

## Insertion of the Carbene $\text{:CH}_2$ into Ni–R Bonds of Mono- and Di-alkylnickel(II) Complexes

By TAKAKAZU YAMAMOTO

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

**Summary** The reaction of alkylnickel(II) complexes  $[\text{NiR}_2(\text{bpy})]$  and  $[\text{NiR}(\text{X})\text{L}_2]$  [ $\text{R} = \text{Me}, \text{Et}$ ;  $\text{X} = \text{imido}, \text{OCOMe}$ ;  $\text{L} = \text{bpy}$  (2,2'-bipyridine), 1,2-bis(diphenylphosphino)ethane], with  $\text{CH}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{I}$ ) afforded  $\text{RCH}_2\text{CH}_2\text{R}$ ,  $\text{RCH}_2\text{R}$ ,  $\text{RMe}$ , and  $\text{R}(-\text{H})=\text{CH}_2$  in addition to the usual degradation products  $\text{R}-\text{R}$ ,  $\text{RH}$ , and  $\text{R}(-\text{H})$ ; these unusual products are considered to be formed through insertion of the carbene  $\text{:CH}_2$  into the Ni–R bond.

complexes with  $\text{CH}_2\text{X}_2$  ( $\text{X} = \text{Cl}, \text{I}$ ) which is known to generate  $\text{:CH}_2$  by reaction with metals<sup>2</sup> and metal compounds.<sup>3,4</sup>

The composition of the products obtained in the reaction of ethylnickel complexes with  $\text{CH}_2\text{X}_2$  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  $\text{CD}_2\text{Cl}_2$  was employed in the reaction with (Ib) and (III), the propene evolved contained two deuterium atoms (mass spectroscopy). Furthermore, the  $^1\text{H}$  n.m.r. spectra ( $\text{CD}_2\text{Cl}_2$ ) of the labelled n-pentane and n-hexane formed showed that they had the structures  $\text{EtCD}_2\text{Et}$  and  $\text{EtCD}_2\text{CD}_2\text{Et}$ , respectively;  $\text{EtCD}_2\text{Et}$ :  $\delta$  0.84 (t, 6H,  $J$  6 Hz,  $\text{CH}_3$ ) and 1.27 (q, 4H,  $J$  6 Hz,  $\text{CH}_2$ );  $\text{EtCD}_2\text{CD}_2\text{Et}$ :  $\delta$  0.90 (t, 6H,  $J$  7 Hz,  $\text{CH}_3$ ) and 1.32 (q, 4H,  $J$  7 Hz,  $\text{CH}_2$ ).

INSERTION of the carbene  $\text{:CH}_2$  into a non-transition metal-carbon bond such as  $\text{Al}-\text{C}^\dagger$  is known. However, only a little is known concerning the insertion of  $\text{:CH}_2$  into a transition metal-carbon bond,<sup>†</sup> in spite of recent developments in transition metal-carbene chemistry. This paper deals with the results of an attempt to insert  $\text{:CH}_2$  into the Ni–R bonds of mono- and di-alkylnickel(II) complexes.  $\text{:CH}_2$  was generated by the reaction of the alkylnickel(II)

<sup>†</sup> *Added to proof:* After this note was submitted, a paper has appeared which describes insertion of  $\text{:CH}_2$  into Pt–C bonds of platinum metallacycles (G. B. Young and G. M. Whitesides, *J. Amer. Chem. Soc.*, 1978, **100**, 5808).

