Five Co-ordination in Isocyanide Insertion Complexes of Pd(II)

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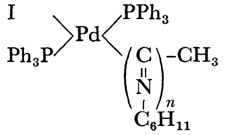
(Received August 29, 1970)

We have already reported that the reaction of cyclohexyl isocyanide (**1**) with *trans*-Pd$(PPh_3)_2I(CH_3)$ underwent the insertion of isocyanide molecules into a methyl-palladium σ-bond, affording imidoyl complexes.[1]



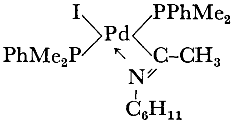
$n = 1$ or 2

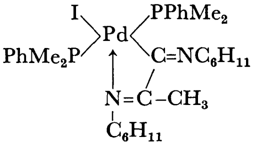
In our further studies of the insertion reaction of isocyanide,[2–4] we concluded that it had a five coordinate structure complexes to palladium through the lone-pair electrons of imino nitrogen atom; our conclusion was based on the NMR spectra of these types of complexes with dimethylphenylphosphine. We wish now to report on this subject.

The treatment of **1** with *trans*-Pd$(PPhMe_2)_2I(CH_3)$ in a 1 :1 or 2 : 1 molar ratio in benzene at 0°C underwent the single or double insertion of isocyanide into a methyl-palladium σ-bond, producing *trans*-Pd$(PPhMe_2)_2I[C(CH_3){=}NC_6H_{11}]$ (**2**)[5] (as very pale yellow crystals, 59%, mp 169—172°C dec., $\nu_{C=N}$(KBr) 1627 cm^{-1}) and *trans*-Pd$(PPhMe_2)_2I[CH_3(C{=}NC_6H_{11})_2]$ (**3**)[5] (as yellow crystals, 54%, mp 223—227°C dec., $\nu_{C=N}$(KBr) 1632 and 1583 cm^{-1}) respectively. The complex **3** was more stable than **2**.

In the NMR spectrum of **2** in C_6D_6 at 23°C, the methyl resonances of dimethylphenylphosphine ligands showed a well-defined 1 : 2 : 2 : 2 : 1 pattern. This may be considered to arise from two overlapping 1 : 2 : 1 patterns (8.47 and 8.35 τ), separated by 7.2 Hz, in which the triplet resonance suggests that the two phosphorus ligands were coordinated to a metal in mutual *trans*-positions.

The presence of two triplet signals indicates that the two methyl groups on the same phosphorus atom are magnetically nonequivalent, for there is no plane of symmetry resulting from the co-ordination of the imino nitrogen to the palladium atom.[6]





An elevation of the temperature might be expected to give the four co-ordinate complex by releasing the imino nitrogen. This would cause the two methyl proton resonances to be magnetically equivalent.

The P–CH_3 protons of **2** at 42°C appeared as two triplets (with the same coupling constant, $|{}^2J_{P,H}+{}^4J_{P,H}|=6$ Hz), and separated by 4.6 Hz. At 63°C and 81°C, the spectra showed 1 : 3 : 3 : 1 and 1 : 1 : 2 : 2 : 1 : 1 patterns, separated by 3 and 1 Hz, respectively, indicating two overlapping 1 : 2 : 1 patterns. At 85°C, the two P–CH_3 resonances converged to a triplet peak, indicating the absence of magnetic nonequivalence.

Analogous NMR behavior was observed in the complex **3**. In the spectrum of **3** in C_6D_6 at 23°C, the methyl proton resonances of the phosphorus ligands showed two triplets at 8.45 ($|{}^2J_{P,H}+{}^4J_{P,H}|=6.5$ Hz) and 8.22 τ ($|{}^2J_{P,H}+{}^4J_{P,H}|=6.5$ Hz), indicating also the presence of magnetic nonequivalence. The magnitude of the chemical-shift difference of the two triplets due to the P–CH_3 resonances decreased with a rise in the temperature without changing their forms. The convergence of the two triplets to a triplet peak was ultimately observed at *ca.* 130°C, indicating that the co-ordination strength of **3** is higher than that of **2**. This indicates a parallel between the co-ordination strength and the difference in stability of the two iminoacyl complexes. Detailed studies are in progress.

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[1] Y. Yamamoto and H. Yamazaki, This Bulletin, **43**, 2653 (1970).

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

[3] Y. Yamamoto and H. Yamazaki, This Bulletin **43**, 143 (1970).

[4] Y. Yamamoto and H. Yamazaki, *J. Organometal. Chem.*, **24**, 717 (1970).

[5] Both complexes gave satisfactory results in elementary analysis and molecular-weight determinations.

[6] The triple-inserted complex, Pd$(PPh_2Me)I[CH_3(C{=}NC_6H_{11})_3]$, obtained from the reaction of *trans*-Pd$(PPh_2Me)_2I(CH_3)$ with **1** in a 1 : 3 molar ratio had a four-co-ordinated structure containimg the five-membered chelate co-ordinated to palladium through the terminal imino nitrogen atom; see Ref. 1. An analogous structure was noted in the nickel complexes; see S. Otsuka, A. Nakamura and K. Yoshida, *J. Amer. Chem. Soc.*, **91**, 7196 (1969).