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TANTALUM-CARBON BOND FORMATION IN THE THERMAL DECOMPOSITION OF TANTALUM DIETHYLAMIDE

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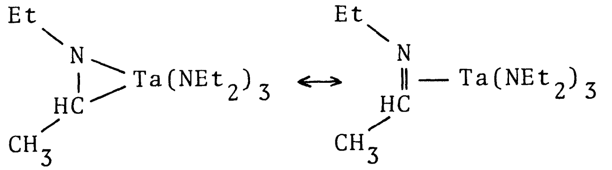
In the thermal decomposition of pentakis(diethylamido)tantalum, a novel organometallic compound, ethylimino(C,N)tris(diethylamido)tantalum (1), is isolated, which reacts with methyl isocyanate affording the insertion product (4). On heating (1) above 100°C, it decomposes to ethylimido-complex (2) and ethylene. The rate of the reaction is first-order with respect to the complex (1). The activation parameters at 144°C are calculated as $\Delta H^{\ddagger} = 26.2$ kcal/mole and $\Delta S^{\ddagger} = -8.3$ e.u.

Metal-carbon bond formation by intramolecular metallation, or co-ordination-directed metallation, is still one of the important subjects in the metal complexes[1). In the course of our investigation[2) concerning metal dialkylamides[3) we found that tantalum diethylamide easily underwent the intramolecular metallation reaction affording a novel compound having a three-membered ring including tantalum-carbon bond.

Treatment of tantalum pentachloride with lithium diethylamide in ether at -10°C and subsequent distillation of the reaction mixture at reduced pressure gave a pale yellow liquid of b.p. 90°/1.2 - 110°C/2.0 Torr. On distillation substantial decomposition occurred evolving gases, which were trapped at Dry Ice temperature and identified as diethylamine including a small quantity of ether. Fractional distillation of the yellow product gave two compounds; one was identified as ethyliminoethyl(C,N)tris(diethylamido)tantalum (1)[4), b.p. 78°C/0.025 Torr, yield 22 % based on tantalum chloride used, and the other as ethylimidotris(diethylamido)tantalum (2)[5), b.p. 65°C/0.025 Torr, yield 31 %.

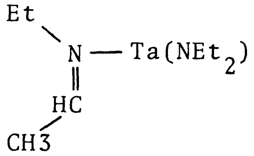
The ^{1}H nmr spectrum of the former compound (1) in C_6D_6 gave well resolved



(1a) (1b)

$EtN=Ta(NEt_2)_3$

(2)



(3)

resonances. In particular, the A_3B pattern expected for $\geq CH-CH_3$ moiety was clearly found at 1.91 (d) and 2.28δ (m) (J_{ab} = 5.0 Hz). According to the chemical shift of the methine proton, structure (3) can be excluded. The methylene protons in the ethylimino group were observed as a multiplet which was assignable to the AB part in an ABX_3 spin system of $CH_3CHH'N<$ (J_{ab} = 13, $J_{ax} = J_{bx}$ = 7.2 Hz, δ_x = 1.36, δ_a or δ_b = 3.95 or 3.80 ppm), suggesting that there should be an asymmetric center in the molecule. The presence of the asymmetric center was further confirmed by the observation that the methylene protons in the diethylamido ligands had two quartets at 3.42 and 3.44δ, and the methyl protons a triplet at 0.98δ ($J_{CH_3-CH_2}$ = 7.2 Hz).

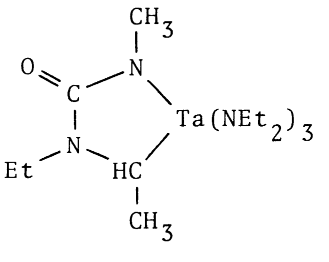
In a $^{13}C\ \{^1H\}$ nmr spectrum of (1) in C_6D_6 six peaks were observed at 16.1 [multiplicity in the absence of ^1H irradiation, and the coupling constant between the carbon and the protons bound to it; q, J = 127 Hz, $(\underline{C}H_3CH_2)_2N-$], 17.1 [q, J = 127 Hz, $\underline{C}H_3CH_2N\geq$], 21.6 [q, J = 127 Hz, $\underline{C}H_3CH\geq$], 45.8 [t, J = 134 Hz, $(CH_3\underline{C}H_2)_2N-$], 50.7 [t, J = 125 Hz, $CH_3\underline{C}H_2N\geq$], and 64.0 ppm [d, J = 147 Hz, $CH_3\underline{C}H\geq$]. The magnitudes of the coupling constant and the chemical shift for the methine carbon resembled those of π-bonded ethylene to platinum metal$^{6,7)}$.

The mass spectrum of (1) showed a strong parent peak (m/e 468), and the intensity ratio of the isotopic peak to the parent peak, (p+1)/p, was 0.188, being in good agreement with the content of isotopic elements in (1) (calcd. for $C_{16}H_{39}N_4\cdot Ta$, 0.194).

The infrared and Raman spectra had no bands above 1500 cm^{-1} attributable to an N-co-ordinated $\geq C=N^-$ double bond, but instead a strong band (particularly in the infrared spectrum) at 1235 cm^{-1} which can be assignable to the stretching vibration of a C-N bond having a partially double bonding character. Therefore, the contribution of the structure (1b) should be taken into consideration.

Hydrolysis of (1) with D_2O under argon and subsequent treatment with a large quantity of diluted hydrochloric acid afforded diethylamine hydrochloride in almost quantitative yield (above 85 %). The mass spectrum of the amine salt showed the parent ion (p; m/e 73) of diethylamine and its isotopic peak (p+1; m/e 74), the intensity ratio of (p+1)/p = 0.32, being much larger than that for normal diethylamine hydrochloride (obsvd. 0.067). The higher intensity of the isotopic peak for the amine salt which was obtained from the complex (1) can be attributed to the incorporation of a deuterium atom through the reaction with D_2O. Other molecular ions of hydrogen chloride (HCl^{35} and HCl^{37}) were, of course, found at the same time as a result of the dissociative evaporation of the hydrochloride. However, no deuterium chloride (DCl^{35} and DCl^{37}) was found since N-deuterated amine $Et_2ND{\cdot}HCl$ which might be formed originally could be converted rapidly to the normal hydrochloride $Et_2NH{\cdot}HCl$ by subsequent H-D exchange reaction with H_2O. Therefore, the site of deuteration can be unambiguously ascribed to the alkyl group in the amine. The analysis of the other fragment ions suggested that it was an α-methylene group, confirming the structure (1).

The compound (1) was found to react very rapidly with methyl and phenyl isocyanates in benzene solution at room temperature. In the ^1H nmr spectrum of the reaction mixture between (1) and methyl isocyanate (the molar ratio 1:1), the A_3B pattern which was originally found for $CH_3CH<$ moiety in (1) changed to A_3X-type resonances, 1.42 (d), 2.99δ (q) (J_{ax} = 7.2 Hz). The absorption of methylene group of ethylimino group $CH_3\underline{CH_2}N<$ had two double quartets at 3.06 and 4.18δ (J_{gem} = 14.0 Hz, J_{vic} = 7.0 Hz) because of the asymmetry. The methyl protons appeared as a triplet at 1.12δ. The resonances of diethylamido ligands had no substantial difference from those of (1) except for broadening of the signals due to methylenes and slight upper field shift of the resonance of the methyl protons [0.84δ, t, $(\underline{CH_3}CH_2)_2N$-; 3.30δ, broad q, $(CH_3\underline{CH_2})_2N$-, $J_{CH_3-CH_2}$ = 7.0 Hz]. The variation in the coupling constants and the chemical shifts of protons in $CH_3\overset{|}{C}H$-$\overset{|}{N}$-Et group suggested that the isocyanate reacted with the group, but not with diethylamido ligands. Hydrolysis of the product gave the N,N-diethyl-N'-methylurea, m.p. 34.5-36°C, in 80 % yield. Therefore it can be concluded that isocyanate inserted into the Ta-N bond to result in the formation of product (4). Formation of (4) was further confirmed by the fact that the deuterated urea $CH_3NDCON(CH_2CH_3)(CHDCH_3)$ was obtained by the decomposition of (4) with D_2O. This result is consistent with Wilkinson's report[8] that the Ta-N bond was more active for the insertion reaction than the Ta-C bond. On the other hand the reaction of phenyl isocyanate with (1) was less selective. It inserted both into Ta-NEt_2 and into Ta-NEt in the three-membered ring at room temperature.



(4)

The complex (1) is relatively thermally stable. In the high temperature nmr spectra (60-80°C) no fluxional behavior was found, but above 100°C it decomposed to ethylimido complex (2) and ethylene. The rate of the decomposition reaction was followed by using an nmr spectroscopy, and found to be first-order with respect to the concentration of the complex (1); the first-order rate constants, $k = 2.70\times10^{-4}$ (117.5°C), 5.41×10^{-4} (127.0°C), 1.20×10^{-3} (136.5°C), and 2.43×10^{-3} min^{-1} (144.0°C). The activation enthalpy and entropy for the reaction at 144°C were calculated as $\Delta H^{\ddagger} = 26.2$ kcal/mole and $\Delta S^{\ddagger} = -8.3$ e.u. The negative activation entropy indicates that a simple mechanism such as a spontaneous elimination of methylcarbene from (1) is not likely. This assumption was confirmed by the fact that even in the presence of cis-2-butene no cyclopropane derivatives were detected by an nmr spectrum.

Throughout our study we could not obtain any evidence for the formation of tetrakis(diethylamido)tantalum $Ta(NEt_2)_4$ which was reported by Bradley and co-workers$^{5b, 9)}$. On the other hand pentakis(dimethylamido)tantalum $Ta(NMe_2)_5$$^{5)}$ was easily prepared, but a compound similar to (1) could not be obtained.

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4) After hydrolysis weight percentages of the tantalum atom and diethylamine were evaluated as follows; tantalum, 37.98 % (calcd. 38.63 %); diethylamine, 61.45 % (calcd. 62.45 %) from the tantalum oxide (Ta_2O_5) and by titration, respectively.

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