Single, Double and Triple Insertion of Cyclohexyl Isocyanide into Methyl-Palladium Sigma Bond

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Recently Otsuka *et al.* reported that the reaction of tetrakis(*tert*-butyl isocyanide)nickel with methyl iodide or benzoyl chloride undergoes multiple successive insertions of isocyanide molecules.[1] They pointed out that the insertion reaction suggested a mechanism for the polymerization of isocyanides. During our studies on the interaction of isocyanide with alkyl transition metal complexes,[2] we found that a similar successive insertion occurred in the reaction of cyclohexyl isocyanide(I) with *trans*-iodo-bis(tertiary phosphine)-methylpalladium. We wish to report on this subject.

Addition of I to *trans*-iodo-bis(methyldiphenylphosphine)methylpalladium(IIa) in benzene at 0°C gave yellow orange crystals IIIa[3] (49%, mp 134—137°C dec.). The dimeric structure was confirmed by molecular weight determination, IR and NMR spectra. Treatment of IIIa with I in the presence of methyldiphenylphosphine produced yellow complex IVa[3] (57%, mp 126—130°C dec.). The IR spectrum showed two carbon - nitrogen double bonds at 1630 and 1585 cm^{-1}. The NMR spectrum[*1] showed a singlet peak at 8.47($C-CH_3$), three broad signals at 8.72, 8.43 and 2.35 (two cyclohexyl and four phenyl groups) and a triplet signal at 8.07 τ($P-CH_3$), indicating the *trans*-configuration for IVa. The complex IVa was also obtained from the reaction of IIa with I in 1 : 2 molar ratio.

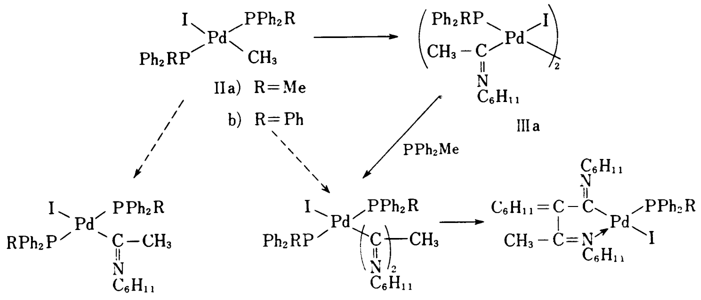
When IVa was treated with I in benzene, stepwise-inserted reaction took place, affording a trisimino complex Va[3] (67%, mp 138—141°C dec.). Va was identified to be the five-membered chelate structure coordinated to palladium through the lone pair electrons of terminal imino nitrogen atom, based on its monomeric nature, electronic configuration of palladium atom and spectroscopic studies.[4] The IR spectrum showed carbon-nitrogen double bonds at 1636 and 1598 cm^{-1}. The NMR spectrum showed a sharp singlet peak at 7.68($C-CH_3$), a doublet resonance at 7.80($P-CH_3$, $J_{P,H}=9.0$Hz) and two broad signals at 8.50 and 2.60 τ(cyclohexyl and phenyl groups), in addition to two broad signals due to α-protons of two internal cyclohexyl groups (7.30 τ) and that of a terminal one(6.50 τ). Complex Va was also obtained from the reaction of IIa with I in 1 : 3 molar ratio. A series of reactions indicates the stepwise-inserted reaction of isocyanides.

The reaction of *trans*-iodo-bis(triphenylphosphine)methylpalladium (IIb) with I in 1 : 1 molar ratio gave an air-sensitive yellow complex VIb[3] (53%, mp 98—102°C dec.). Treatment of IIb with I in 1 : 2 molar ratio produced yellow crystals IVb[3] (51%, mp 117—119°C dec.). The IR and NMR spectra were in complete agreement with the suggested structure.

No reaction of I with VIb was observed, indicating that the reaction did not proceed stepwise as IIb→VIb→IVb.

It is interesting to note that the insertion proceeds stepwise or nonstepwise depending on the nature of tertiary phosphine ligand.

Detailed studies will be reported in the near future.



VIb IVa, b Va

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[1] S. Otsuka, A. Nakamura and T. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).

[2] Y. Yamamoto, H. Yamazaki and N. Hagihara, This Bulletin, **41**, 532 (1968); *J. Organometal. Chem.* **18**, 189 (1969); Y. Yamamoto and H. Yamazaki, This Bulletin, **43**, 143 (1970).

[3] All complexes gave satisfactory results in elementary analysis.

[*1] measured in $CDCl_3$ with TMS as the internal standard.

[4] A similar structure has been postulated in the nickel complex; see Ref. 1.