably could not yield conclusive results for MN_4 and MN_5 compounds because of their reactivity. MN_5 are known to coordinate $HNMe_2$ and TiN_4 apparently reacts with LiR. However, we have found that WN_6 does not react with LiR, which made WN_6 suitable for studies of eq 40. Addition of MeLi to a solution of WN_6 in ether inhibited the reaction between WN_6 and CO_2; no reaction was found after 25 h at 25 °C. However, attempts to inhibit this reaction using Me_3CCH_2Li failed. Presumably Me_3CCH_2Li was not an efficient trap for $HNMe_2$.

Conclusive evidence in support of amine catalyzed CO_2 insertion came from the following experiments. We had prepared $W_2(O_2CNEt_2)_4Me_2$ via reaction 41 and noted that the reaction proceeded rapidly.[21] At a later date, we reacted a hexane solution of *freshly prepared* $W_2(NEt_2)_4Me_2$ with a 25% excess of $^{13}CO_2$ at 25 °C for 24 h and observed no reaction. Upon addition of a small amount of $HNEt_2$ (ca. 0.05 equiv), CO_2 insertion occurred and was complete within ca. 10 min.

$$W_2(NEt_2)_4Me_2 + 4CO_2 \rightarrow W_2(O_2CNEt_2)_4Me_2 \quad (41)$$

These observations provide the strongest possible evidence that the reactions between $W_2(NEt_2)_4Me_2$ and CO_2, and WN_6 and CO_2, are catalyzed by trace amounts of amine. There is no evidence to suggest that the reaction between CO_2 and any other $M(NR_2)_n$ compound proceeds differently.

Amine Exchange Reactions. In the course of our studies of CO_2 exchange and insertion reactions we carried out reaction 42a for a number of $MN_{n-m}L_m$ compounds in order to study the facility of amine exchange reactions 42b and c.

$$MN_{n-m}L_m + HN' \quad (42a)$$

$$M\text{-}N + HN' \rightleftarrows M\text{-}N' + HN \quad (42b)$$

$$M\text{-}L + HN' \rightleftarrows ML' + HN \quad (42c)$$

Table VIII. Product Distribution as a Function of Time for the Reaction: $TiN_4 + 2COS$[a]

	mol % $TiN_{4-n}(OSCNMe_2)_n$[c]				
Time, h	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$
0.5	20	20	21	22	17[b]
12	1	29	47	19	4[b]
15	0	21	62	16	0
40	0	5	95	0	0
88	0	4	96	0	0

[a] Carried out in benzene at 25 °C, monitored via ^1H NMR; N = NMe_2. [b] Calculated; $Ti(OSCNMe_2)_4$ is sparingly soluble in benzene. [c] See experimental section for chemical shifts of $TiN_{4-n}(OSCNMe_2)_n$.

Exchange reactions of type 42b and/or 42c were not observed (in benzene, at 25 °C) for WN_6, W_2N_6, WN_3L_3, or NbL_5. TiN_2L_2 (in benzene at 25 °C) underwent an exchange reaction of type 42b but not 42c, thus yielding TiN'_2L_2. TiN_4 and TaN_5 also underwent facile aminolysis, eq 42b. These results are consistent with aminolysis occurring via a simple associative mechanism 43.

$$MN + HN' \rightleftarrows \begin{bmatrix} N'\text{-}H \\ M\text{-}N \end{bmatrix} \rightleftarrows MN' + HN \quad (43)$$

Only the sterically crowded molecules WN_6, W_2N_6, and WN_3L_3 do not undergo this reaction. Significantly the absence of aminolysis for these compounds also rules out a dissociative mode of reaction 44 which might have been expected for electron rich and crowded molecules such as WN_6.

$$MN_n \rightleftarrows MN_{n-1}{}^+N^- \quad (44)$$

Ligand Exchange Reactions. During this work we have noted that $TiN_{4-n}L_n$ compounds undergo facile ligand exchange reactions (see reactions 5, 12, 13, 15, 17, and 19), of both N and L groups. These facile ligand exchange reactions are responsible for the rapid attainment of thermodynamic control of the reaction between TiN_4 and nCO_2 ($n < 4$). We made use of these ligand exchange reactions to prepare the unusual compound $Ti(NMe_2)_2(O_2CNEt_2)_2$ from reaction 45.

$$TiN_4 + Ti(O_2CNEt_2)_4 \rightarrow 2Ti(NMe_2)_2(O_2CNEt_2)_2 \quad (45)$$

We have also noted that $TaN_{5-n}L_n$ compounds undergo ligand exchange reactions only slowly (see reactions 20 and 21). Thus, the apparent lack of thermodynamic control of the reaction between TaN_5 and nCO_2 ($n < 5$) is not surprising.

Facile ligand exchange reactions of the type observed for $TiN_{4-n}L_n$ have also been observed for $M(\text{chelate})_{4-n}X_n$ compounds (M = Ti, Zr).[22-24]

Mono- and Dithiocarbamato Compounds of Titanium: $Ti(NMe_2)_4$ + 2COS, $2CS_2$. We carried out a study of these reactions to check the feasibility of isolating the compounds $TiN_2(OSCNMe_2)_2$ and $TiN_2(S_2CNMe_2)_2$ for comparisons with TiN_2L_2.

A solution of TiN_4 reacted rapidly with COS (2 equiv) to yield an initial mixture of $TiN_{4-n}(OSCNMe_2)_n$ (n = 0, 1, 2, 3, 4) which slowly reacted further to yield a solution of $TiN_2(OSCNMe_2)_2$. See Table VIII. Thus thermodynamic product control is attained.

A solution of TiN_4 reacted with CS_2 to yield a mixture of $TiN_{4-n}(S_2CNMe_2)_n$ (n = 0, 1, 2, 3, 4). The relative concentrations of these products changed only slightly over 7 days. These reactions were not pursued further.

The ability of the compounds $Ti(OSCNMe_2)_4$ and $Ti(S_2CNEt_2)_4$ to undergo COS and CS_2 exchange reactions

analogous to eq 3 and 4 was noted in the previous paper.[2] These exchange reactions may well occur via amine catalyzed mechanisms analogous to that established for eq 3 and 4.

Conclusions

Compounds of the form $MN_{n-m}L_m$ have been isolated and characterized from reactions between MN_n and CO_2 ($<n$ equiv). Labeling studies have shown that CO_2 exchange reactions 3 and 4 do not occur via eq 6. Indeed we have never observed extrusion of CO_2 from a carbamate ligand. Exchange reactions 4 occur via 3 due to the presence of fortuitous CO_2 in solutions of ML_n. All our observations indicate that CO_2 exchange, eq 3, is amine catalyzed and occurs by the reactions 26a and 27a.

Further observations concerning the reaction between MN_n compounds and CO_2 indicate an amine catalyzed mechanism of insertion. This has been unequivocally demonstrated for WN_6 and $W_2Me_2(NEt_2)_4$. From our studies it is clear that the mechanism of insertion of CO_2 into M-NR_2 bonds need not be analogous to the insertions of unsaturated hydrocarbons into M-C (alkyl) bonds.

One can propose a generalized mechanism for the insertion of an A=B dipole into a metal nitrogen bond, 46.

$$A{=}B + HNR_2 \rightleftarrows H\text{-}A\text{-}B\text{-}NR_2 \qquad (46a)$$

$$M{-}NR_2 + H\text{-}A\text{-}B\text{-}NR_2 \rightarrow M\text{-}A\text{-}B\text{-}NR_2 + HNR_2 \qquad (46b)$$

Reaction 46a has been observed for many A=B dipoles[25] and reaction 46b is certainly reasonable.[8] While, on the basis of our studies and the results of Breederveld,[19] one can hardly generalize that all insertion reactions of all M-NR_2 bonds are catalyzed by HNR_2, there is as yet no conclusive evidence to suggest otherwise.

Finally, we note that a number of exchange reactions of the type represented by eq 47 may also occur via an amine catalyzed mechanism.

$$M\text{-}A\text{-}B\text{-}NR_2 + X{=}Y \rightleftarrows M\text{-}X\text{-}Y\text{-}NR_2 + A{=}B$$

where A = B, X = Y = CO_2, COS, CS_2, RCN, etc. If an A=B or X=Y dipolar molecule reacts reversibly with amine, as in eq 46a, and the acid H-X-Y-NR_2 reacts with a coordinated M-A-B-NR_2 ligand to give M-X-Y-NR_2 and H-A-BNR_2, the exchange reaction 47 becomes possible and thermodynamic control of products may occur. Reactions of this type have been noted: $Me_3Sn(O_2CNMe_2)$ and $Ti(O_2CNMe_2)_4$ react with CS_2 to yield $Me_3Sn(S_2CNMe_2)$[20] and $Ti(S_2CNMe_2)_3(O_2CNMe_2)$,[7] respectively.

Experimental Section

General Procedures. The preparation of starting materials and our basic experimental techniques have been described previously (see immediately preceding paper).[1]

Manipulation of Air- and Moisture-Sensitive Compounds. One of the basic conclusions of this paper is that several facile reactions are caused by trace amounts of decomposition, either of $M(NMe_2)_n$ or ML_n. Therefore, the care with which we have prepared and handled these compounds must be emphasized. All preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere (purified over BTS catalyst and P_2O_5 columns) or in vacuo (ca. 10^{-3} Torr) using standard Schlenk techniques.[26] Solvents were carefully purified (see previous paper) and stored under N_2 and over CaH_2 or molecular sieves (4 Å). The purities of $M(NMe_2)_n$, $MN_{n-x}L_x$, and ML_n were verified via elemental analyses, and no hydrolysis products could be observed via ^1H NMR spectroscopy.

X-ray Crystallography. The single-crystal structural determination of $Ti(NMe_2)_2(O_2CNMe_2)_2$ was carried out by Molecular Structures Corp., College Station, Texas.

Crystal data: $Ti(NMe_2)_2(O_2CNMe_2)_2$; M = 312.23; triclinic; a = 8.954 (4), b = 9.841 (5), c = 10.686 (5) Å; α = 106.22 (4), β = 110.35 (4), γ = 70.48 (4)°; Z = 2; d_{calcd} = 1.268 g/cm^2; space group $P\bar{1}$. Intensity data were collected on a Syntex $P\bar{1}$ computer controlled diffractometer using Mo Kα radiation. In the refinement of the structure, 1729 independent reflections having $F_o^2 > 3\sigma(F_o^2)$ were used to give the final agreement factors R_1 = 0.086 and R_2 = 0.115. See paragraph at the end of the paper regarding supplementary data.

$W(NMe_2)_6 + 2CO_2$. CO_2 (0.02 mmol) was condensed into an NMR tube containing WN_6 (0.01 mmol) in benzene (0.5 ml). Upon warming to 25 °C, the solution darkened. A ^1H NMR spectrum taken after ca. 30 min (see Table I) indicated the presence of $WN_{6-n}L_n$ (n = 0, 1, 2, 3). After ca. 24 h, the only observable product was a small amount of WN_3L_3; WN_5L and WN_4L_2 had apparently decomposed.

$M(NMe_2)_5 + nCO_2$ (M = Nb, Ta; n = 1, 2, 4). Aliquots of NbN_5 (0.13 mmol per tube) and TaN_5 (0.061 mmol per tube) in toluene-d_8 (with HMDS as an internal reference) were placed in NMR tubes. The appropriate amount of CO_2 (1, 2, or 4 equiv) was condensed into each tube with liquid N_2. The tubes were kept at −78 °C for 3 h, then warmed to ambient temperatures and examined via ^1H NMR. See Tables II and III for ^1H NMR shifts and product distributions. The $MN_{5-n}L_n$ compounds thus formed were more stable in solution for M = Ta than M = Nb. Significant decomposition was detected for $NbN_{5-n}L_n$ within 2-3 days whereas $TaN_{n-5}L_n$ were stable for ca. 2 weeks in solution.

$Zr(NMe)_4 + 2CO_2$. CO_2 (0.15 mmol) was condensed into an NMR tube containing $Zr(NMe_2)_4$ (20.3 mg, 0.075 mmol) in benzene. A rapid reaction occurred when the tube was warmed to 25 °C, and a white precipitate formed (presumably ZrL_4); the solution remained colorless. A ^1H NMR spectrum (60 MHz, 40 °C) taken after 10 min exhibited an intense singlet (at δ 2.39 ppm in the O_2CNMe_2 region not due to ZrL_4 which is nearly insoluble in benzene). The M-NMe_2 region of the spectrum exhibited several very broad resonances (δ 2.9 ± 0.3 ppm). These resonances became even broader with time.

$Ti(NMe_2)_4 + nCO_2$, 2COS, $2CS_2$. Aliquots (0.5 ml) of a stock solution of TiN_4 in benzene (29.2 mg, 0.13 mmol per aliquot) were placed into four NMR tubes; 0.13 mmol of CO_2 (1 equiv), 0.39 mmol of CO_2 (3 equiv), 0.25 mmol of COS (2 equiv), and 0.26 mmol of CS_2, respectively, were condensed into the tubes, which were then sealed. The samples were warmed to ca. 25 °C and their ^1H NMR spectra were monitored periodically. For the reactions $TiN_4 + nCO_2$ (n = 1, 3) equilibrium was reached rapidly. Initial spectra obtained within 30 min showed the product distributions indicated in Table V. At t = 30 min the TiN_4 + 2COS reaction was dark red with a bright red precipitate. Its ^1H NMR spectrum indicated it was a mixture of $TiN_{4-n}(OSCNMe_2)_n$ (n = 0, 1, 2, 3, 4). The precipitate dissolved within ca. 15 h; the product distribution changed slowly with time. See Table VIII. ^1H NMR shifts for $TiN_{4-n}(OSCNMe_2)_n$ (n = 0, 1, 2, 3) in benzene: n = 0, $\delta(NMe_2)$ 3.03; n = 1, $\delta(NMe_2)$ 3.28, $\delta(OSCNMe_2)$ 2.43, 2.52; n = 2, $\delta(NMe_2)$ 3.54, $\delta(OSCNMe_2)$ 2.45, 2.54; n = 3, $\delta(NMe_2)$ 3.67, $\delta(OSCNMe_2)$ 2.53, 2.57. δ in parts per million downfield from HMDS. The $TiN_4 + 2CS_2$ reaction yielded an orange-brown solution with an orange precipitate. The precipitate did not dissolve and the product distribution changed only slightly over 7 days. Distribution (mole percent) of benzene soluble products, $TiN_{4-n}(S_2CNMe_2)_n$: t = 30 min, n = 0 (16%), n = 1 (35%), n = 2 (38%), n = 3 (12%); t = 7 day, n = 0 (9%), n = 1 (39%), n = 2 (36%), n = 3 (15%). ^1H NMR data for $Ti(NMe_2)_{4-n}(S_2CNMe_2)_n$ in benzene: n = 0, $\delta(NMe_2)$ 3.03; n = 1, $\delta(NMe_2)$ 3.19, $\delta(S_2CNMe_2)$ 2.70; n = 2, $\delta(NMe_2)$ 3.61, $\delta(S_2CNMe_2)$ 2.62; n = 3, $\delta(NMe_2)$ 4.52, $\delta(S_2CNMe_2)$ 2.60. δ in parts per million downfield from HMDS.

Preparation (in situ) of $Ti(NMe_2)_3(O_2CNMe_2)$. CO_2 (4.66 mmol) was condensed into a solution of $Ti(NMe_2)_4$ (1.044 g, 4.66 mmol in toluene (25 ml)). Upon warming to 25 °C the solution turned orange. The solvent was stripped off leaving an orange oil which solidified upon cooling to −20 °C. A ^1H NMR spectrum (in benzene) revealed that the oil was a mixture of $Ti(NMe_2)_4$, $Ti(NMe_2)_3(O_2CNMe_2)$, and $Ti(NMe_2)_2(O_2CNMe_2)_2$ in the ratio 1:6:1. An attempt to recrystallize the oil from hexane yielded only a small amount of $Ti(NMe_2)_2(O_2CNMe_2)_2$ (the least soluble fraction of the mixture). The reaction, $Ti(NMe_2)_4 + 1CO_2$, was also followed via ^1H NMR. Equilibrium (ca. 1:6:1 mixture) was reached before the first spectrum was recorded (ca. 5 min at 25 °C). Integration of the ^1H NMR spectra indicated that K_{eq} = 38 for the equilibrium: $Ti(NMe_2)_4 + Ti(NMe_2)_2(O_2CNMe_2)_2 \rightleftarrows Ti(NMe_2)_3(O_2CNMe_2)_3$.

Preparation of $Ti(NMe_2)_2(O_2CNMe_2)_2$. CO_2 (7.4 mmol) was condensed into a solution of $Ti(NMe_2)_4$ (0.870 g, 3.88 mmol in toluene

(20 ml)). The solution turned bright red upon warming to room temperature. After stirring for 12 h the solvent was stripped off. The residue was recrystallized from hexane, yielding bright red crystals.

Preparation of $Ti(NMe_2)(O_2CNMe_2)_3$. CO_2 (8.69 mmol) was condensed into a solution of $Ti(NMe_2)_4$ (0.649 g, 2.90 mmol in toluene (25 ml)). The solution turned red, then brown upon warming to room temperature. After stirring for 12 h at 25 °C, the solvent was stripped off. The brown residue was washed with 30 ml of 3:1 hexane/toluene, then dried (1 h, 10^{-3} Torr).

Preparation of $Ti(NMe_2)_2(O_2CNEt_2)_2$. $Ti(NMe_2)_4$ (0.164 g, 0.732 mmol) in benzene (10 ml) was added to $Ti(O_2CNEt_2)_4$ (0.375 g, 0.732 mmol), the solution immediately turned bright red. After stirring for ca. 3 h, the solvent was stripped off. The residue was recrystallized from hexane yielding bright red crystals.

Preparation of $Ta(NMe_2)_2(O_2CNMe_2)_3$. CO_2 (12.2 mmol) was condensed into a solution of $Ta(NMe_2)_5$ (1.68 g, 4.08 mmol in toluene (50 ml)). The solution was warmed to room temperature and stirred (24 h). The solvent was stripped off leaving a pale yellow residue which was recrystallized from toluene (20 ml)/hexane (35 ml) yielding pale yellow crystals.

A slightly modified preparation was carried out in hexane: CO_2 (2 equiv, 3.85 mmol) was condensed into a solution of $Ta(NMe_2)_5$ (0.773 g, 1.92 mmol) in hexane (50 ml). The solution was warmed to 25 °C and stirred; a precipitate formed which was redissolved by warming the solution to ca. 60 °C. The solution was then slowly cooled to −20 °C; nearly colorless crystals formed. They were filtered off and dried. A ^1H NMR spectrum verified that they were $Ta(NMe_2)_2(O_2CNMe_2)_3$.

Infrared Data. Unless otherwise noted spectra were recorded as Nujol mulls, 250–2000 cm^{-1}. **$Ti(NMe_2)_2(O_2CNMe_2)_2$.** 353 m, 377 m, 433 m sh, 453 s, 581 s, 614 w, 660 s, 788 s, 792 s, 861 m, 945 s, 961 s, 1048 m, 1066 w, 1116 w, 1146 m, 1245 m, 1269 s, 1410 vs, 1496 s, 1575 vs, 1597 sh, 1705 w. **$Ti(NMe_2)_2(O_2{}^{13}CNMe_2)_2$.** 353 m, 379 m, 433 msh, 453 s, 582 s, 613 w, 662 s, 766 s, 770 ssh, 790 w, 794 wsh, 859 m, 946 s, 962 s, 1049 m, 1067 w, 1116 w, 1146 m, 1244 s, 1261 s, 1409 s, 1496 w, 1555 vs, 1589 sh, 1705 w. **$Ti(N(CD_3)_2)_2(O_2{}^{13}CN(CD_3)_2)_2$.** 325 w, 341 m, 357 m, 385 m, 426 s, 525 s, 588 w, 633 s, 764 s, 766 sh, 802 s, 812 sh, 817 sh, 822 s, 829 s, 899 s, 918 wsh, 1027 m, 1057 s, 1090 sh, 1100 s, 1128 s, 1151 s, 1160 sh, 1211 s, 1225 s, 1245 w, 1500 vs, 1520 sh, 1540 sh, 1563 sh. **$Ti(NMe_2)(O_2CNMe_2)_3$.** 318 w, 361 m, 375 wsh, 442 s, 583 m, 624 msh, 652 s, 670 sh, 789 s, 860 w, 869 w, 952 m, 1038 m, 1055 m, 1145 w, 1255 sh, 1265 s, 1402 s, 1490 m, 1504 w, 1576 vs, 1693 wsh. **$Ta(NMe_2)_2(O_2CNMe_2)_3$.** 263 m, 344 sh, 375 s, 410 sh, 429 s, 559 s, 594 s, 634 s, 661 vs, 678 m, 775 m, 786 m, 797 m, 841 m, 870 w, 960 vs, 972 s, 1034 m, 1047 m, 1131 w, 1206 vs, 1245 w, 1270 vs, 1410 s, 1608 vs, 1630 vs, 1645 vs. In benzene: 374 m, 426 s, 558 s, 600 s, no window 650–1200 cm^{-1}, 1219 vs, 1277 vs, 1369 vs, 1418 vs, 1603 vs, 1610 sh, 1637 sh, 1650 vs. **$Ti(NMe_2)(O_2CNMe_2)_3 + Ti(O_2{}^{13}CN(CD_3)_2)_4$.** $TiNL_3$ and TiL'^*_4 (ca. 15 mg each) were placed in an NMR tube and dissolved in CH_2Cl_2. A ^1H NMR spectrum taken within 10 min indicated that ligand exchange had occurred. No peaks due to $O_2{}^{13}CNMe_2$ were observed and no further changes in the spectrum occurred (over 48 h). See Figure 2.

Effect of Inhibiter ($TiNL_3$) on the CO_2 Exchange Reaction: TiL_4 + TiL'^*_4. Stock solutions of TiL_4 and TiL'^*_4 (ca. 15 mg each) in CH_2Cl_2 (ca. 0.5 ml each) were prepared. Two separate reactions were carried out: A, 0.25 ml of each stock solution was placed in an NMR tube. ^1H NMR spectra taken within 10 min showed that $^{13}CO_2$ exchange was complete. B, a trace amount of $TiNL_3$ (0.1–0.5 mg) was added to 0.25 ml of the TiL_4 solution, then 0.25 ml of the TiL'^*_4 solution was added and the mixture was placed in an NMR tube. ^1H NMR spectra taken over an hour indicated the absence of $^{13}CO_2$ exchange. The amount of $TiNL_3$ present was not observable via ^1H NMR; however, solution B was very pale brown. $TiNL_3$ is brown and solution A was colorless. After 12 h the color due to $TiNL_3$ had disappeared and $^{13}CO_2$ exchange was complete. See Figure 3.

$Ti(NMe_2)(O_2{}^{12}CNMe_2)_3 + Ti(N(CD_3)_2)_2(O_2{}^{13}CN(CD_3)_2)_2$. $TiNL_3$ (19 mg, 0.05 mmol) and $TiN'_2L'^*_2$ (30 mg, 0.09 mmol) were placed in an NMR tube and dissolved in toluene-d_8. ^1H NMR spectra taken over 6 days indicated that exchange of dimethylamido and carbamato ligands occurred. No $O_2{}^{13}CNMe_2$ was observed. Carbamato ligand exchange was complete within 30 min and dimethyamido ligand exchange was complete within 5 h.

Note: Toluene-d_8 was used as a solvent instead of benzene because the $TiNL_3$ and TiN_2L_2 carbamato resonances are accidentally magnetically degenerate in benzene. In toluene-d_8 their chemical shifts are slightly different ($\Delta\nu$ = 0.8 Hz at 60 MHz).

$Ti(NMe_2)_2(O_2{}^{12}CNMe_2)_2 + Ti(N(CD_3)_2)_2(O_2{}^{13}CN(CD_3)_2)_2$. TiN_2L_2 (24 mg, 0.08 mmol) and $TiN'_2L'^*_2$ (30 mg, 0.09 mmol) were placed in an NMR tube and dissolved in benzene (0.5 ml). ^1H NMR spectra taken over 73 h indicated that no $O_2{}^{13}CNMe_2$ had formed. *Note:* Although ligand exchange presumably occurs, it would not be observable via ^1H NMR spectroscopy.

$Ta(O_2{}^{13}CN(CD_3)_2)_5 + TaN_2L_3$. TaN_2L_3 and TaL'^*_5 (ca. 10 mg each) were placed in an NMR tube and dissolved in benzene (0.5 ml). ^1H NMR spectra taken over a period of 5 days at 25 °C indicated that ligand exchange slowly took place, producing some $TaNL_4$. After 5 days $[TaNL_4]/[TaN_2L_3]$ = 1.20. The carbamato region showed no peaks due to $O_2{}^{13}CNMe_2$.

$TaN_2L_3 + TaN_5$. TaN_2L_3 and TaN_5 (ca. 20 mg each) were reacted in benzene (0.5 ml) in an NMR tube. After 11 h at 25 °C, the only species observable via ^1H NMR were TaN_5 and TaN_2L_3.

$TaN'_5 + NbL_5$. TaN'_5 and NbL_5 (ca. 15 mg each) were reacted in benzene in an NMR tube. After 18 h at 25 °C, considerable ligand exchange had occurred. However, no M–NMe_2 species were observed.

$WN'_6 + CO_2/HNMe_2$; Preparation of $W(N(CD_3)_2)_3(O_2CNMe_2)_3$. CO_2 (0.50 mmol) and $HMNe_2$ (0.30 mmol) were condensed into an NMR tube containing $W(N(CD_3)_2)_6$ (55 mg, 0.11 mmol) in toluene-d_8 (0.5 ml) with HMDS as an internal reference. An immediate reaction occurred; a ^1H NMR spectrum taken within 15 min at 25 °C indicated the presence of $W(N(CD_3)_2)_3(O_2CNMe_2)_3$ and excess $HNMe_2$. No further change was observed. Note that no incorporation of $HNMe_2$ into the dimethylamido ligands of WN'_3L_3 was observed. The tube was cooled to −20 °C, orange WN'_3L_3 crystallized from solution and was isolated and used for the following reaction.

$W(N(CD_3)_2)_3(O_2CNMe_2)_3 + {}^{13}CO_2$. $^{13}CO_2$ (0.34 mmol) was condensed into an NMR tube containing WN'_3L_3 (ca. 15 mg, 0.025 mmol) in toluene-d_8. The tube was placed in a bath at 40 °C. ^1H NMR spectra taken over 124 h indicated (1) $^{13}CO_2$ exchange was complete within 40 h. (2) Over the reaction period (124 h) no increase in the intensity of the resonance due to W–NMe_2 was observed (i.e., no NMe_2–$N(CD_3)_2$ exchange occurred). See Figure 4.

$W(N(CD_3)_2)_3(O_2CN(CD_3)_2)_3 + HNMe_2$. $HNMe_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing $WN'_3L'_3$ (ca. 10 mg, 0.02 mmol) in benzene (0.5 ml). ^1H NMR spectra, taken over 4 days indicated that aminolysis of W–$N(CD_3)_2$ and W–$O_2CN(CD_3)_2$ did not occur.

$WN_3L^*_3 + HN(CD_3)_2/{}^{12}CO_2$. $^{12}CO_2$ (0.42 mmol) and $HN(CD_3)_2$ (0.48 mmol) were condensed into an NMR tube containing $WN_3L^*_3$ (ca. 15 mg, 0.03 mmol) in benzene (0.5 ml). ^1H NMR spectra indicated that aminolysis of the $O_2{}^{13}CNMe_2$ ligand occurred (complete within ca. 24 h) and that $^{13}CO_2$ exchange occurred (after 24 h, $[L^*]/[L] \approx 2.3$). Aminolysis of the W–NMe_2 group did not occur.

$WN_3L^*_3 + 18{}^{12}CO_2 + xHN(CD_3)_2$ (x = 0, 3.6, 90). A stock solution of $WN_3L^*_3$ (24.5 mg, 0.042 mmol) in benzene (1.5 ml) was divided into three equal portions and placed in NMR tubes; each tube contained 0.014 mmol of $WN_3L^*_3$: reaction A, stock solution + 0.25 mmol of $^{12}CO_2$; reaction B, stock solution + 0.25 mmol of $^{12}CO_2$ and 0.05 mmol of $HN(CD_3)_2$; reaction C, stock solution + 0.25 mmol of $^{12}CO_2$ and 1.25 mmol of $HN(CD_3)_2$. The tubes were kept at ca. 25 °C and their ^1H NMR spectra were monitored over a period of 9 days. See Figure 6. From reaction A we observed the expected CO_2 exchange reaction (complete within ca. 50 h). For reaction B we observed amine exchange and CO_2 exchange. The *observable* CO_2 exchange (i.e., % $O_2{}^{12}CNMe_2$) was less for reaction B than reaction A, at all times less than $t = \infty$. After equilibrium had been reached (t = 226 h) % L was the same for A and B (80%). Amine exchange for B was complete within ca. 72 h. Reaction C: No CO_2 exchange or amine exchange was observed over 50 h. A white precipitate was formed in the NMR tube, possibly $((CD_3)_2NH_2)^+(O_2CN(CD_3)_2)^-$.

$Nb(O_2CNMe_2)_5 + HN(CD_3)_2$ in Benzene. $HN(CD_3)_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing NbL_5 (ca. 17 mg, 0.03 mmol) in benzene (0.5 ml). The tube was warmed to 25 °C. Spectra taken over 10 days indicated that no amine exchange occurred.

$Nb(O_2CNMe_2)_5 + HN(CD_3)_2/{}^{13}CO_2$ in Benzene. $HN(CD_3)_2$ (0.36 or 0.82 mmol) and $^{13}CO_2$ (0.36 mmol) was condensed into each of two NMR tubes containing NbL_5 (ca. 10 mg, 0.02 mmol) in benzene (0.5 ml). Upon warming to 25 °C, amine exchange occurred immediately;

in both cases exchange was complete within 3-4 min as indicated by ^{1}H NMR spectra.

$Nb(O_2CNMe_2)_5$ + $HNMe_2/^{13}CO_2$ in Toluene-d_8. $HNMe_2$ (ca. 0.12 mmol) and $^{13}CO_2$ (0.28 mmol) were condensed into a solution of NbL_5 (ca. 10 mg, 0.02 mmol) in toluene-d_8 (0.5 ml). ^{1}H NMR spectra were recorded over the temperature range −25 to 80 °C. At −25 °C, resonances assignable to Nb-L/Nb-L* (δ 2.49) and [$HNMe_2$ + $^{12}CO_2/^{13}CO_2$] (δ 2.32) were observed which showed $^3J(^{13}C-H)$ = 3.2 and 3.0 Hz, respectively. At 80 °C broad resonances at δ 2.57 (Nb-L) and 2.37 ppm were observed, $^3J(^{13}C-H)$ was not visible. See Figure 5 for spectra.

$W(NMe_2)_6$ + MeLi + CO_2. MeLi (1.5 mmol) was added to $W(NMe_2)_6$ (181 mg, 0.40 mmol) in ether (30 ml). After stirring at 25 °C for ca. 5 min, CO_2 (3 mmol) was added. No reaction was observed after 11 h at 25 °C. Additional CO_2 was added (1.3 mmol) and the solution was stirred another 14 h. The solvent was stripped off and the residue was extracted with benzene (15 ml). A ^{1}H NMR spectrum of the orange benzene solution indicated the presence of *only* $W(NMe_2)_6$.

Preparation of $W_2(O_2{}^{13}CNEt_2)_4Me_2$. This preparation, although similar to that reported for the unlabeled compound,[21] is described because it provides important insight into the mechanism of CO_2 "insertion." $^{13}CO_2$ (1.25 mmol) was condensed into a solution of freshly prepared $W_2(NEt_2)_4Me_2$[21] (187 mg, 0.27 mmol) in hexane (10 ml). The bright red solution was stirred at room temperature for 24 h; no noticeable reaction occurred. $HNEt_2$ (ca. 1 mmol) was condensed into the solution. Immediately upon warming the solution to room temperature, the solution turned from red to yellowish brown and a yellow precipitate formed. The supernatant was decanted via syringe and the yellow precipitate $W_2Me_2(O_2{}^{13}CNEt_2)_4$ was dried in vacuo.

$Ti(N(CD_3)_2)_4$ + $HNMe_2$. $HNMe_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing TiN'_4 (22 mg, 0.09 mmol) in benzene (0.5 ml). The tube was warmed to 25 °C and ^{1}H NMR spectra, were taken over a period of 98 h. Amine exchange was complete within ca. 2 h. After 72 h we observed a greenish precipitate. However, the ^{1}H NMR spectra showed no new resonances.

$Ta(NMe_2)_5$ + $HN(CD_3)_2$. $HN(CD_3)_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing TaN_5 (15 mg, 0.04 mmol) in benzene (0.5 ml). Amine exchange was complete within ca. 70 min, as shown by the ^{1}H NMR spectra. Further spectra, taken over 10 days showed no change. The NMR spectra indicate that the compound in solution is probably $Ta(NMe_2)_5(HNMe_2)$: $\delta(NMe_2)$ 3.17; $\delta(HNMe_2)$ 3.19 ppm.[27]

$W(NMe_2)_6$ + $HN(CD_3)_2$. $HN(CD_3)_2$ (ca. 0.5 mmol) was condensed into an NMR tube containing $W(NMe_2)_6$ (ca. 4 mg, 0.01 mmol) in benzene (0.5 ml). No amine exchange was observed after 48 h at 25 °C.

$Ti(N(CD_3)_2)_2(O_2{}^{13}CN(CD_3)_2)_2$ + $HNMe_2$. $HNMe_2$ (ca. 0.4 mmol) was condensed into an NMR tube containing $TiN_2L'^*_2$ (17 mg, 0.05 mmol) in benzene (0.5 ml). ^{1}H NMR spectra were taken over a period of 121 h. Exchange of $M-N(CD_3)_2$ with $HNMe_2$ was complete within 1 h. Exchange of $M-O_2CN(CD_3)_2$ with $HNMe_2$ was never observed.

Acknowledgment. We thank Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. GPS73-05016) for their support of this work. M.E. gratefully acknowledges the American Can Company for a fellowship.

Supplementary Material Available: A listing of data and structural factor amplitudes (22 pages). Ordering information is available on any current masthead page.

References and Notes

(1) Part 3, M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, preceding paper in this issue.
(2) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972, p 777.
(3) W. Wojcicki, *Adv. Organomet. Chem.*, 11, 87 (1973).
(4) A. Wojcicki, *Adv. Organomet. Chem.*, **12**, 31 (1974).
(5) M. F. Lappert and B. Prokai, *Adv. Organomet. Chem.*, **5**, 224 (1967).
(6) P. L. Bock, D. J. Boschetto, J. R. Rasmussen, J. P. Demers, and G. M. Whitesides, *J. Am. Chem. Soc.*, **96**, 2814 (1974).
(7) G. Chandra, A. D. Jenkins, M. F. Lappert, and R. C. Srivastava, *J. Chem. Soc. A*, 2550 (1970).
(8) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15**, 259 (1972).
(9) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **96**, 6214 (1974).
(10) M. H. Chisholm and M. W. Extine, *J. Am. Chem. Soc.*, **97**, 1623 (1975).
(11) M. H. Chisholm and M. W. Extine, *J. Chem. Soc., Chem. Commun.*, 438 (1975).
(12) Structural studies in progress in collaboration with M. B. Hursthouse, Queen Mary College.
(13) D. F. Lewis and R. C. Fay, *J. Am. Chem. Soc.*, **96**, 3843 (1974).
(14) D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 282 (1969).
(15) P. Finocchiaro, *J. Am. Chem. Soc.*, **97**, 4443 (1975).
(16) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4477 (1976).
(17) C. Airoldi and D. C. Bradley, *Inorg. Nucl. Chem. Lett.*, 11, 155 (1974).
(18) A. Jensen, M. B. Jensen, and C. Faurhold, *Acta Chem. Scand.*, **8**, 1129 (1954).
(19) H. Breederveld, *Recl. Trav. Chim. Pays-Bas*, **81**, 276 (1962).
(20) T. A. George, K. Jones, and M. F. Lappert, *J. Chem. Soc.*, 2157 (1965).
(21) M. H. Chisholm, F. A. Cotton, M. W. Extine, and B. R. Stults, *J. Am. Chem. Soc.*, **98**, 4683 (1976).
(22) A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 228 (1966).
(23) T. J. Pinnavaia and R. C. Fay, *Inorg. Chem.*, **5**, 233 (1966).
(24) R. C. Fay and R. N. Lowry, *Inorg. Chem.*, **13**, 1309 (1974).
(25) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, pp 672-675.
(26) D. F. Shriver, "The Manipulations of Air Sensitive Compounds", McGraw-Hill, New York, N.Y., 1969.
(27) D. C. Bradley, private communication.

Vinyl Ether Hydrolysis. 7. Isotope Effects on Catalysis by Aqueous Hydrofluoric Acid[1]

A. J. Kresge,*[2] H. J. Chen, and Y. Chiang[2]

Contribution from the Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois 60616. *Received April 26, 1976*

Abstract: Comparison of rates of hydrolysis of three vinyl ethers catalyzed by HF in H_2O and DF in D_2O at 25 °C gives primary isotope effects in the range k_H/k_D = 3.3-3.5. The unexpectedly small size of these effects may be attributed to strong, ω = 1325-1450 cm^{-1}, hydrogenic bending vibrations in the proton transfer transition states of these reactions along with the lack of compensatory bending vibrations in the diatomic proton donor.

Hydrogen fluoride is unique among the hydrohalogen acids in that it remains largely undissociated and therefore diatomic in dilute aqueous solution. It is nevertheless a moderately strong acid, pK_a = 3.17, which makes it an effective proton donor whose catalytic activity can be studied conveniently. This gives it a number of interesting properties,