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Insertion of the Carbene :CH₂ into Ni–R Bonds of Mono- and Di-alkylnickel(11) Complexes

Βυ Τακακάζυ Υλημηστο

(Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227, Japan)

Summary The reaction of alkylnickel(II) complexes $[NiR_2-(bpy)]$ and $[NiR(X)L_2]$ $[R = Me, Et; X = imido, OCOMe; L = bpy (2,2'-bipyridine), 1,2-bis(diphenyl-phosphino)ethane], with <math>CH_2X_2$ (X = Cl, I) afforded RCH_2CH_2R, RCH_2R, RMe, and $R(-H)=CH_2$ in addition to the usual degradation products R-R, RH, and R(-H); these unusual products are considered to be formed through insertion of the carbene: CH_2 into the Mi-R bond.

INSERTION of the carbene: CH_2 into a non-transition metalcarbon bond such as $Al-C^1$ is known. However, only a little is known concerning the insertion of : CH_2 into a transition metal-carbon bond, \dagger in spite of recent developments in transition metal-carbene chemistry. This paper deals with the results of an attempt to insert : CH_2 into the Ni-R bonds of mono- and di-alkylnickel(II) complexes. : CH_2 was generated by the reaction of the alkylnickel(II) complexes with CH_2X_2 (X = Cl, I) which is known to generate : CH_2 by reaction with metals² and metal compounds.^{3,4}

The composition of the products obtained in the reaction of ethylnickel complexes with CH₂X₂ is shown in the Table. The reaction was completed in 1 h at room temperature and almost all the Et groups bonded to Ni were incorporated into the products given in the Table. The reaction gives n-hexane, n-pentane, propane, and propene in addition to the ordinary degradation products (ethane, ethene, and n-butane). When CD₂Cl₂ was employed in the reaction with (Ib) and (III), the propene evolved contained two deuterium atoms (mass spectroscopy). Furthermore, the ¹H n.m.r. spectra (CD₂Cl₂) of the labelled n-pentane and n-hexane formed showed that they had the structures EtCD₂Et and EtCD₂CD₂Et, respectively; EtCD₂Et: δ 0.84 (t, 6H, J 6 Hz, CH₃) and 1.27 (q, 4H, J 6 Hz, CH₂); EtCD₂- $CD_2Et: \delta 0.90$ (t, 6H, J 7 Hz, CH_3) and 1.32 (q, 4H, J 7 Hz, CH₂).

† Added to proof: After this note was submitted, a paper has appeared which describes insertion of :CH₂ into Pt-C bonds of platinum metallacycles (G. B. Young and G. M. Whitesides, J. Amer. Chem. Soc., 1978, 100, 5808).

CH₂X₂ Compound^a Distribution of gaseous and liquid products Normal degradation products C_2H_4 х $n-C_6H_{14}$ $n-C_{\delta}H_{12}$ C₃H₈ C₃H₆ C_4H_{10} C_2H_6 Cl $6 \cdot 3$ (Ia) 53trace 19 17 3.4 1.4 ÌIb) Cl 18 55trace **3**∙8 $\mathbf{22}$ 0.60.5. . • • • • 7.6(Ic) Cl $5 \cdot 6$ 16 46 9.214 1.5 •• Ċl 6·4 122.67.6(III) 69 1.1 0.5. I 23 · 7·0 $2 \cdot 5$ (III)15 11 1.241 Normal degradation products C_2H_6 CH₄ $n-C_4H_{10}$ $C_{3}H_{8}$ C_2H_4 NiMe(succinimido)(dpe) Cl 29 67 trace trace 4.3NiMe(succinimido)(bpy) Cl trace trace 71 $\mathbf{24}$ 5.4NiMe₂(bpy) C11516trace 62 7.4. .

TABLE. Products of the reaction of alkylnickel complexes with CH₂X₂

^a dpe = 1,2-bis(diphenylphosphino)ethane.

These data clearly indicate that : CH₂ is inserted into the Ni-Et bond [reactions (1)---(5)].

$$[\text{NiEt}(X)(\text{bpy})] + :CH_2 \longrightarrow [\text{NiCH}_2\text{Et}(X)(\text{bpy})] \quad (1)$$
(I)
(II)

X =succinimido (Ia), phthalimido (Ib), OCOMe (Ic) bpy = 2,2'-bipyridine.

$$[\text{NiEt}_2\text{bpy})] + :CH_2 \longrightarrow [\text{NiCH}_2\text{Et}(\text{Et})(\text{bpy})]$$
(2)
(III) (IV)

$$(IV) + :CH_2 \longrightarrow [Ni(CH_2Et)_2(bpy)]$$
(3)
(V)

coupling

$$C_{3}H_{8} + C_{3}H_{6}$$
 (4b)

(4a)

(5a)

n-C5H12

(IV)
or (I) +
(II)
disproportionation
disproportionation
$$C_3H_8 + C_2H_4$$
 (5b)
 $C_3H_6 + C_8H_6$ (5c)

coupling

It is known that :CH₂ is inserted into a C-H bond of an alkyl group bonded to a metal.⁵ In the present reactions, however, the insertion into the C-H bond does not seem to occur since branched alkanes such as isopentane and 2,3dimethylbutane were not formed and the α -position of n-hexane and n-pentane obtained in the reaction with CD_2Cl_2 was not deuteriated. In the reaction of (IV) with :CH₂ the carbene may be inserted into the Ni-CH₂Et bond to give a species having a Ni-Buⁿ bond. In fact, the thermolysis product, but-1-ene, of this species was detected. However, the amount was very small, indicating that :CH₂ is preferably inserted into the Ni-Et bond of (IV). The precipitate formed in the reaction of (III) with CH₂Cl₂ was identified as [NiCl₂(bpy)] by comparing its i.r. spectrum with that of an authentic sample.⁶ No indication of attack by :CH₂ at ligands such as bpy and imido was obtained.

The reaction of CH₂Cl₂ with methylnickel(II) complexes gave butane, propane, and ethene in addition to the usual degradation products. When CD₂Cl₂ was employed in the reaction with Ni(Me)(succinimido)(bpy) the ethene evolved was found to contain two deuterium atoms (mass spectroscopy). Ikariya and Yamamoto reported the evolution of $CH_2 = CD_2$ in the reaction of a methyliron complex with $\mathrm{CD}_2\mathrm{Cl}_2$.⁷ They proposed abstraction of the α -hydrogen of Me by iron and coupling between the CH₂ thus formed and CD_2 generated by the reaction of CD_2Cl_2 with the methyliron complex in order to account for the formation of CH₂=CD₂, as well as other facts obtained in the thermolysis of the methyliron complex. The same mechanism also explains the formation of $C_2H_2D_2$ in the reaction of the methylnickel complexes with CD₂Cl₂. However, if we take into account the results of the reaction of the ethylnickel(II) complexes with CD_2Cl_2 , the $C_2H_2D_2$ evolved in the present reaction seems to be formed through insertion of :CD₂ into the Ni-Me bond and abstraction of the β -hydrogen by nickel.

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- ⁵ C. J. Mazac and J. W. Simons, J. Amer. Chem. Soc., 1968, 90, 2484.
- ⁶ J. A. Broomhead and F. P. Dwyer, *Austral. J. Chem.*, 1961, 14, 250. [†]T. Ikariya and A. Yamamoto, *J.C.S. Chem. Comm.*, 1974, 720.

¹ H. Hoberg, Annalen, 1966, 695, 1; 1962, 656, 1; Angew. Chem. Internat. Edn., 1966, 5, 513. ² H. E. Simmons and R. D. Smith, J. Amer. Chem. Soc., 1958, 80, 5323; N. Kawabata, M. Naka, and S. Yamashita, ibid., 1976, 98, 2676.

S. Takakashi, Y. Suzuki, K. Sonogashira, and N. Hagihara, Chem. Letters, 1976, 515.

⁴ W. E. Volz and L. A. Paquette, *J. Org. Chem.*, 1976, **41**, 57; J. Nishimura, N. Kawabata, and J. Furukawa, VIIIth Internat. Conference on Organometallic Chem., 3C 24, Kyoto, Japan, 1977.