Bis[cyclopentadienyl(cyclohexyl isocyanide)nickel]

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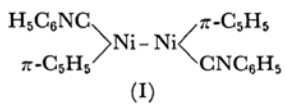
It has already been well established that isocyanides, analogous to carbon monoxide, produce various isocyanide complexes of transition metals. Pauson and Stubbs[1] have prepared bis[cyclopentadienyl(phenyl isocyanide)nickel] by means of the reaction of nickelocene with tetrakis(phenyl isocyanide)nickel; they have suggested the sturucture I on the basis of the peak of the infrared spectrum at 2175 cm^{-1}.



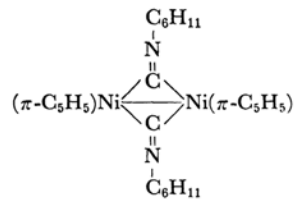
(I)

Recently, Pauson and his co-workers[2] have reported an iron complex with a bridging isocyanide group and have also established that bis[cyclopentadienyl(phenyl isocyanide)nickel] has a bridged structure in a solid state, but these points have not been discussed in detail.

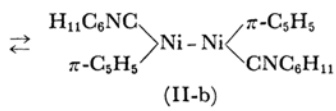
We wish to report the direct preparation of a similar compound from nickelocene by means of cyclohexyl isocyanide. During the studies of the polymerization of cyclohexyl isocyanide using various metallocenes as catalysts, we found that the use of nickelocene as a catalyst was very favorable to the polymerization; in this case bis[cyclopentadienyl(cyclohexyl isocyanide)nickel] (II) was isolated as an intermediate of the polymerization reaction.

When nickelocene was treated with cyclohexyl isocyanide at room temperature, the reaction took place instantaneously, as was shown by the rapid color change from green to red brown, and gave a 38% yield of bis[cyclopentadienyl(cyclohexyl isocyanide)nickel] as red brown needles. The infrared spectrum of this compound in Nujol mull showed two peaks, at 1870 and 1830 cm^{-1}; these peaks were analogous to those of bis[cyclopentadienyl(carbonyl-nickel] with bridging carbonyl groups. The spectrum in benzene showed a strong peak at 2140 cm^{-1} and two weak peaks, at 1880 and 1840 cm^{-1}, while in *n*-hexane it showed only a strong peak at 2140 cm^{-1}.

It was concluded from the infrared spectrum that bis[cyclopentadienyl(cyclohexyl isocyanide)nickel] had a bridged isocyanide structure II-a in a solid state and that it existed in an equilibrium between a bridged isocyanide structure II-a and a terminal isocyanide structure II-b in solutions, in which the former should make a greater contribution than the latter.



(II-a)



(II-b)

The reaction of cyclohexyl isocyanide with bis[cyclopentadienyl(carbonyl)nickel] took place readily at room temperature, and it also gave a 15% yield of bis[cyclopentadienyl(cyclohexyl isocyanide)-nickel]. Analogously, dicyclopentadienyl(acetylene)dinickel gave a 12% yield of the same compound.

Experimental

Materials.—Cyclohexyl isocyanide,[3] nickelocene,[4] bis[cyclopentadienyl(carbonyl)nickel],[5] and dicyclopentadienyl(acetylene)dinickel[6] were prepared by methods described in the literature.

The Reaction of Cyclohexyl Isocyanide with Nickelocene. — A solution of 1.0 g. (5.3 mmol.) of nickelocene in 40 ml. of a benzene - *n*-hexane mixture (1 : 1) was treated with 0.6 g. (5.5 mmol.) of cyclohexyl isocyanide at room temperature and then kept for 3 hr. The reaction mixture was evaporated to about 10 ml. under reduced pressure and chromatographed on alumina. Eluting with a benzene - *n*-hexane mixture gave raw products, from which bis[cyclopentadienyl(cyclohexyl isocyanide)nickel] was obtained as red brown needles by recrystallization from the benzene - *n*-hexane mixture (1 : 5). (Yield. 38%; m. p. 155—156°C (decomp.)) This compound was sensitive to air, so all the procedures mentioned above were performed under a nitrogen atmosphere.

1) P. L. Pauson and W. H. Stubbs, *Angew. Chem.*, **74**, 466 (1962).
2) K. K. Joshi, O. S. Mills, P. L. Pauson, B. W. Shaw and W. H. Stubbs, *Chem. Comm.*, **1965**, 181.
3) I. Ugi and R. Mayr, *Chem. Ber.*, **93**, 239 (1960).
4) J. F. Cordes, ibid., **95**, 3084 (1962).
5) E. O. Fischer and C. Palm, ibid., **91**, 1725 (1958).
6) M. Dubeck, *J. Am. Chem. Soc.*, **82**, 502 (1960).
* By the cryoscopic benzene method.

Found: C, 61.59; H, 7.01. Calcd. for $[Ni(C_5H_5)(CNC_6H_{11})]_2$ C, 61.85; H, 6.87%. M. w. 451* (466).

The Reaction of Cyclohexyl Isocyanide with Bis[cyclopentadienyl(carbonyl)nickel] (III) or Dicyclopentadienyl(acetylene)dinickel (IV) $(C_5H_5)Ni(HC{\equiv}CH)Ni(C_5H_5)$.—The procedure was similar to the reaction described above except that dry benzene was used as the solvent. The working-up of the reaction mixture gave bis[cyclopentadienyl(cyclohexyl isocyanide)nickel]. The yields of II from III and IV were 12% and 15% respectively.