Carbon Dioxide Exchange Reactions Involving Early Transition-metal *NN*-Dimethylcarbamato Compounds: Reversible Insertion of Carbon Dioxide into Transition-metal–Nitrogen σ-Bonds

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Summary Transition-metal *NN*-dimethylcarbamato compounds ML^*_n, (where M = Ti, Zr and $n = 4$; M = Nb, Ta and $n = 5$), $W_2L^*_6$ and $W(NMe_2)_3L^*_3$, ($L^* = O_2{}^{13}CNMe_2$), react with $^{12}CO_2$ to give ML_n, W_2L_6 and $W(NMe_2)_3L_3$, where ($L = O_2{}^{12}CNMe_2$), with an energy of activation ranging from *ca.* 54 ± 8kJ mol^{-1} for ZrL_4 to *ca.* 96kJ mol^{-1} for $W(NMe_2)_3L_3$; mixtures of ML_n and ML^*_n scramble CO_2 in the absence of an applied CO_2 atmosphere.

Early transition-metal dimethylamides[1] $M(NMe_2)_n$ (where M = Ti, Zr, $n = 4$; M = Nb, Ta, $n = 5$ and M = W, $n = 3$ and 6) react[2,3] with carbon dioxide to give *NN*-dimethylcarbamato compounds ML_n except $W(NMe_2)_6$ which gives $W(NMe_2)_3L_3$, (where $L = O_2{}^{12}CNMe_2$). The compounds $W(NMe_2)_3L_3$[2] and NbL_5[4] have been shown to contain six co-ordinate tungsten, *fac*-WN_3O_3, and eight co-ordinate niobium respectively. We now find that in solution all these compounds are labile towards CO_2 exchange (equation 1).

$$ML^*_n + x^{12}CO_2 \rightleftharpoons ML_mL^*_{n-m} + m^{13}CO + (x-m)^{12}CO_2 \qquad (1)$$

(where $L = O_2{}^{12}CNMe_2$ and $L^* = O_2{}^{13}CNMe_2$)

The reactions were carried out in dichloromethane for M = Zr and Ti, and in $[^2H_8]$-toluene and benzene for M = Nb, Ta and W. The reactions were followed by ^1H n.m.r. spectroscopy using the fact that the ^{13}C labelled ligand $O_2{}^{13}CNMe_2$ shows $^3J_{^{13}C-H}$ *ca.* 3 Hz (Figure). The reactions are remarkable in both their generality and lability. When ZrL^*_4 was dissolved in dichloromethane and allowed to react with 8 mol. equiv. of $^{12}CO_2$ in a sealed n.m.r. tube at −43 °C, its half-life was *ca.* 20 min. From variable temperature ^1H n.m.r. studies we estimate the energy of activation of the reaction to be *ca.* 54 ± 8kJ mol^{-1} for M = Zr. The reaction occurs with equal ease for M = Ti, Nb and Ta. The rate of exchange for $W(NMe_2)_3L_3$ is, however, significantly slower (E_{act} *ca.* 96 kJ mol^{-1}) which makes it more amenable to detailed kinetic studies using the ^1H n.m.r. technique.

A plausible mechanism for the reaction involves an initial de-insertion (expulsion) of CO_2 from a carbamato ligand (equation 2). Consistent with this proposal are the

$$M(O_2CNMe_2)_n \rightleftharpoons M(O_2CNMe_2)_{n-1}(NMe_2) + CO_2 \qquad (2)$$

following observations:

(1)[4] Solutions of NbL_5 in $[^2H_8]$-toluene contain significant (n.m.r. detectable) concentrations of $NbL_4(NMe_2)$. The concentration of the latter is dependent on CO_2 pressure.

(2) Preliminary kinetic studies involving $W(NMe_2)_3L_3$ indicate that the CO_2 exchange reaction is first-order in tungsten and *ca.* zero-order in CO_2 concentrations.

(3) When a mixture of ZrL^*_4 and TiL_4 was dissolved in dichloromethane scrambling occurred (equation 3).

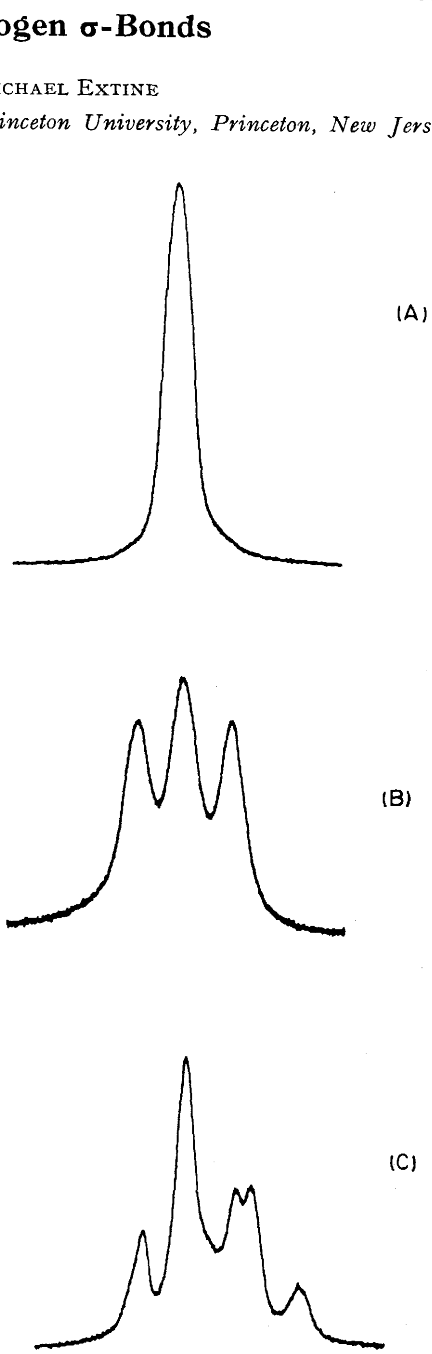

Figure. ^1H n.m.r. spectra (CH_2Cl_2, 100 MHz, 30°C), of the *N*-methyl resonances of (A) $Zr(O_2{}^{12}CNMeEt)_4$ δ = 2·90 p.p.m. (rel. Me_4Si), (B) $Zr(O_2{}^{12}CNMeEt)_4$ + $4^{13}CO_2$ after 5 min, $^4J_{^{13}C-H}$ 3·0 Hz, (C) $Zr(O_2{}^{13}CNMe_2)_4$ + $Zr(O_2{}^{12}CNMeEt)_4$ showing scrambling of CO_2 between the carbamato ligands; the O_2CNMe_2 resonance is to low field of the O_2CN*Me*Et resonance.

$$ZrL^*_4 + TiL_4 \rightleftharpoons ZrL_xL^*_{4-x} + TiL^*_xL_{4-x} \qquad (3)$$

Similar scrambling occurred when a mixture of ZrL^*_4 and NbL_5 was dissolved in dichloromethane.

(4) A mixture of ZrL^*_4 and $Zr(O_2{}^{12}CNMeEt)_4$ in dichloromethane scrambled CO_2 to give $ZrL_xL^*_{4-x}$ and $Zr(O_2{}^{12}CNMeEt)_{4-x}(O_2{}^{13}CNMeEt)_x$ (Figure).

(5) A mixture of ZrL_4' and NbL_5 reacted in dichloromethane to give ZrL_xL_{4-x} and $NbL_{5-x}L_x'$ where $L' = {}^{18}O_2{}^{12}CNMe_2$ (indicated by i.r. spectroscopy[4]).

(6) The organic ester $MeO_2{}^{12}CNMe_2$ does not react with either ${}^{13}CO_2$ or NbL^*_5 under comparable conditions to those above.

Whilst all these observations are entirely consistent with an initial mechanism as in equation 2 we recognize that our present data do not exclude all alternate mechanisms for the reaction. However, we believe that the most plausible mechanism is given in equation 2 and it provides a rationale for the observation that $W(NMe_2)_3L_3$ has the slowest rate of exchange. It should be noted that the displacement of CO_2 in the reaction between $Me_3SnO_2CNMe_2$ and CS_2, which gives[5] $Me_3SnS_2CNMe_2$, could also proceed *via* the initial step shown in equation 2.

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