Reactions of Transition Metal–Nitrogen σ Bonds. 3.[1] Early Transition Metal *N,N*-Dimethylcarbamates. Preparation, Properties, and Carbon Dioxide Exchange Reactions

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Abstract: Early transition metal dimethylamides $M(NMe_2)_n$ (where M = Ti, Zr, V and $n = 4$; M = Nb, Ta and $n = 5$) and $W_2(NMe_2)_6$ react with carbon dioxide to give *N,N*-dimethylcarbamato compounds ML_n and W_2L_6, where $L = O_2CNMe_2$, respectively. $W(NMe_2)_6$ reacts with CO_2 to give only $W(NMe_2)_3L_3$ even in the presence of excess CO_2. These compounds have been characterized by a number of physicochemical techniques. On the basis of vibrational studies of isotopically labeled compounds we predict that ML_4 compounds (M = Ti, Zr) and W_2L_6 contain only bidentate carbamate ligands. Single-crystal structural determinations show (i) that $W(NMe_2)_3L_3$ contains a *fac*-WN_3O_3 octahedral moiety with very short W–N bond distances, 1.922 (7) Å, and (ii) that NbL_5 contains eight-coordinated niobium. The NbO_8 polyhedron ($NbO_2(O\text{-}O)_3$) does not conform to any idealized MX_8 geometry. Variable temperature NMR studies reveal interesting dynamical solution behavior for ML_5 (M = Nb, Ta) and W_2L_6. All the carbamato compounds are labile towards CO_2 exchange reactions of the type $ML^* + CO_2 \rightleftarrows ML + {}^{13}CO_2$, where $L^* = O_2{}^{13}CNMe_2$ and $L = O_2{}^{12}CNMe_2$. In addition the group 4A metals (Ti, Zr) show exchange reactions of the type $MO_2{}^{13}CNMe_2 + MO_2{}^{12}CNR_2 \rightleftarrows MO_2{}^{12}CNMe_2 + MO_2{}^{13}CNR_2$ and $ML + M'L' \rightleftarrows ML' + M'L$, where $L = O_2CNMe_2$ and $L' = O_2CN(CD_3)_2$.

The facile formation and rupture of M–H, M–C, C–H, and C–C bonds within the coordination sphere of transition metals form the basis for hydrocarbon catalysis. In principle an extension to include M–N and M–O bonds seems possible and is certainly desirable. With this in mind we set out to study the basic reactions of transition metal complexes containing M–N and M–O σ bonds.

Early transition metal dialkylamides, $M(NR_2)_n$, provide a suitable starting point for studying the reactions of covalent metal-nitrogen σ-bonds. These compounds have already been shown to be reactive toward substitution and insertion reactions.[2-4]

A number of considerations led us to examine the reactivity of these compounds towards carbon dioxide: (1) There is currently a general interest in carbon dioxide fixation and the reactions of carbon dioxide with transition metal complexes.[5] (2) The reaction between carbon dioxide and $M(NR_2)_n$ compounds has received little previous attention, although insertion has been established for $Ti(NMe_2)_4$[3b] and $Cr(N\text{-}i\text{-}Pr_2)_3$.[6] (3) The coordination properties of $M(O_2CNR_2)_n$ compounds would be of considerable interest, especially in comparison with the related dithiocarbamates, $M(S_2CNR_2)_n$. (4) The physical properties of carbon dioxide and its commercial availability in varying isotopically labeled forms make it ideally suited for detailed mechanistic and spectroscopic studies.

In this paper we describe the preparation and properties of $M(O_2CNMe_2)_n$ (where M = Ti, Zr, V and $n = 4$; Nb, Ta and $n = 5$; W, $n = 3$) and $W(NMe_2)_3(O_2CNMe_2)_3$. We also note the remarkable lability of these compounds towards CO_2 exchange reactions. In the following paper we describe studies aimed at delineating the mechanism of CO_2 insertion into the M–N bond and of the carbon dioxide exchange reactions involving these carbamato complexes.

Preliminary results, reporting the crystal structures of $W(NMe_2)_3(O_2CNMe_2)_3$[7] and $Nb(O_2CNMe_2)_5$[1] and a discussion of the carbon dioxide exchange reaction[8] have been published.

Results and Discussion

Synthesis. Solutions of early transition metal *N,N*-dimethylamides $M(NMe_2)_n$ (where M = Ti,[3b] Zr, V and $n = 4$; Nb, Ta and $n = 5$) and $W_2(NMe_2)_6$, react rapidly and quantitatively (via ^1H NMR) with carbon dioxide ($\geq n$ equiv) to yield the corresponding dimethylcarbamates $M(O_2CNMe_2)_n$ as shown in eq 1.

$$M(NMe_2)_n + nCO_2 \rightarrow M(O_2CNMe_2)_n \quad (1)$$

Although we concentrated on characterizing dimethylcarbamates, other dialkylamides $M(NRR')_n$ (R, R' = Me, Et) of Ti(IV), Zr(IV), and W(III) were found to react with CO_2 to yield $M(O_2CNRR')_n$. $W(NMe_2)_6$, however, reacts differently, as is shown in eq 2.

$$W(NMe_2)_6 + 3CO_2 \rightarrow W(NMe_2)_3(O_2CNMe_2)_3 \quad (2)$$

$W(NMe_2)_3(O_2CNMe_2)_3$ is the only product observed, even in the presence of excess CO_2 (ca. 10 atm at 25 °C).

Most of these reactions were initially carried out on a small scale in NMR tubes and monitored via ^1H NMR spectroscopy. The quantitative nature of eq 1 and 2 was confirmed. In some cases transient species were observed, probably $M(NMe_2)_{n-x}(O_2CNMe_2)_x$. We obtained a qualitative measure of the speed of eq 1 and 2. Equation 1 is complete within ca. 5 min at 25 °C for $M(NMe_2)_4$ (M = Ti, Zr, V) and $M(NMe_2)_5$ (M = Nb, Ta). $W_2(NMe_2)_6$ and $W(NMe_2)_6$ react somewhat more slowly (complete within ca. 10–20 min).

Reactions of $M(NMe_2)_n$ with CO_2 were usually carried out in toluene or benzene using standard vacuum line techniques to add the CO_2. $M(O_2CNMe_2)_4$ (M = Ti, Zr, V) precipitated from the benzene or toluene solution. $W_2(O_2CNMe_2)_6$, $W(NMe_2)_3(O_2CNMe_2)_3$, and $M(O_2CNMe_2)_5$ (M = Nb, Ta) were crystallized by concentrating the solution and adding hexane.

Characterization. Dimethylcarbamato compounds are air- and moisture-sensitive crystalline solids. ML_4, where $L = O_2CNMe_2$ and M = Ti, Zr, or V, are stable indefinitely at 25 °C in the absence of water and oxygen. NbL_5, TaL_5, and $W(NMe_2)_3L_3$ decompose slowly over a period of weeks at 25 °C but are stable indefinitely when stored, sealed, in vacuo at −20 °C, in the dark.

Satisfactory elemental analyses (Table I) were obtained for all compounds except $W(NMe_2)_3L_3$ and W_2L_6. However, all other experimental data, including single-crystal x-ray studies indicate that $W(NMe_2)_3L_3$ and W_2L_6 are authentic compounds.

Table I. Characterization[a,b] of Some Early Transition Metal Dimethylcarbamato Complexes

Compound	Color	Carbon Found (calcd)	Hydrogen Found (calcd)	Nitrogen Found (calcd)	Mol wt Found (calcd)
$Ti(O_2CNMe_2)_4$	Pale yellow	35.86 (36.01)	6.03 (6.04)	13.78 (14.00)	
$Zr(O_2CNMe_2)_4$	White	32.78 (32.49)	5.58 (5.45)	12.54 (12.63)	443 ± 20 (443)
$V(O_2CNMe_2)_4$	Green	35.53 (35.74)	6.08 (6.00)	13.67 (13.89)	
$Nb(O_2CNMe_2)_5$	Pale yellow	33.49 (33.78)	5.50 (5.67)	12.79 (13.13)	534 ± 15 (533)
$Ta(O_2CNMe_2)_5$	White	28.75 (28.99)	4.80 (4.87)	10.99 (11.27)	
$W(NMe_2)_3(O_2CNMe_2)_3$[c]	Orange	33.70 (31.04)	6.82 (6.25)	14.14 (14.48)	
$W_2(O_2CNMe_2)_6$[d]	Orange	36.29 (35.57)[e]	4.79 (4.85)[e]	8.65 (7.78)[e]	858 ± 80 (896)

[a] Elemental analyses performed by Alfred Bernhardt Mikro. Lab., Elbach, W. Germany. [b] Molecular weights determined cryoscopically in benzene. [c] Tungsten, found (calcd) = 30.63 (31.68). [d] Tungsten, found (calcd) = 34.83 (34.04), see *e* below. [e] Calcd for $W_2(O_2CNMe_2)_6(toluene)_2$.

Table II. Solubilities and ^1H NMR Data for Some Metal *N,N*-Dialkylcarbamates

	Solubility			^1H NMR data			
Compound	Hexane	C_6H_6	CH_2Cl_2	Solvent	Temp (°C)	δ (ppm)[a]	$^3J_{^{13}C-H}$ (Hz)[b]
TiL_4[c]	i	ss	s	CH_2Cl_2	45	2.85	3.2
				C_6H_6	45	2.33	
$Ti(O_2CNEt_2)_4$	i	s	s	CH_2Cl_2	45	3.27 (q, 2), 1.04 (t, 3)	
				C_6H_6	45	3.12 (q, 2), 0.88 (t, 3)	
ZrL_4[c]	i	ss	s	CH_2Cl_2	45[d]	2.87	3.2
				C_6H_6	45	2.39	
NbL_5[c]	i	s	s	CH_2Cl_2	45	2.83	3.2
				C_6H_6	45	2.55	
				$C_6D_5CD_3$	−80[e]	2.50, 2.32 (2:3)	
TaL_5[c]	i	s	s	CH_2Cl_2	45	2.85	3.2
				C_6H_6	45	2.55	
				$C_6D_5CD_3$	−80[e]	2.53, 2.30 (2:3)	
$W(NMe_2)_3(L_3)$[c]	s	s	s	C_6H_6	45	4.75, 2.82 (1:1)[f]	3.0
				$C_6D_5CD_3$	−30	4.57, 2.78, 2.74 (2:1:1)[g]	
W_2L_6[c]	i	s	ss	C_6H_6	45	2.58	3.0
				CH_2Cl_2	45	3.15, 2.90 (1:2)	
				CH_2Cl_2	−70	3.16, 3.03, 2.83, 2.63 (2:2:1:1)	

[a] Shifts in ppm downfield from hexamethyldisiloxane at 60 MHz. [b] $^3J_{^{13}C-H}$ for $(O_2{}^{13}CNR_2)$. [c] L = O_2CNMe_2. [d] Spectrum unchanged at ca. −120 °C in 1:1 CH_2Cl_2–Freon 11. [e] $T_c = -65$ °C. [f] $\delta(NMe_2)$ 4.75, $\delta(L)$ 2.82. [g] $\delta(NMe_2)$ 4.57, $\delta(L)$ 2.74, 2.78, $T_c = -1$ °C.

^1H NMR data and solubility data for ML_n and $W(NMe_2)_3L_3$ are given in Table II. Molecular weight determinations indicate that ZrL_4 and NbL_5 are monomeric and W_2L_6 is dinuclear in benzene (Table I).

In general these compounds did not sublime, or yield molecular ions, $ML_n{}^+$, in the mass spectrometer. However, $W(NMe_2)_3L_3$ and $W_2(O_2CNMeEt)_6$ yielded parent ions corresponding to loss of NMe_2 and NMeEt, respectively. For $W(NMe_2)_3L_3$ this was apparent from a comparison of the mass spectra of $W(NMe_2)_3({}^{18}O_2{}^{12}CNMe_2)_3$ and $W(NMe_2)_3({}^{16}O_2{}^{12}CNMe_2)_3$.

In general, the carbamato compounds $M(O_2CNR_2)_n$ are considerably less soluble than the parent dialkylamides $M(NR_2)_n$ but more soluble than the corresponding dithiocarbamato compounds $M(S_2CNR_2)_n$.

Infrared Spectra. Carbamato compounds show strong absorptions in the 1560–1685-cm^{-1} region assignable to the O_2CN moiety (Table III). The effect of isotopic substitution (${}^{18}O_2CN$ and $O_2{}^{13}CN$) on the positions of these absorptions has been studied (see Table III). A comparison of $\Delta^{18}O$ with the known coordination of the ligands in $W(NMe_2)_3L_3$[7] and NbL_5[1] leads us to the conclusion that a small $\Delta^{18}O$ (<5 cm^{-1}) is indicative of a bidentate ligand and a relatively large $\Delta^{18}O$ (ca. 20 cm^{-1}) of a monodentate ligand. The magnitudes of $\Delta^{13}C$ and $\Delta^{18}O$ may be rationalized by assuming that $\nu_{str}(O_2CN)$ for a bidentate ligand is mostly C=N in character while $\nu_{str}(O_2CN)$ for a monodentate ligand has a significant contribution from the C=O moiety. A consideration of $\Delta^{18}O$ leads us to predict that ZrL_4 is eight coordinate and W_2L_6 contains only bidentate ligands.

Very weak bands are observed at ca. 1700 cm^{-1} for TiL_4 and ZrL_4. Lappert and co-workers[3b] suggested that the weak shoulder observed at 1690 cm^{-1} for TiL_4 might be due to a monodentate Me_2NCO_2 ligand. For TiL_4 and ZrL_4 these bands are present both in solid state (Nujol mull) and solution (CH_2Cl_2) spectra ($\Delta^{18}O$ = 30 cm^{-1} for ZrL_4). $Ti(NMe_2)_2L_2$ (see following paper) has been shown by x-ray crystallography to contain only bidentate carbamato ligands, yet its solid state (Nujol mull) infrared spectrum also shows a very weak band at 1705 cm^{-1}. Thus, it seems that little can be inferred about the coordination properties of a Me_2NCO_2 ligand from this very weak high frequency band.

The infrared absorptions observed in the 250–700-cm^{-1} region for ML_4 and W_2L_6 are listed in Table IV. These compounds we believe contain only bidentate ligands. Considerations of $\Delta^{13}C$, $\Delta^{18}O$, and the infrared spectra of $M(S_2CNR_2)_4$[4] (ν_{str}(M–S) $\simeq$ 360 cm^{-1}), $Zr(O_2NO)_4$,[9] and $Co(NH_3)_4(O_2CO)Cl$[10] lead us to assign the strong bands at 428–459 cm^{-1} to ν_{str}(M–O). By analogy to $CH_3CO_2{}^-$,[11] the strong bands at ca. 650 cm^{-1} are assigned to bending vibrations of the O_2CN moieties.

Table V summarizes the infrared maxima in the 250–700-cm^{-1} region for NbL_5, TaL_5, and $W(NMe_2)_3L_3$. NbL_5 and TaL_5 contain monodentate as well as bidentate ligands

Table III. Infrared Absorption Maxima in the 1700–1550-cm^{-1} Region Characteristic of $\nu_{str}(O_2CN)$

Compound[a]	$\nu_{str}(^{16}O_2{}^{12}CN)$[b]	$\Delta^{13}C$ (cm^{-1})[c]	$\Delta^{18}O$ (cm^{-1})[d]	Ligand coordination[e]
ZrL_4	1587	22	4	Bidentate
TiL_4	1599			
$Ti(O_2CNEt_2)_4$	1564			
VL_4	1525[f]			
NbL_5	1611	19	1	Bidentate[g]
	1680	35	22	Monodentate[g]
TaL_5	1619			
	1682			
$W(NMe_2)_3L_3$	1636	39	21	Monodentate[g]
W_2L_6	1575	20	4	Bidentate
	1629	29	3	Bidentate

[a] $L = O_2CNMe_2$. [b] As Nujol mulls, uncertainty in peak positions is ca. 4 cm^{-1}. [c] $\Delta^{13}C = \nu(^{16}O_2{}^{12}CN) - \nu(^{16}O_2{}^{13}CN)$. [d] $\Delta^{18}O = \nu(^{16}O_2{}^{12}CN) - \nu(^{18}O_2{}^{12}CN)$. [e] Predicted on the basis of $\Delta^{18}O$. [f] Extremely broad. [g] Confirmed by crystal structure.

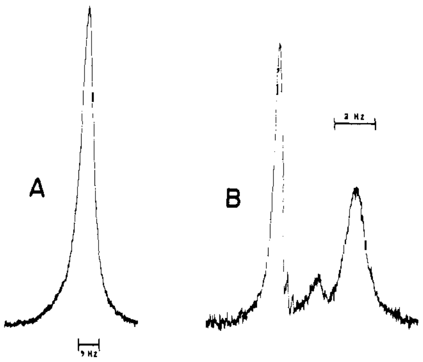


Figure 1. ^1H NMR spectra in CH_2Cl_2, at 60 MHz and at 40 °C: (A) $Ti(OS^{12}CNMe_2)_4$, (B) $Ti(OS^{13}CNMe_2)_4$, average $^3J(^{13}C-H) = 3.8$ Hz.

(from x-ray studies—see later). Based on the same arguments which were made for ML_4 compounds, we assign the strong bands at 437 ± 5 cm^{-1} to the bidentate $\nu_{str}(M-O)$. The bands at 590 ± 3 cm^{-1} show relatively large $\Delta^{18}O$ and are assigned to $\nu_{str}(M-O)$ of a monodentate ligand. This is in agreement with the values obtained for metal alkoxides, $\nu_{str}(M-O)$ 571 cm^{-1} for $Nb(OEt)_5$.[12] $W(NMe_2)_3L_3$ is a distorted fac-octahedron and should exhibit $\nu_{str}(M-N)$ and $\nu_{str}(M-O)$. On the basis of $\Delta^{18}O$ we make the assignments: $\nu_{str}(W-N)$ 576 cm^{-1} and $\nu_{str}(W-O)$ 604 cm^{-1}. These assignments are in basic agreement with the values obtained for $W(NMe_2)_6$ ($\nu_{str}(W-N)$ 545 cm^{-1})[13] and for $W(O\text{-}i\text{-}Pr)_6$ ($\nu_{str}(W-O)$ 600 cm^{-1}).[13] Since $\nu(W-N)$ and $\nu(W-O)$ are of similar energy, one might expect some coupling of these modes. However, values obtained for $\Delta^{18}O$ argue against extensive coupling of $\nu_{str}(W-N)$ and $\nu_{str}(W-O)$. As was the case for ML_4 compounds, the bands at 625–690 cm^{-1} are assigned to bending vibrations of the O_2CN moieties.

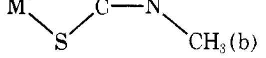
There were no significant differences between solid state (Nujol mull) and solution (CH_2Cl_2 or benzene) infrared spectra of these compounds. The absorptions in the 1550–1685-cm^{-1} region shifted less than 10 cm^{-1} and $\Delta^{18}O$ remained constant. Complete infrared data for all compounds are recorded in the experimental section.

$Zr(O_2CNMe_2)_4$, $Ti(O_2CNMe_2)_4$, and $Ti(O_2CNEt_2)_4$. $Zr(O_2CNMe_2)_4$ is monomeric in benzene (Table I) and contains only bidentate ligands (Table III) and thus must contain eight-coordinated zirconium. A comparison of the infrared spectra of ZrL_4, TiL_4, and $Ti(O_2CNEt_2)_4$ suggests that in the latter two compounds titanium is also eight-coordinated. The closely related compound $Ti(S_2CNEt_2)_4$ has been shown by x-ray crystallography to contain eight-coordinated titanium.[14] The TiS_8 moiety is dodecahedral, containing two "types" of sulfur coordination sites (designated A and B). This type of coordination geometry is common for tetrakis chelate complexes.[15]

In theory, if the TiO_8 and ZrO_8 geometries are dodecahedral, one should observe two methyl resonances via NMR spectroscopy. However, as is the case for the dithiocarbamates $M(S_2CNR_2)_4$ (M = Ti or Zr),[16,17] only a single resonance is observed at temperatures as low as −120 °C for ZrL_4 (Table II).

These results are consistent with either stereochemical nonrigidity or accidental magnetic degeneracy. Our experience indicates that the proton chemical shifts of the carbamate ligands can be insensitive to their coordination environment, although they are solvent dependent. For example, the methyl resonances of TiL_4, ZrL_4, NbL_5, and TaL_5 in CH_2Cl_2 at 40 °C are nearly magnetically degenerate ($\Delta\nu$ = 2 Hz at 60 MHz).

An interesting example of near accidental magnetic degeneracy is seen in the ^1H NMR spectrum of $Ti(OSCNMe_2)_4$ which, in CH_2Cl_2 at 40 °C, shows only a slightly broad single resonance ($\Delta\nu_{1/2}$ = 0.8 Hz) at 60 MHz. However, the labeled compound $Ti(OS^{13}CNMe_2)_4$ shows an asymmetric doublet. See Figure 1. The doublet is asymmetric because (i) $CH_3(a)$ and $CH_3(b)$ as depicted in I are not degenerate ($\Delta\nu \approx 0.3$ Hz)



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and (ii) $^3J(^{13}C-H_a) \neq {}^3J(^{13}C-H_b)$ ($\Delta^3J \approx 0.3$ Hz). The ^1H NMR spectra of $Ti(OSCNMe_2)_4$ shown in Figure 1 demonstrate two important points. Firstly, they unambiguously show that two chemically different methyl groups may appear degenerate (as seen in Figure 1A). Secondly, the fact that $CH_3(a)$ and $CH_3(b)$ are not degenerate (as seen in Figure 1B) indicates that rotation about the C–N bond is slow on the ^1H NMR time scale at 40 °C.

These observations demonstrate that tetrakis chelates of the type TiL_4 and ZrL_4 are prone to accidental magnetic degeneracy. Our ^1H NMR data on ZrL_4 and TiL_4 are inconclusive. (i) The molecules may be stereochemically nonrigid at −120 °C or (ii) the methyl resonances may be accidentally magnetically degenerate.

Fay and co-workers have recently reported the first example of stereochemical rigidity of a tetrakis chelate.[18] The ^1H NMR spectrum of $Ta(S_2CNMe_2)_4{}^+$ exhibits two methyl resonances ($\Delta\nu$ = 7.2 Hz at 60 MHz) below −62 °C in CH_2Cl_2-CD_3CN. The interconversion process has a free energy of activation, $\Delta G^{\ddagger} = 11.05\ (8)$ kcal mol^{-1}.

$V(O_2CNMe_2)_4$. The infrared spectrum of VL_4 indicates significant structural differences from ML_4 (M = Ti, Zr). The only absorption of VL_4 in the $\nu_{str}(O_2CN)$ region is an extremely broad band centered at ca. 1525 cm^{-1}. Although there are some similarities between the infrared spectra of VL_4 and TiL_4 in the 250–700-cm^{-1} region, VL_4 exhibits a strong band at 605 cm^{-1} not found in TiL_4. See Table IV. VL_4 is insoluble in hydrocarbon solvents which hindered further characterization of this compound.

$Nb(O_2CNMe_2)_5$ and $Ta(O_2CNMe_2)_5$. Molecular weight determinations showed $Nb(O_2CNMe_2)_5$ to be monomeric in

Table IV. Infrared Absorption Maxima for ML_4[a] and W_2L_6[a] in the 250-700-cm^{-1} Region

ZrL_4 ν (cm^{-1}) ($\Delta^{13}C$, $\Delta^{18}O$)[b]	TiL_4 ν (cm^{-1})	$Ti(O_2CNEt_2)_4$ ν (cm^{-1})	VL_4 ν (cm^{-1})	W_2L_6 ν (cm^{-1})	Assignment[c]
260 w (−3, 0)	250 w		283 s	262 s	
303 s (−1, 2)	352 m	348 m	354 m	355 w	
		356 sh			
409 sh (0, 14)				400 w	
428 s (0, 8)	446 s	449 s, br	456 s	450 s	ν(M-O)
625 w (1, 23)			605 s	608 w	
				625 w	$\delta(O_2CN)$
659 s (0, 21)	650 s	641 s	669 s	662 s	

[a] As Nujol mulls, $L = O_2CNMe_2$. [b] $\Delta^{13}C = \nu(M^{16}O_2{}^{12}CNMe_2) - \nu(M^{16}O_2{}^{13}CNMe_2)$, $\Delta^{18}O = \nu(M^{16}O_2{}^{12}CNMe_2) - \nu(M^{18}O_2{}^{12}CNMe_2)$. [c] See text for a discussion of assignments.

Table V. Infrared Absorption Maxima for ML_5[a] and $W(NMe_2)_3L_3$[a] in the 250-700-cm^{-1} Region

NbL_5 ν (cm^{-1}) ($\Delta^{13}C$, $\Delta^{18}O$)[b]	TaL_5 ν (cm^{-1}) ($\Delta^{13}C$)[b]	$W(NMe_2)_3L_3$ ν (cm^{-1}) ($\Delta^{13}C$, $\Delta^{18}O$)[b]	Assignment[c]
320 m (−3, 4)	260 m (0)	372 w	
		433 s (−1, 0)	
442 s (0, 7)	432 s (4)		ν(M-O)
587 s (−2, 18)	592 s (2)	604 m (−2, 21)	ν(M-O)
		576 s (−1, 0)	ν(M-N)
626 w (−2, 21)	628 w (2)		
666 vs (−2, 19)	665 vs (0)	649 vs (2, 20)	$\delta(O_2C$-N)
690 w (0, 22)	690 w (0)	666 s (2, 26)	

[a] As Nujol mulls. $L = O_2CNMe_2$. [b] $\Delta^{13}C = \nu(M^{16}O_2{}^{12}CNMe_2) - \nu(M^{16}O_2{}^{13}CNMe_2)$, $\Delta^{18}O = \nu(M^{16}O_2{}^{12}CNMe_2) - \nu(M^{18}O_2{}^{12}CNMe_2)$. [c] See text for a discussion of assignments.

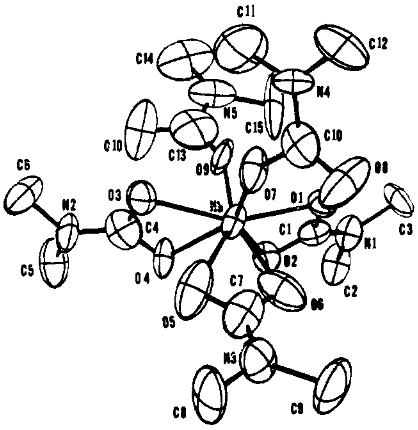
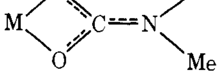


Figure 2. A view of the $Nb(O_2CNMe_2)_5$ molecule showing 50% probability ellipsoids and the atomic numbering scheme.

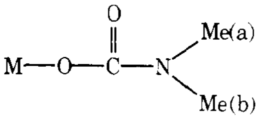
benzene (Table I). ^1H NMR spectra of NbL_5 and TaL_5 (Table II) consisted of a single resonance at ambient temperatures and two resonances in the integral ratio 2:3 at low temperatures (T_c = −65 °C). Infrared spectra of NbL_5, TaL_5, and $Nb(^{18}O_2CNMe_2)_5$ indicated the presence of both bidentate and monodentate ligands (Table III). These data could be interpreted in terms of seven- or eight-coordinated niobium or tantalum. To resolve this question and to determine the interesting structural possibilities which seven- or eight-coordination offer, we resorted to a single-crystal x-ray structural determination for $Nb(O_2CNMe_2)_5$.[1]

An ORTEP view of the molecular structure of NbL_5 is shown in Figure 2 and the pertinent bond distances and bond angles for the immediate coordination geometry of niobium are given in Table VI. Niobium is eight-coordinate having three bidentate and two monodentate $Me_2NCO_2^-$ ligands. All Me_2NCO_2 moieties are planar, as expected. The NbO_8 moiety does not correspond to any idealized MX_8 polyhedron.[15,19] This is clearly evident from the fact that two almost mutually perpendicular planes contain Nb and *five* of the NbO_8 oxygens. See Table VI. Of course, for a $MO_2(O\text{-}O)_3$ structure a departure from an idealized MX_8 geometry is expected due to the constraints imposed by the chelating ligands. In this context it is interesting to compare the structure of NbL_5 with eight-coordinate U(VI) compounds $UO_2(O\text{-}O)_3$ (e.g., $RbUO_2(NO_3)_3$).[20] The latter adopt a trans O-U-O geometry whereas for NbL_5 the monodentate ligands are cis; the O(7)-Nb-O(9) angle is 90.5 (7)°. Note also that the Nb-O bond distances are much shorter for the monodentate ligands (average monodentate Nb-O = 1.91 (2) Å) than for the bidentate ligands which are bonded asymetrically (average bidentate Nb-O = 2.08 (4) and 2.19 (2) Å). Oxygen to niobium π-bonding may be significant in NbL_5 since niobium attains only 16 valence electrons via NbO_8 σ-bonding.

Unfortunately, the structure of NbL_5 provides little insight into its dynamical behavior. In the solid state structure *none* of the methyl groups is stereochemically equivalent. Even if one assumes that methyls associated with each bidentate ligand are accidentally degenerate by virtue of the high local symmetry of the MO_2CNMe_2 moiety II, it is more difficult to presume degeneracy of the methyls of the monodentate ligands III. Furthermore one must explain the 2:3 ratio of the methyl resonances observed at temperatures as low as −120 °C in the ^1H NMR spectra (in 1:1 CH_2Cl_2/Freon 11 at 100 MHz).



II



III

Variable temperature ^1H NMR spectra have been obtained for the carbamate esters $Me_2NC(O)OR$[21] which are closely related to III. The *N*-methyl resonances of these compounds are solvent dependent and are sometimes degenerate (60 MHz). The barrier to rotation about the N-C bond in $Me_2NC(O)OR$ is about 16 kcal mol^{-1}. A barrier of ca. 16 kcal mol^{-1} would be too large to explain the equivalence of Me(a) and Me(b) in III at −120 °C and 100 MHz.

Solution infrared spectra (CH_2Cl_2 and benzene) of NbL_5 and TaL_5 are entirely consistent with the solid state structure indicating the presence of both bidentate and monodentate ligands ($\Delta^{18}O$ = 3 and 20 cm^{-1}).

At this point we felt that a ^{13}C NMR study would be more definitive since carbon resonances are less likely to be accidentally degenerate.

Table VI. Bond Distances (Å), Bond Angles (deg), and Least-Squares Planes for the NbO_5 Moiety of $Nb(O_2CNMe_2)_5$

Bond distances		Bond angles	
Nb-O1	2.17 (1)	O1-Nb-O2	61.5 (5)
Nb-O2	2.10 (1)	O1-Nb-O3	154.5 (5)
Nb-O3	2.20 (1)	O1-Nb-O4	134.7 (6)
Nb-O4	2.11 (1)	O1-Nb-O5	130.6 (6)
Nb-O5	2.20 (2)	O1-Nb-O6	74.8 (6)
Nb-O6	2.02 (2)	O1-Nb-O7	82.2 (6)
Nb-O7	1.91 (1)	O1-Nb-O9	80.8 (6)
Nb-O9	1.91 (2)	O2-Nb-O3	133.0 (6)
		O2-Nb-O4	74.3 (6)
Bond angles			
		O2-Nb-O5	112.9 (7)
O4-Nb-O6	106.2 (6)	O2-Nb-O6	78.1 (6)
O4-Nb-O7	141.8 (6)	O2-Nb-O7	143.6 (6)
O4-Nb-O9	87.2 (6)	O2-Nb-O9	85.8 (6)
O5-Nb-O6	56.9 (7)	O3-Nb-O4	60.6 (6)
O5-Nb-O7	88.6 (7)	O3-Nb-O5	68.2 (6)
O5-Nb-O9	148.0 (7)	O3-Nb-O6	124.8 (7)
O6-Nb-O7	91.4 (7)	O3-Nb-O7	81.4 (6)
O6-Nb-O9	155.1 (7)	O3-Nb-O9	80.0 (6)
O7-Nb-O9	90.5 (7)	O4-Nb-O5	74.2 (6)

Least-Squares Planes

Atoms	Equation of plane
1 Nb, O1, O2, O3, O4, O7	$-0.872x - 0.028y - 0.489z = -1.725$
11 Nb, O1, O3, O5, O6, O9	$0.141x - 0.958y - 0.250z = -3.441$

Distance of Atoms from Plane

1		11	
Nb	−0.16	Nb	0.11
O1	0.19	O1	−0.21
O2	−0.02	O3	−0.18
O3	0.22	O5	0.02
O4	−0.08	O6	0.09
O7	−0.15	O9	0.18
O5	−2.03	O2	1.78
O6	−1.99	O4	1.79
O9	1.75	O7	−1.81

Variable temperature ^{13}C NMR spectra of $Nb(O_2{}^{13}CNMe_2)_5$ and $Ta(O_2{}^{13}CNMe_2)_5$ in CD_2Cl_2 have been recorded over the temperature range −80 to +30 °C. The spectra of the methyl carbons and the carbamate carbons were recorded simultaneously. The carbamate carbons were enriched to 90% ^{13}C to enable achievement of the desired signal/noise in a reasonable amount of time. The low temperature limiting spectra of both the carbamate carbons and the methyl carbons for both complexes were simply two resonances with relative intensity 3:2. See Table VII. No spin-spin coupling between the two types of carbons was observed.

The calculations were performed with a computer program (provided by P. Meakin) which utilized first-order matrix formalism. The problem was represented as a single-spin two-site problem with the populations of the two sites appropriately weighted for an A_2B_3 spin system. Relevant activation parameters were calculated from a least-squares fit of the data. See Table VII. The barrier to intramolecular rearrangement is the same within experimental error for the methyl carbons and the carbamate carbons for both NbL_5 and TaL_5. The barrier is slightly higher (1 kcal mol^{-1}) for TaL_5 than NbL_5.

If we ignore the possibility of accidental magnetic degeneracy, which is unlikely to occur in both ^1H and ^{13}C NMR spectra, then, *on the NMR time scale* all ligands are "apparently" bidentate via a rapid exchange of bonding and nonbonding oxygens, passing through a bidentate transition state or intermediate. This process would have to be rapid, even at −81 °C (^{13}C NMR). However, in order to attain a 3:2 ratio of ligands (assuming Figure 2 represents the solution ground state geometry) other skeletal rearrangements must be operative. It is fruitless to speculate further upon the dynamical solution behavior of ML_5 (N = Nb, Ta).

Table VII. ^{13}C NMR Data for $M(O_2{}^{13}CNMe_2)_5$

M	T (°C)	Resonance	Relative intensity	δ (ppm)[a]	Interconversion barrier: $\Delta G^{\ddagger}$ (kcal/mol)[b]
Nb	−81	CO_2	2	157.4	11.2 (4)
			3	166.0	
		Methyl	2	35.0	10.9 (2)
			3	33.5	
Ta	−60	CO_2	2	157.6	11.9 (2)
			3	165.5	
		Methyl	2	35.1	11.9 (2)
			3	33.9	

[a] δ in ppm downfield from Me_4Si, in CD_2Cl_2. [b] In all cases $\Delta S^{\ddagger} \leq 5.6$ eu.

It should be emphasized that even though all ligands may be effectively bidentate on the NMR time scale, this is not the case for the infrared time scale; the compounds in solution contain both monodentate and bidentate ligands.

$W_2(O_2CNMe_2)_6$. The reaction of carbon dioxide (≥6 equiv) with $W_2(NMe_2)_6$ in toluene yields an orange crystalline solid containing solvent of crystallization (seen via ^1H NMR). Although elemental analyses were not satisfactory for $W_2L_6(toluene)_x$, the observed N to W ratio of 2.94 to 1 was as expected (Table I). A molecular weight measurement in benzene of a sample *crystallized from benzene* was in good agreement with the formula W_2L_6 (Table I). The ^1H NMR spectra of W_2L_6 in benzene at 40 °C exhibits a single resonance. Variable temperature ^1H NMR spectra of W_2L_6 in CH_2Cl_2 are shown in Figure 3. The low temperature limiting spectrum consists of four resonances in the integral ratio 2:2:1:1. This spectrum is consistent only with a compound containing 6*n* methyl groups.

Thus, while satisfactory elemental analyses have not been obtained for W_2L_6, all other experimental data indicate that W_2L_6 is an authentic compound.

Infrared spectra of W_2L_6 indicate the presence of at least two types of bidentate carbamato ligands as well as the absence of monodentate ligands.

The variable temperature ^1H NMR spectra would seem to rule out a structure containing four bridging bidentate ligands which is so often found in dinuclear metal tetraacetates, e.g., $Mo_2(O_2CCF_3)_4 \cdot 2L$.[22]

A single-crystal x-ray structural determination has recently been carried out on the related compound $W_2(O_2CNEt_2)_4Me_2$.[23] This molecule has virtual C_{2v} symmetry and contains two terminal W-Me groups, two terminal bidentate carbamato ligands, and a tungsten-tungsten triple bond (W-W = 2.27 Å) bridged by two bidentate carbamato ligands.

It is possible to interpret the variable temperature ^1H NMR spectra of W_2L_6 by assuming that W_2L_6 adopts a structure akin to that of $W_2(O_2CNEt_2)_4Me_2$, but in which the two W-Me groups are replaced by terminal bidentate carbamato ligands, retaining the overall molecular symmetry C_{2v}.

Thus, at high temperatures all ligands are exchanging rapidly on the ^1H NMR time scale (Figure 3a). On cooling to ca. 30 °C two resonances, integral ratio 1:2, are observed (Figure 3c) and are assigned to the bridging and terminal ligands, respectively. Upon further cooling, the resonance assigned to the bridging ligands sharpens, while the resonance

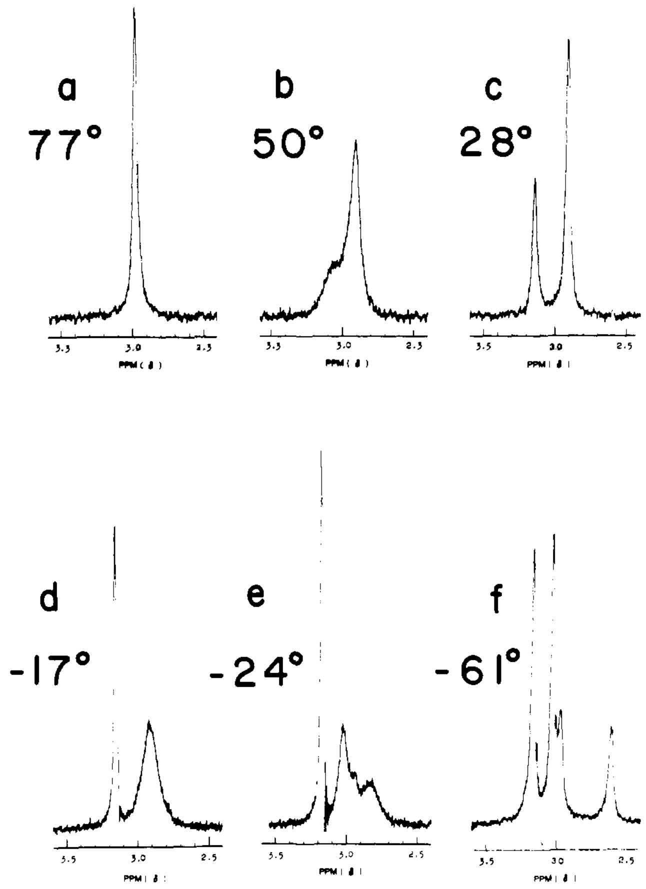


Figure 3. ^{1}H NMR spectra of $W_2(O_2CNMe_2)_6$ at various temperatures, in CH_2Cl_2 and at 60 MHz.

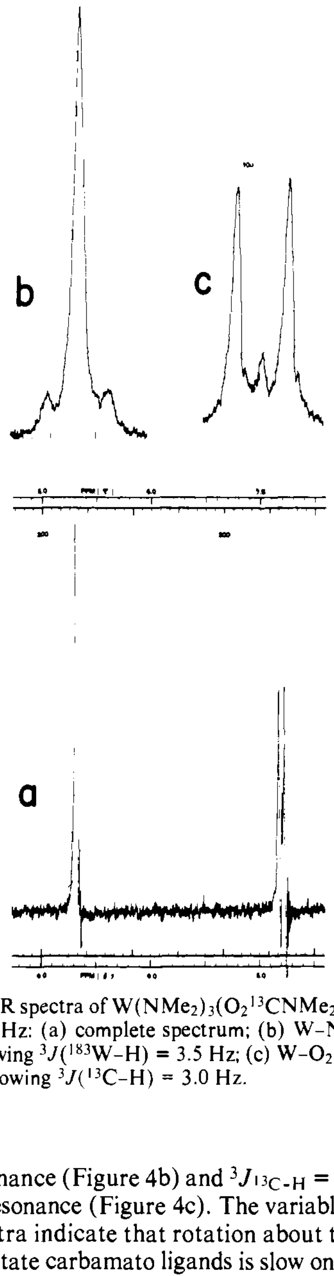


Figure 4. ^{1}H NMR spectra of $W(NMe_2)_3(O_2{}^{13}CNMe_2)_3$ in benzene, at 40 °C and 60 MHz: (a) complete spectrum; (b) W–NMe_2 region expanded 50×, showing $^3J(^{183}W\text{–}H) = 3.5$ Hz; (c) W–$O_2{}^{13}CNMe_2$ region expanded 50× showing $^3J(^{13}C\text{–}H) = 3.0$ Hz.

assigned to the terminal ligands broadens (Figure 3d and 3e), then splits into three resonances, integral ratio 2:1:1 (Figure 3f). Thus, four resonances are observed at low temperatures in the ratio 2:2:1:1 (Figure 3f), equivalent to 4, 4, 2, and 2 methyl groups, respectively. The low field resonance (4 methyls) is assigned to the bridging ligands which are apparently symmetry equivalent while the other three resonances (4, 2, and 2 methyls, respectively) are assigned to the terminal ligands. The relatively large chemical shift separation of these resonances is probably due to the diamagnetic anisotropy of the tungsten–tungsten triple bond; cf. the proximal and distal methyl resonances of $W_2(NMe_2)_6$ which are separated by ca. 2 ppm (^{1}H NMR at −60 °C).[24]

As the temperature of a CH_2Cl_2 solution of W_2L_6 is increased from −70 to 80 °C two processes become rapid on the ^{1}H NMR time scale. The first makes equivalent the four terminal ligands and the second, higher energy process, exchanges terminal and bridging ligands. Thus, ^{1}H NMR data are at least entirely consistent with our formulation of W_2L_6 as a derivative of the $W_2(O_2CNEt_2)_4Me_2$ structure.

$W(NMe_2)_3(O_2CNMe_2)_3$. An orange crystalline solid was isolated from the reaction of $W(NMe_2)_6$ and carbon dioxide. Although elemental analyses were not satisfactory, the formulation of this compound as $W(NMe_2)_3(O_2CNMe_2)_3$ has been verified by a single-crystal structural determination[7] (see following). The infrared spectra of $W(NMe_2)_3L_3$ indicates that the carbamato ligands are monodentate (Table III). At 40 °C the ^{1}H NMR spectrum of $W(NMe_2)_3L_3$ shows two singlets of equal intensity at δ 4.75 and 2.82 ppm. Below −1 °C the high field singlet splits into a doublet ($\Delta\nu = 2$ Hz at 60 MHz). See Table II. We assign the high field resonance (δ 2.82 ppm) to the carbamato-methyl protons. These assignments are substantiated by the observation of $^3J_{^{183}W\text{–}H} = 3.5$ Hz for the W–NMe_2 resonance (Figure 4b) and $^3J_{^{13}C\text{–}H} = 3.0$ Hz for the $O_2{}^{13}CNMe_2$ resonance (Figure 4c). The variable temperature ^{1}H NMR spectra indicate that rotation about the C–N bond of the monodentate carbamato ligands is slow on the ^{1}H NMR time scale below −1 °C ($\Delta G^{\ddagger} \gtrsim 15$ kcal mol^{-1}). Furthermore, the ^{1}H NMR spectra support the formulation that the WN_3O_3 moiety adopts the facial isomer in solution.

We reacted $W(NMe_2)_3L_3$ in benzene with excess CO_2 (ca. 10 atm) in a sealed NMR tube. The only compound observed (via ^{1}H NMR) in this reaction mixture was $W(NMe_2)_3L_3$. This experiment does not indicate whether the failure of $W(NMe_2)_3L_3$ to react with excess CO_2 is due to kinetic or thermodynamic factors.

This was the only carbamato compound prepared which presumably contained only monodentate ligands and thus it served as one of our model compounds for the investigation of $\Delta^{18}O$ and $\Delta^{13}C$ (Table III).

We undertook a single-crystal x-ray structural determination for $W(NMe_2)_3L_3$[7] because (i) it was important to unambiguously characterize a compound containing only monodentate carbamato ligands and (ii) we hoped it might provide some insight as to why $W(NMe_2)_3L_3$ failed to react further with CO_2.

An ORTEP view of the molecular structure of $W(NMe_2)_3L_3$ is shown in Figure 5 and pertinent bond distances and bond angles are given in Table VIII. The molecular structure belongs to the symmetry point group C_3. Tungsten is six-coordinated

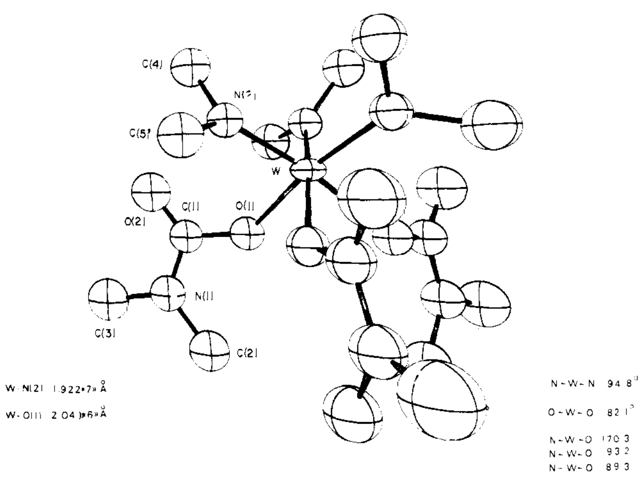


Figure 5. A view of the $W(NMe_2)_3(O_2CNMe_2)_3$ molecule showing 50% probability ellipsoids and the atomic number scheme. The molecule possesses C_3 symmetry; the three NMe_2 ligands are equivalent as are the three O_2CNMe_2 ligands. Also listed are some important structural parameters.

and the local geometry about the metal, WN_3O_3, is a slightly distorted fac-octahedron. Of particular note are the following observations: (i) the N(2)-W-N(2) angles (94.8 (3)°) are greater than the O(1)-W-O(1)′ angles (82.1 (2)°), (ii) W-N(2) bond distances (1.922 (7) Å) are considerably shorter than the W-O bond distances (2.041 (6) Å), and (iii) the O_2CNMe_2 and $W-NMe_2$ moieties are planar.

A comparison of the structures of $W(NMe_2)_3L_3$ and $W(NMe_2)_6$[25] yields two important observations. Firstly, tungsten in $W(NMe_2)_3L_3$ is apparently less crowded than in $W(NMe_2)_6$. This is indicated by the N-W-N angles: compare N-W-N = 94.8 (3)° in $W(NMe_2)_3L_3$ with N-W-N = 90.0° in $W(NMe_2)_6$. Secondly, reaction of $W(NMe_2)_6$ with CO_2 is accompanied by a considerable decrease in the W-N bond lengths of the dimethylamido ligands: compare W-N = 2.032 (25) Å in $W(NMe_2)_6$ with W-N = 1.922 (7) Å in $W(NMe_2)_3L_3$. It is also interesting that ${}^3J({}^{183}W\text{-}H)$ is observed for $W(NMe_2)_3L_3$ (${}^3J({}^{183}W\text{-}H)$ = 3.5 Hz) but not for $W(NMe_2)_6$ or $W_2(NMe_2)_6$.

A consideration of these observations leads us to believe that steric factors do not limit the further reaction of $W(NMe_2)_3L_3$ with CO_2. We suggest that insertion is limited by the nucleophilicity of the NMe_2 ligands. Six dimethylamide ligands, Me_2N^-, offer tungsten a total of 24 electrons although the available metal valence orbitals can accomodate only 18 electrons. Thus for $W(NMe_2)_6$ ligand to metal π-bonding may lead to a maximum W-N bond order of 1.5. However, in $W(NMe_2)_3L_3$ replacement of three NMe_2 ligands by weaker π-donating oxygen ligands leads to greater N to W π-bonding as evidenced by the decrease of 0.11 (3) Å in the W-N bond length. The *fac*-WN_3O_3 geometry allows for maximum W-N π-bonding. The nucleophilic character of the dimethylamide lone pairs is thus diminished and further insertion of CO_2 is not favored, at least by kinetic factors. The mechanism of this insertion reaction is discussed in the following paper.

Monothiocarbamato Compounds. We have initiated a study of the early transition metal monothiocarbamato compounds $M(OSCNMe_2)_n$. The preparations and properties of $M(OSCNMe_2)_4$ (M = Ti, Zr), $Ti(OSCNEt_2)_4$, and $Ta(OSCNMe_2)_5$ are listed in the experimental section.

As discussed previously, the ${}^1H$ NMR chemical shifts of the methyl groups of $Ti(OSCNMe_2)_4$ are nearly degenerate in CH_2Cl_2. The methyl resonances of $Zr(OSCNMe_2)_4$ and $Ta(OSCNMe_2)_5$ are 1:1 doublets at 40 °C in CH_2Cl_2; $\Delta\nu$ = 1.1 and 2.4 Hz, respectively.

Table VIII. Bond Distances (Å) and Bond Angles (deg) for $W(NMe_2)_3(O_2CNMe_2)_3$

W-O(1)	2.041 (6)	N(1)-C(2)	1.44 (1)
W-N(2)	1.922 (7)	N(1)-C(3)	1.47 (1)
O(1)-C(1)	1.30 (1)	N(2)-C(4)	1.48 (1)
C(1)-O(2)	1.24 (1)	N(2)-C(5)	1.50 (1)
C(1)-N(1)	1.35 (1)		
O(1)-W-O(1)′	82.1 (2)	O(1)-C(1)-O(2)	122.8 (9)
O(1)-W-N(2)	93.2 (3)	O(1)-C(1)-N(1)	114.9 (9)
O(1)-W-N(2)′	89.3 (3)	O(2)-C(1)-N(1)	122.3 (9)
O(1)-W-N(2)″	170.7 (3)	C(1)-N(1)-C(2)	123.3 (8)
N(2)-W-N(2)′	94.8 (3)	C(1)-N(1)-C(3)	119.9 (9)
W-O(1)-C(1)	133.7 (6)	C(2)-N(1)-C(3)	116.6 (9)
W-N(2)-C(4)	125.7 (6)	C(4)-N(2)-C(5)	107.6 (7)
W-N(2)-C(5)	126.5 (6)		

Weighted Least-Squares Planes (Å)

Plane I		Plane II	
O(1)	0.012	N(2)	0.0
C(1)	−0.015	C(4)	0.0
O(2)	−0.003	C(5)	0.0
N(1)	−0.026		
C(2)	0.003		
C(3)	0.061		

W distance from plane I = 0.79 Å
W distance from plane II = 0.10 Å

The infrared spectra of $M(OSCNMe_2)_4$ (M = Ti, Zr) show strong absorptions at 1550 cm^{-1} which we assign to ν_{str}(NCOS) of the bidentate ligand. Bands at 346 and 409 cm^{-1} may be due to ν(M-S) and ν(M-O), respectively.

$W(NMe_2)_6$ reacts with COS or CS_2 to yield reduced tungsten compounds, which, although not well characterized, are probably $W(OSCNMe_2)_4$[26] and $W(S_2CNMe_2)_4$,[13] respectively.

Further studies on early transition metal *N,N*-dimethylmonothiocarbamates are in progress. It will be most interesting to compare the solid state structures and dynamical solution behaviors of $Ta(OSCNMe_2)_5$ and $Ta(O_2CNMe_2)_5$.

Carbon Dioxide Exchange Reactions. While attempting to determine why $W(NMe_2)_3L_3$ failed to react further with CO_2 we sealed a solution of the labeled compound $W(NMe_2)_3L^*_3$ ($L^* = O_2{}^{13}CNMe_2$) in an NMR tube with an excess of ${}^{12}CO_2$. ^{1}NMR spectra of the solution revealed that the carbon dioxide exchange reaction (eq 3) was occurring ($t_{1/2} \approx$ 13 h at 21 °C).

$$W(NMe_2)_3L^*_3 + \text{excess}\,{}^{12}CO_2 \rightarrow W(NMe_2)_3L_3 + 3\,{}^{13}CO_2 \quad (3)$$

See Figure 6. Further experiments demonstrated the generality of the CO_2 exchange reaction. ML_4 (M = Ti, Zr), $Ti(O_2CNEt_2)_4$, $Zr(O_2CNMeEt)_4$, ML_5 (M = Nb, Ta), and W_2L_6 are labile towards CO_2 exchange in solution as indicated by eq 4.

$$ML^*_n + \text{excess}\,{}^{12}CO_2 \rightarrow ML_n + n\,{}^{13}CO_2 \quad (4)$$

These reactions are all much faster than eq 3. Attempts to follow eq 4 via ${}^1H$ NMR at 25 °C indicated that exchange was complete in less than ca. 5 min (i.e., $t_\infty \leq$ 5 min at 25 °C). However, it was possible to follow eq 4 at low temperatures via ${}^1H$ NMR. For the reactions, (i) $NbL^*_5 + 20CO_2$ ([Nb] ≈ 0.03 M in toluene-d_8) and (ii) $ZrL_4 + 8\,{}^{12}CO_2$ ([Zr] ≈ 0.09 M in CH_2Cl_2), at −40 °C, the half-life of eq 4 was ca. 24 min. Reactions 3 and 4 were followed by ${}^1H$ NMR spectroscopy using the fact that ${}^3J_{{}^{13}C\text{-}H}$ = 3 Hz for $O_2{}^{13}CNMe_2$.

Reactions 3 and 4 are, of course, reversible ($k_1 = k_{-1}$) and must be treated by exchange kinetics.[27] We have ignored any ${}^{12}C/{}^{13}C$ isotope effects in these reactions since these are pre-

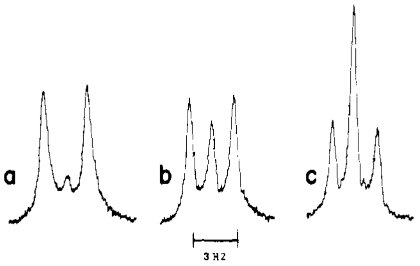


Figure 6. ^{1}H NMR spectra (60 MHz) of the carbamato region during the reaction: $WN_3L^*_3 + 6^{12}CO_2$, carried out at 20.2 °C in toluene-d_8: (a) t = 0 (90% L*), (b) t = 350 min (70% L*), (c) t = 1505 min (45% L*).

sumably very small. The CO_2 exchange reaction can be represented by eq 5,

$$L + C^* \rightleftharpoons L^* + C \quad (5)$$

where L = O_2CNMe_2, L* = $O_2{}^{13}CNMe_2$, C* = $^{13}CO_2$, and C = $^{12}CO_2$. At equilibrium $[L^*]/[L] = [C^*]/[C]$. If R is defined as the gross overall exchange rate for eq 5, a plot of ln $\{[\%\ L_\infty/(\%\ L_\infty - \%\ L_t]\}$ vs. time, where % L_t = mole percent $O_2{}^{12}CNMe_2$ at time = t, should yield a straight line with slope = $R[(LT + CT)]/[(LT)(CT)]$ where LT = [L] + [L*] and CT = [C] + [C*], assuming that all CO_2 is in solution. This assumption is valid if exchange between gaseous and dissolved CO_2 is much faster than eq 5. While this is almost certainly the case for eq 3, it may not be true for the extremely rapid CO_2 exchange reactions of NbL^*_5 or ZrL^*_4.

Kinetic studies of eq 3 indicated that the rate of CO_2 exchange was first order in tungsten, doubling [W] increased R by a factor of 2.04, and ca. zeroth order in CO_2, use of 6, 12, and 18 mole equiv of CO_2 yielded relative rates of exchange: 1.00, 1.03, and 1.26, respectively.

Kinetic studies of eq 4, carried out at ca. −40 °C and followed via ^{1}H NMR spectroscopy, yielded only qualitative results. However, ***reproducible*** experiments indicated that the rate of CO_2 exchange for ZrL^*_4 and NbL^*_5 was ca. first order in CO_2 concentration.

Carbon dioxide exchange reactions have even been observed in the absence of applied CO_2 pressure. $Zr(O_2{}^{13}CNMe_2)_4$ and $Zr(O_2{}^{12}CNMeEt)_4$ react as depicted in eq 6. See Figure 7c.

$$MO_2{}^{13}CNMe_2 + MO_2{}^{12}CNMeEt \rightleftharpoons MO_2{}^{12}CNMe_2 + MO_2{}^{13}CNMeEt \quad (6)$$

The reaction between TiL'^*_4 and ZrL_4 (L'^* = $O_2{}^{13}CN(CD_3)_2$) was followed by ^{1}H NMR spectroscopy: both CO_2 exchange and ligand exchange reactions occurred. In CH_2Cl_2 equilibrium was reached within 5 min at 25 °C. See Figure 8. This reaction may be represented by the sum of eq 7 and 8 since at equilibrium a complex mixture containing statistical combinations of Ti and Zr with L, L*, L′, and L′* are present.

$$ML'^* + M'L \rightleftharpoons ML' + M'L^* \quad (7)$$

$$ML' + M'L \rightleftharpoons ML + M'L' \quad (8)$$

Of course, L′ and L′* are not observable by ^{1}H NMR.

Facile ligand exchange reactions of type 8 have also been observed for other metal tetrakis chelate compounds.[28]

Since all our studies of eq 4 and 6 described thus far have monitored $^3J_{^{13}C-H}$ = 3 Hz in $O_2{}^{13}CNMe_2$ ligands we have only demonstrated that C–N bonds are reversibly formed and broken in thse reactions. We have, however, shown that the analogous reaction 9 occurs. Moreover, in eq 9, CO_2 metathesis, eq 10, does not occur. This demonstrates that the carbon dioxide moiety remains intact during these exchange reactions.

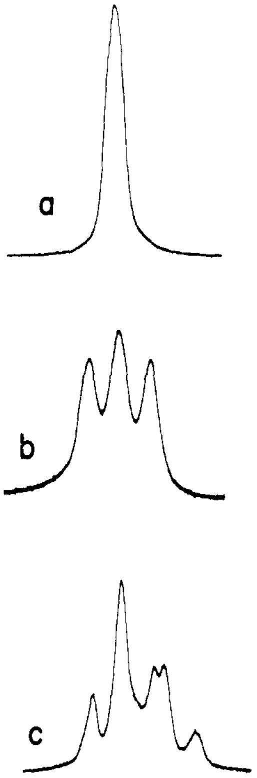


Figure 7. ^{1}H NMR spectra (CH_2Cl_2, 100 MHz, 30 °C) of the N-methyl resonances of (a) $Zr(O_2{}^{12}CNMeEt)_4$ (δ 2.79 ppm), (b) $Zr(O_2{}^{12}CNMeEt)_4 + 4^{13}CO_2$ after 5 min, $^3J(^{13}C-H)$ = 3.0 Hz, and (c) $Zr(O_2{}^{13}CNMe_2)_4 + Zr(O_2{}^{12}CNMeEt)_4$ showing exchange of CO_2 between the carbamato ligands; the O_2CNMe_2 resonance is slightly downfield from the O_2CNMeEt resonance.

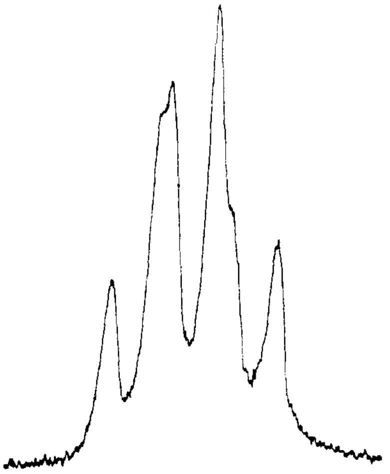


Figure 8. ^{1}H NMR spectrum (CH_2Cl_2, 60 MHz, 40 °C) of the reaction $Zr(O_2{}^{12}CNMe_2)_4 + Ti(O_2{}^{13}CN(CD_3)_2)_4$, after ca. 5 min, showing that ligand exchange as well as CO_2 exchange has occurred. The Ti–L and Ti–L* resonances are slightly upfield (ca. 1.5 Hz) from the Zr–L and Zr–L* resonances.

$$M^{18}O_2CNMe_2 + C^{16}O_2 \rightleftharpoons M^{16}O_2CNMe_2 + C^{18}O_2 \quad (9)$$

$$C^{16}O_2 + C^{18}O_2 \rightleftharpoons 2C^{16}O^{18}O \quad (10)$$

We found that the organic ester, $MeO_2{}^{12}CNMe_2$, does not react with $^{13}CO_2$ under comparable conditions to eq 4.

These observations led us to propose a mechanism for CO_2 exchange reactions involving initial deinsertion of CO_2 from the carbamate ligand, eq 11.[1,8]

$$ML_n \underset{+CO_2}{\overset{-CO_2}{\rightleftharpoons}} M(NMe_2)L_{n-1} \underset{-^{13}CO_2}{\overset{+^{13}CO_2}{\rightleftharpoons}} ML_{n-1}L^* \quad (11)$$

While all of our observations are consistent with a mechanism involving eq 11, they do not rule out all alternate mechanisms.

In the following paper we will discuss further experiments which show that eq 11 is *not* the mechanism for CO_2 exchange reactions. Furthermore, these additional experiments indicate that the rate of deinsertion of CO_2 (11) is extremely small in comparison to the rate of CO_2 exchange (reactions 3 and 4).

Similar exchange reactions have been observed for COS and CS_2. The exchange reactions: (i) $Ti(OS^{13}CNMe_2)_4$ + excess^{12}COS and (ii) $Ti(OS^{13}CNMe_2)_4$ + $Ti(OS^{12}CNEt_2)_4$, carried out in CH_2Cl_2 at 25 °C, were complete within 5 min and 90 h, respectively. The CS_2 exchange reaction, $Ti(S_2CNEt_2)_4$ + excess$^{13}CS_2$ in CH_2Cl_2, was much slower. Only ca. 10% exchange was observed after 70 h at 25 °C.

Conclusions

Carbon dioxide reacts readily with $M(NMe_2)_n$ to give $M(O_2CNMe_2)_n$, except for $W(NMe_2)_6$ which gives only $W(NMe_2)_3(O_2CNMe_2)_3$. It remains to be shown whether the latter compound is formed under kinetic or thermodynamic control.

The carbamate ligand is capable of stabilizing metals in both high oxidation states and high coordination numbers. The bite of the bidentate carbamate ligand, 2.15 (5) Å (averaged over NbL_5 and $Ti(NMe_2)_2L_2$), is comparable to that of the bidentate nitrate ligands in $Ti(NO_3)_4$, 2.13 Å,[29] and is considerably less than that of the dithiocarbamate ligand (2.84 (3) Å in $Ti(S_2CNEt_2)_4$.[14] The carbamate ligand is not oxidized by either Nb(V) or W(VI) whereas the dithiocarbamato ligand is oxidized to $(Me_2NCS_2)_2$.

The carbamato complexes are labile towards CO_2 exchange, and, in addition, the ML_4 compounds (M = Ti, Zr) undergo facile ligand exchange reactions.

Experimental Section

Materials. Dialkylamides, $M(NMe_2)_4$ (M = Ti,[30] Zr,[30] V[31]), $Ti(NEt_2)_4$,[30] $Nb(NMe_2)_5$,[32] $Ta(NMe_2)_5$,[33] $W(NMe_2)_6$,[24] and $W_2(NMe_2)_6$[24] were prepared according to published procedures. "Bone-dry" carbon dioxide was purchased from Matheson. $^{13}CO_2$ (90% ^{13}C) was purchased from Prochem Limited and Merck and Company. $C^{18}O_2$ (94% ^{18}O) was purchased from Miles Laboratories and Prochem Limited. $^{13}CS_2$ (91% ^{13}C) was purchased from Prochem Limited. ^{13}COS (90% ^{13}C) and $(CD_3)_2NH$ (99% D) were purchased from Merck and Company.

General Procedures. Due to the highly reactive nature of $M(NMe_2)_n$, $M(O_2CNMe_2)_n$, and related compounds, all preparations and other operations were carried out under a dry and oxygen-free nitrogen atmosphere or in vacuo using standard Schlenk techniques.[34] Solvents (pentane, hexane, benzene, toluene, THF, and ether) were dried and freed from dissolved molecular oxygen by distillation from a solution of the solvent, benzophenone, sodium, and phenyl ether (Ph_2O not added to ether or THF), then stored over CaH_2 under nitrogen until used. After preparation samples were stored and handled in a Vacuum Atmospheres Company Dri Lab system.

Carbon dioxide was usually measured (ca. 2% accuracy) on a calibrated vacuum manifold, then condensed into the reaction flask with liquid N_2.

Isotopically Labeled Compounds. Labeled compounds, $M(N(CD_3)_2)_n$, $M(O_2{}^{13}CNMe_2)_n$, $M(^{18}O_2CNMe_2)_n$, $M(O_2{}^{13}CN(CD_3)_2)_n$, etc., were prepared similarly to the respective unlabeled compounds, although usually on a smaller scale.

Physical and Analytical Measurements. Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, using drybox sampling techniques.

Molecular weights were determined cryoscopically in benzene, under a purified nitrogen atmosphere, in a jacketed all-glass, cryoscopic apparatus incorporating a thermister bridge.

Infrared spectra were obtained from Nujol mulls between CsI, KBr, or polyethylene plates or from CH_2Cl_2 or benzene solutions in KBr cells using a Beckman IR-12 spectrophotometer.

^1H NMR spectra were obtained from Varian A-60 and HA-100 instruments equipped with variable temperature probes. Temperatures were calibrated with methanol (low temperatures) or ethylene glycol (high temperatures). ^1H chemical shifts are reported as parts per million downfield from HMDS (hexamethyldisiloxane), used as an internal reference.

Variable temperature ^{13}C NMR spectra of $M(O_2{}^{13}CNMe_2)_5$ (M = Nb, Ta) were recorded in the Fourier mode on a Bruker WH90 instrument in the PAPS mode and on a Bruker HFX90/Digilab NMR-3 system. The temperature in both cases was regulated by a copper-constantan thermocouple located directly beneath the NMR tube. Temperatures were calibrated via a second thermocouple held coaxially in a spinning NMR tube. The solvent used was CD_2Cl_2 and this solvent also served as an internal standard for chemical shift measurements ($\delta_{CD_2Cl_2}$ 53.6 ppm). Chemical shifts are reported as parts per million downfield from Me_4Si.

Mass spectra were obtained using an AEI MS9 mass spectrometer and the method of direct insertion (80–120 °C).

Structural Determinations. The single-crystal x-ray structural determinations of $W(NMe_2)_3L_3$ and NbL_5 were carried out by Molecular Structure Corp., College Station, Texas.

Preparation of $M(O_2CNMe_2)_4$ (M = Ti, Zr, V). CO_2 (11.4 mmol) was condensed into a solution of $Zr(NMe_2)_4$ (0.758 g, 2.84 mmol) in toluene (20 ml). The solution was warmed to 25 °C and stirred (ca. 2 h). The white precipitate was filtered off and dried (1 h, 10^{-3} Torr). TiL_4 and VL_4 were prepared similarly.

Preparation of $M(O_2CNMe_2)_5$ (M = Nb, Ta). CO_2 (6.45 mmol) was condensed into a solution of $Nb(NMe_2)_5$ (0.357 g, 1.14 mmol in hexane (20 ml)/toluene (20 ml)). The flask was warmed to room temperature, stirred ca. 1 h, then cooled to −20 °C. The pale yellow solid was filtered off and dried (30 min, 10^{-3} Torr). TaL_5 was prepared similarly.

Preparation of $Ti(O_2CNEt_2)_4$. CO_2 (12 mmol) was condensed into a solution of $Ti(NEt_2)_4$ (0.782 g, 2.33 mmol) in toluene (20 ml). The solution was warmed to room temperature, it turned pale brown, and was stirred (12 h at 25 °C). The solution was concentrated to ca. 5 ml and hexane (20 ml) was added. The pale brown solid was filtered off and dried (1 h, 10^{-3} Torr).

Preparation of $W_2(O_2CNMe_2)_6$. $W_2(NMe_2)_6$ (0.71 g, 1.1 mmol) in toluene (40 ml) was stirred under CO_2 (1 atm pressure) for ca. 45 min at 50 °C. The solution initially turned red, then yellow, and a yellow precipitate formed. The precipitate was redissolved by stirring the solution at ca. 70 °C. The solution was slowly cooled to 25 °C; crystals formed. The orange crystals were filtered off and dried in vacuo (45 min, 10^{-2} Torr). ^1H NMR spectra in CH_2Cl_2 indicated the presence of toluene of crystallization. W_2L_6 was also prepared in benzene and was precipitated by adding hexane.

Preparation of $W(NMe_2)_3(O_2CNMe_2)_3$. CO_2 (8.5 mmol) was condensed into a 250-ml flask containing $W(NMe_2)_6$ (0.64 g, 1.4 mmol in benzene (50 ml)). The solution was warmed to room temperature and stirred for 10 h; it turned from red to orange. The solvent was stripped off and the residue was extracted with warm hexane (150 ml at 50 °C). The filtrate was concentrated to ca. 40 ml at 50 °C then slowly cooled to −20 °C. The orange crystals were filtered off and dried.

Infrared data. Infrared spectra were recorded of Nujol mulls over the 200–2000-cm^{-1} region unless otherwise noted: **$Ti(O_2CNMe_2)_4$.** 250 w, 352 m, 446 s, 650 s, 784 m, 865 m, 950 w, 1042 m, 1058 wsh, 1153 vs, 1170 vw, 1266 s, 1408 s, 1503 m, 1512 m, 1589 vs, 1690 vw, 1738 vw. **$Ti(O_2CN(CD_3)_2)_4$.** (spectra not recorded <400 cm^{-1}), 417 s, 623 s, 786 m, 803 w, 828 w, 904 m, 917 wsh, 974 w, 1017 w, 1055 m, 1068 w, 1096 s, 1150 vw, 1169 vw, 1229 m, 1246 wsh, 1269 w, 1556 vs. **$Zr(O_2CNMe_2)_4$.** 260 w, 303 s, 428 s, 625 w, 659 s, 794 s, 861 m, 1044 m, 1059 m, 1265 vs, 1409 s, 1509 s, 1587 vvs, 1696 vw, 1726 vw. In CH_2Cl_2: 1591 vs, 1700 vw. **$Zr(O_2{}^{13}CNMe_2)_4$.** 263 w, 304 s, 428 s, 624 w, 659 s, 770 s, 793 w, 859 m, 1044 m, 1060 m, 1253 vs, 1405 s, 1498 s, 1565 vs. **$Zr(^{18}O_2CNMe_2)_4$.** 260 w, 301 s, 395 msh, 420 s, 602 m, 638 s, 698 w, 786 s, 833 m, 1028 w, 1060 m, 1248 vs, 1405 s, 1484 s, 1583 vvs, 1666 vw. In CH_2Cl_2: 424 s, 638 s, 1485 s, 1588 vs, 1667 vw. **$V(O_2CNMe_2)_4$.** 283 s, 354 m, 456 s, 605 s, 669 s, 800 s, 850 m, 975 vw, 1056 m, 1155 vw, 1275 vs, ca. 1525 vs, vvbr. **$Ti(O_2CNEt_2)_4$.** 348 s, 356 sh, 459 s, 641 s, 791 s, 840 s, 940 m, 977 m, 1076 m, 1084 m, 1099 m, 1168 w, 1212 s, 1261 w, 1505 s, 1564 vs. **$Nb(O_2CNMe_2)_5$.** 320 m, 442 s, 587 m, 596 wsh, 626 wsh, 666 vs, 690 wsh, 770 m, 782 m, 842 s, 865 w, 877 w, 1038 s, 1064 w, 1142 vs, 1193 s, 1268 s, 1410 m, 1418 m, 1611 vs, 1680 vs. In benzene: 1611 vs, 1677 vs. In CH_2Cl_2: 1618 vs, 1668 vs. **$Nb(^{18}O_2CNMe_2)_5$.** 316 m, 435 s, 569 m, 579 wsh, 605 w, 647 vs, 668 wsh, 763 m, 775 m, 822 s, 1020 s, 1063 w, 1142 vs, 1180 vs, 1258 s, 1409 m, 1418 m, 1610 vs, 1658 vs. In CH_2Cl_2: 1615 vs, 1650 ssh. **$Nb(O_2{}^{13}CNMe_2)_5$.** 323 m, 442 s, 589 m, 599 wsh, 628 w, 668 vs, 690 wsh, 749 m, 761 m, 843 s, 865 w, 875 w, 1038 s, 1066 w, 1127 vs, 1180 s, 1263 s, 1414 m, 1592 vs, 1645 vs. **$Ta(O_2CNMe_2)_5$.** 260 m, 287 wsh, 432 s, 592 m, 598 m, 630 wsh, 665 vs, 774 s, 783 s, 845 s, 871 w, 884 w, 1043 s, 1150 vs, 1166 ssh, 1209 s, 1270 s, 1410 m, 1415 m, 1619 vs, 1682 vs. **$Ta(O_2{}^{13}CNMe_2)_5$.** 262 m, 288 wsh, 428 s, 590 s, 599 msh, 626 wsh, 665 vs, 748 s, 759 s, 840 s, 866 w, 878 w, 1043 s, 1131 s, 1152 ssh, 1184 s, 1259 s, 1405 m, 1414 m, 1589 vs, 1630 vs. **$W_2(O_2CNMe_2)_6(toluene)_x$.** 220 w, 263 m, 330 w, 355 w, 400 w, 450 s (asymmetric), 609 w, 625 w, 663 s, 695 w, 700 w, 709 w, 728 w, 748 m, 761 m, 771 m, 792 m, 841 w, 850 w, 875 w, 975 w, 1032 mbr, 1062 mbr, 1084 w, 1151 w, 1176 w, 1237 s, 1265 s, 1410 m, 1510 w, 1575 vs, 1591 ssh, 1629 vs, 1708 vw, 1751 vw. **$W_2(O_2{}^{13}CNMe_2)_6$.** (1500–1650 cm^{-1} region) 1555 vs, 1600 vs. **$W_2(^{18}O_2CNMe_2)_6$.** (1500–1650 cm^{-1} region), 1571 vs, 1626 vs. **$W(NMe_2)_3(O_2CNMe_2)_3$.** 372 w, 433 s, 576 m, 604 m, 649 s, 666 m, 785 m, 791 m, 836 m, 958 s, 965 sh, 1020 m, 1039 m, 1059 m, 1133 w, 1190 s, 1228 s, 1276 m, 1568 w, 1580 w, 1636 vs. In benzene: 1576 w, 1643 vs. **$W(NMe_2)_3(O_2{}^{13}CNMe_2)_3$.** 373 w, 434 s, 577 m, 606 s, 647 s, 664 m, 763 m, 770 m, 834 m, 961 s, 969 sh, 1023 m, 1038 m, 1060 m, 1135 w, 1172 s, 1217 s, 1277 m, 1597 s. **$W(NMe_2)_3(^{18}O_2CNMe_2)_3$.** 433 s, 577 (hidden), 583 s, 629 s, 640 sh, 782 m, 788 m, 820 m, 962 s, 970 sh, 1025 m, 1064 w, 1177 s, 1217 s, 1274 s, 1560 w, 1570 w, 1615 vs.

Preparation of $M(OSCNMe_2)_n$. $Ti(OSCNMe_2)_4$, $Zr(OSCNMe_2)_4$, $Ti(OSCNEt_2)_4$, and $Ta(OSCNMe_2)_5$ were prepared similarly; only the preparation of $Ti(OSCNMe_2)_4$ will be described in detail. COS (13.0 mmol) was condensed into a solution of $Ti(NMe_2)_4$ (0.693 g, 3.09 mmol) in toluene (20 ml). Upon warming to room temperature, the solution turned blood red and a red precipitate formed. After stirring the solution at 25 °C for 8 h, the red solid was filtered off and dried in vacuo. Anal. Calcd for $Ti(OSCNMe_2)_4$: C, 31.03; H, 5.21; N, 12.06. Found: C, 30.90; H, 5.29; N, 11.97. Infrared absorptions of $Ti(OSCNMe_2)_4$ (300–2000 cm^{-1}, Nujol mull): 328 m, 346 m, 409 s, 471 w, 482 w, 553 s, 664 w, 705 sh, 712 s, 740 m, 938 w, 1127 vs, 1249 s, 1400 m, 1494 w, 1550 vs, 1600 vs. $Zr(OSCNMe_2)_4$ (a white solid) was prepared similarly. ^1H NMR spectroscopy indicated the presence of solvent of crystallization. Anal. Calcd for $Zr(OSCNMe_2)_4(toluene)_{1.1}$: C, 38.84; H, 5.42; N, 9.20. Found: C, 38.85; H, 5.73; N, 9.02. Infrared absorptions of $Zr(OSCNMe_2)_4$ (Nujol mull, 400–2000 cm^{-1}): 410 cm^{-1} s, 470 w, 482 w, 554 s, 655 w, 708 s, 749 m, 938 w, 1053 w, 1128 s, 1252 s, 1395 m, 1494 w, 1546 vs. $Ta(OSCNMe_2)_5$ is a pale yellow solid. Anal. Calcd for $Ta(OSCNMe_2)_5$: C, 25.67; H, 4.31; N, 9.98; S, 22.85. Found: C, 25.46; H, 4.18; N, 9.83; S, 22.67. ^1H NMR data at 60 MHz, 40 °C: $Ti(OSCNMe_2)_4$ in CH_2Cl_2; δ 2.96 (s). $Ti(OSCNEt_2)_4$ in CH_2Cl_2; δ 3.49 (q, 2), 1.11 (t, 3), $^3J_{H\text{-}H} = 7$ Hz. $Zr(OSCNMe_2)_4$ in CH_2Cl_2–Freon 11; δ 3.13 (s, 1), 3.11 (s, 1). $Ta(OSCNMe_2)_5$ in benzene; δ 2.81 (s, 1), 2.77 (s, 1). δ in parts per million downfield from HMDS.

Carbon Dioxide and Ligand Exchange Reactions of ML_n. Qualitative information concerning the CO_2 exchange reactions, $M(O_2CNR_2)_n$ + excess$^{13}CO_2$, was obtained for $M(O_2CNMe_2)_4$ (M = Ti, Zr), $Ti(O_2CNEt_2)_4$, $Zr(O_2CNMeEt)_4$, $M(O_2CNMe_2)_5$ (M = Nb, Ta), and $W_2(O_2CNMe_2)_6$ in CH_2Cl_2, benzene, or toluene-d_8 (depending upon solubility). $^{13}CO_2$ (0.3–0.5 mmol) was condensed (using liquid N_2) into a solution of ML_n (ca. 10–20 mg, 0.01–0.05 mmol in 0.5 ml of solvent) in an NMR tube. The sample tube was sealed in vacuo, warmed to room temperature, and examined immediately. In all cases initial ^1H NMR spectra, taken within 3–20 min at ca. 30 °C, indicated that the CO_2 exchange reaction was complete. See Figure 7b. No further changes were observed over a period of days.

The exchange reaction, $Zr(O_2{}^{13}CNMe_2)_4 + Zr(O_2{}^{12}CNMeEt)_4$, was carried out by dissolving a mixture of the two compounds (ca. 10–20 mg each) in CH_2Cl_2 (0.5 ml). Initial ^1H NMR spectra (see Figure 7c) indicated that the reaction was complete.

Other exchange reactions were carried out at ca. 25 °C and monitored similarly ($L' = O_2CN(CD_3)_2$, $L^* = O_2{}^{13}CNMe_2$): $TiL'_4 + ZrL_4$, ligand exchange complete within 5 min; $TiL'^* + ZrL_4$, ligand exchange and CO_2 exchange complete within 25 min; $TiL_4 + TiL'^*_4$, CO_2 exchange complete within 10 min; $TiL'^*_4 + NbL_5$, ligand exchange complete within 6 h, CO_2 exchange not apparent until ca. 20 h but complete within 44 h.

Similarly, we observed that for the exchange reaction, $Ti(OS^{13}CNMe_2)_4 + 2Ti(OSCNEt_2)_4$, COS exchange was complete within ca. 90 h. The exchange reaction $Ti(OS^{13}CNMe_2)_4 + 12{}^{12}COS$ was complete within 5 min. The CS_2 exchange reaction $Ti(S_2CNEt_2)_4$ + excess$^{13}CS_2$ in CH_2Cl_2 was slow. Only ca. 10% exchange occurred in 70 h at 25 °C.

Kinetics of $W(NMe_2)_3(O_2{}^{13}CNMe_2)_3 + nCO_2$. A stock solution of $W(NMe_2)_3(O_2{}^{13}CNMe_2)_3$ (30.4 mg, 0.052 mmol) in toluene (2.5 ml, with HMDS as internal reference) was prepared; [W] = 0.021 M. Aliquots (0.5 ml, measured via syringe) were placed in three NMR tubes (5 mm o.d.). Either 6, 12, or 18 mole equiv of $^{12}CO_2$ (0.063, 0.125, or 0.188 mmol, respectively) was condensed into each NMR tube, then the tubes were sealed in vacuo. The tubes were placed in a constant temperature bath. The reactions were quenched periodically by cooling to 0 °C, examined via ^1H NMR (probe temperature = 16 °C, total time needed to obtain spectrum <5 min), then returned to the temperature bath. See Figure 6 for representative ^1H NMR spectra. The percentages of L and L* were determined by resolving and integrating the ^1H NMR spectra with a Dupont 310 curve resolver.

Raw data for $W(NMe_2)_3L^*_3 + n{}^{12}CO_2$ at 20.8 °C, t in min (% L): n = 6, 0 (14.5), 115 (18), 350 (28.5), 725 (41.8), 1505 (54.4); n = 12, 0 (14.5), 115 (18.0), 350 (29.5), 725 (42.7), 1505 (59.8); n = 18, 0 (14.5), 115 (18.8), 350 (31.8), 725 (48.5), 1505 (66.6). Gross overall exchange rates, $R = 6.06 \times 10^{-7}$, 6.27×10^{-7}, and 7.63×10^{-7} mol s^{-1}, and rate constants, $k = R/[\text{total ligand}] = 9.68 \times 10^{-6}$, 1.00×10^{-5}, and 1.22×10^{-5} s^{-1}, respectively.

A similar experiment was carried out in which the amount of CO_2 (0.25 mmol) was kept constant and the temperature and [L] were varied ($[L] \equiv 3[W(NMe_2)_3L_3]$): [L] = 0.0612 M, T = 15.5 °C, $k = 9.35 \times 10^{-6}$ s^{-1}; [L] = 0.0612 M, T = 26.0 °C, $k = 2.12 \times 10^{-5}$ s^{-1}; [L] = 0.0306 M, T = 26.0 °C, $k = 2.08 \times 10^{-5}$ s^{-1}; [L] = 0.0612 M, T = 36.5 °C, $k = 7.75 \times 10^{-5}$ s^{-1}.

Kinetics of NbL^*_5 and ZrL^*_4 + excessCO_2. It was necessary to follow the exchange reactions, NbL^*_5 + excess$^{12}CO_2$ and ZrL^*_4 + excess$^{12}CO_2$, via ^1H NMR at low temperatures (ca. −40 °C). Considerable experimental difficulties were encountered. Most serious was the difficulty of maintaining a constant probe temperature. Therefore, these results were not as accurate as those for eq 3. However, they were reproducible.

The solutions were prepared as for $W(NMe_2)_3L_3$ (see previous section) and were stored at −198 °C. The NMR tubes were rapidly transferred into the cooled (ca. −40 °C) NMR probe at the beginning of the reaction. Results: NbL^*_5 (0.013 mmol in 0.4 ml toluene-d_8) + $n{}^{12}CO_2$ at −40 °C (±2 °C): n = 16, $t_{1/2}$ = 26 min; n = 62, $t_{1/2}$ = 6.5 min. NbL^*_5 (0.013 mmol in 0.4 ml toluene-d_8) + nCO_2 at −30 °C (±2 °C): n = 16, $t_{1/2}$ = 13 min; n = 62, $t_{1/2}$ = 4 min. ZrL^*_4 (0.022 mmol in 0.4 ml of CH_2Cl_2) + $n{}^{12}CO_2$ at −56 °C (±2 °C): n = 10, $t_{1/2}$ = 87 min; n = 40, $t_{1/2}$ = 34 min. $t_{1/2}$ is defined as the time at which % L* = % L.

$W(NMe_2)_3(O_2{}^{13}CNMe_2)_3$ + excessCO_2. $^{12}CO_2$ (1.0 mmol) was condensed into an NMR tube (5 mm o.d. × 3 mm i.d.; *CAUTION: High pressure*) containing $WN_3L^*_3$ (28.0 mg, 0.050 mmol) in toluene-d_8 (0.3 ml). The NMR tube was sealed carefully with a hand torch and warmed to 25 °C. ^1H NMR spectra taken over a period of 7 days indicated that $^{13}CO_2$ exchange occurred, no species other than WN_3L_3 and $WN_3L^*_3$ was observed.

Acknowledgments. We thank Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation (Grant No. MPS 73-05016) for their support of this work. M. Extine is grateful to the American Can Company for a fellowship 1973–1975. We also thank Dr. Alan English, Experimental Station, Du Pont, Wilmington, for carrying out ^{13}C NMR studies on the ML_5 compounds.

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

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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.

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

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 $W(NMe_2)_3$-