CHEMISTRY LETTERS, pp. 1387-1388, 1977. Published by the Chemical Society of Japan

INSERTION OF DIMETHYL ACETYLENEDICARBOXYLATE AND 2,5-NORBORNADIENE INTO THE Pd-C BOND OF THIOMETHOXYMETHYL-PALLADIUM DERIVATIVES

Gohei YOSHIDA*, Hideo KUROSAWA, and Rokuro OKAWARA

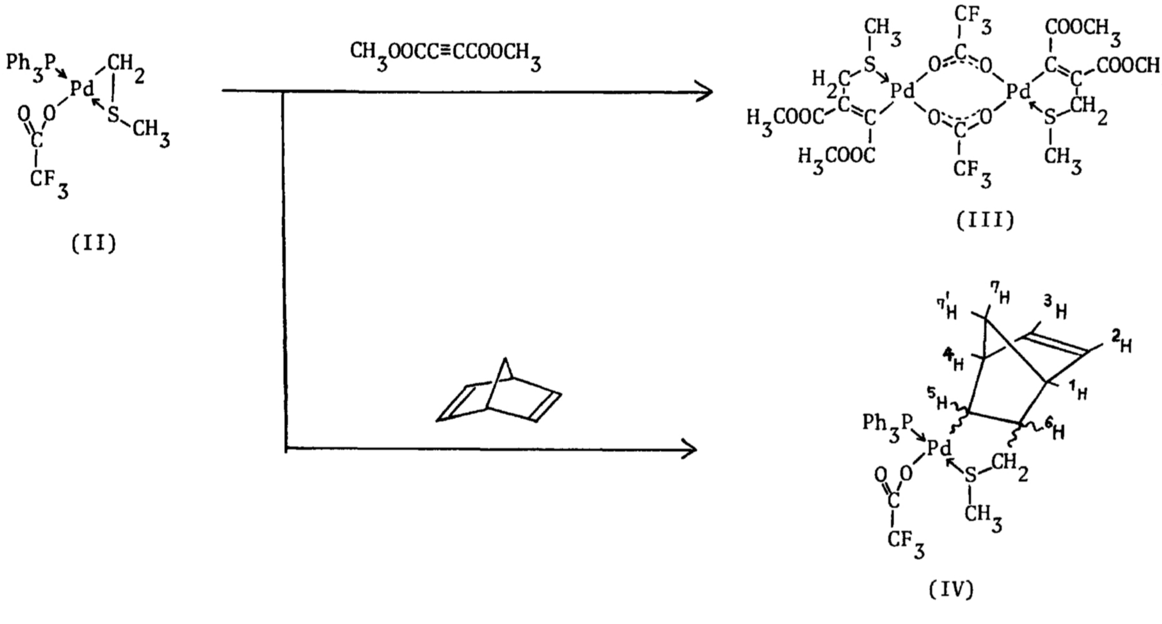
Department of Applied Chemistry, Osaka University, Suita, Osaka 565

Insertion of RC≡CR (R= $COOCH_3$) or 2,5-norbornadiene into the Pd-C bond of $Pd(Ph_3P)(CH_2SCH_3)(OCOCF_3)$ gave the corresponding cis-addition product in good yield. $Pd(Ph_3P)(CH_2SCH_3)Cl$ was unreactive toward RC≡CR (R= $COOCH_3$), however, the reaction between these two compounds occurred readily by addition of catalytic amount of $AgClO_4$ to give $[Pd(CR{=}CRCH_2SCH_3)Cl]_2$ (R= $COOCH_3$).

There has been widespread interest in insertion of unsaturated hydrocarbons into metal-carbon bonds of organometal complexes$^{1)}$. It is particularly interesting to investigate the reaction involving thiomethoxymethyl-palladium complexes$^{2)}$, for these complexes are considered to have some strained energy within the three-membered Pd-C-S ring and such reaction, if occurred, would represent one of few examples of insertion reactions involving metal alkyls bearing functional groups$^{3)}$.

The complex (II)$^{4)}$ was easily obtained from $Pd(Ph_3P)(CH_2SCH_3)Cl$ (I) on treatment with $AgOCOCF_3$ in CH_2Cl_2-acetone as pale yellow needles. The molecular weight measurement showed (II) to be monomeric, and a doublet signal of the (S)CH_3 protons (J(P-H)= 5 Hz) in the ^1H NMR spectrum indicates that the CH_3SCH_2 group coordinates in an intramolecular bidentate fashion.

As shown below, (II) reacted with RC≡CR (R= $COOCH_3$) in CH_2Cl_2 over a period of 2 days at room temperature to form (III), in marked contrast to the inertness of (I) toward the acetylenic compound. The configuration of (III) has been suggested from the molecular weight measurement (found 810; calcd., 846), the appearance of the methylene proton resonance as an AB pattern (δ 4.10 and 3.79 ppm, J_{AB}= 16 Hz), and a strong IR band at 1650 cm^{-1} due to the bridging carboxylate group. Also, (II)



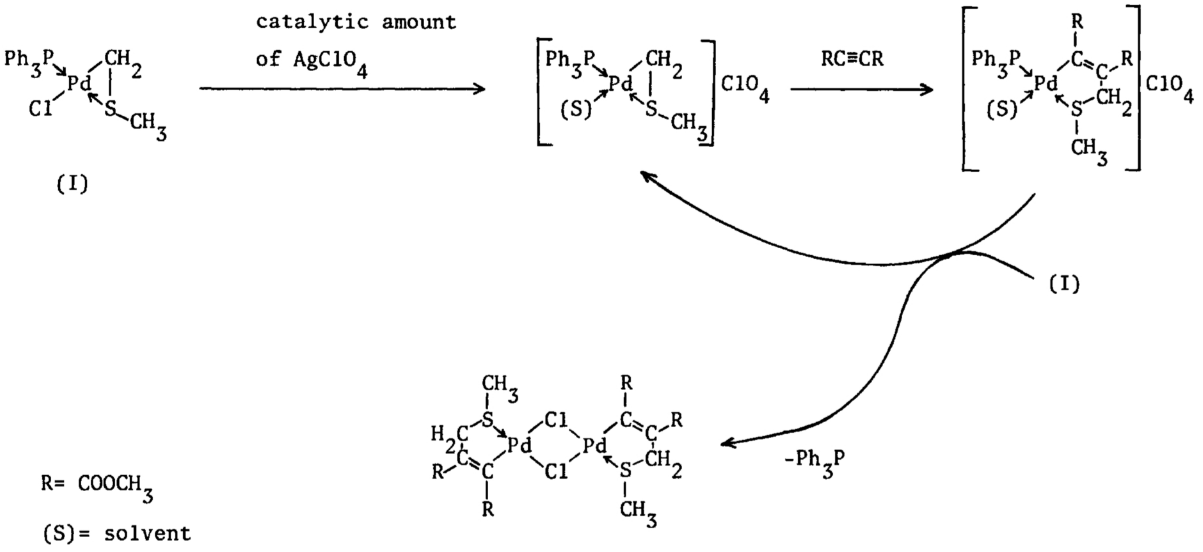
(II)

(III)

(IV)

and 2,5-norbornadiene gave (IV) under a similar reaction condition. Somewhat broad AB pattern (δ 3.14 and 2.96 ppm, J_{AB}= 12 Hz) of the methylene and a doublet signal (J(P-H)= 4 Hz) of the (S)-CH_3 proton resonances of (IV) suggest the intramolecular coordination of sulfur to palladium, and the value of J(^{5}H-^{6}H) (9 Hz) indicates a cis configuration for these protons$^{5)}$. However, it is not certain at present whether the insertion occurred through endo- or exo-addition. The reason for the difference of the reactivities of (I) and (II) may be that the CF_3OCO ligand of (II) can vacate the coordination site more easily than the chloride ligand of (I) on the attack of the unsaturated molecules to the palladium atom.

It is particularly interesting that the addition of catalytic amount of $AgClO_4$ (0.1 mol/Pd-atom) to a mixture of (I) and RC≡CR (R= $COOCH_3$) resulted in the formation of a chloro-bridged palladium complex (V) in good yield. The reaction path to form (V) may be depicted as shown in scheme. The scheme shows that the vacant coordination site induced by removal of the chloride anion of (I) with $AgClO_4$ plays an important role in the insertion of the acetylenic compound to the Pd-C bond. The IR spectrum (Nujol) of (V) showed ν(C=C) at 1592 cm^{-1}, ν(Pd-Cl) at 285 cm^{-1} and ν(CO) at 1700 cm^{-1}. The ^{1}H NMR spectrum of (V), however, could not be measured because of the limited solubility. The monomeric complex $Pd(CR{=}CRCH_2SCH_3)(acac)$ (R= $COOCH_3$, acac= acetylacetonate) (VI) was derived from (V) on treatment with Tl(acac) in $CHCl_3$. The AB pattern (δ 4.15 and 3.63 ppm, J_{AB}= 16 Hz) of the methylene proton resonance of (VI) again suggests the intramolecular coordination of sulfur to palladium.



(I)

(I)

(V)

R= $COOCH_3$

(S)= solvent

Scheme

REFERENCES

1) R. F. Heck 'Organotransition Metal Chemistry' Academic Press, New York (1974).
2) G. Yoshida, H. Kurosawa and R. Okawara, J. Organometal. Chem., 113 85 (1976).
3) T. Tohda, K. Sonogashira, and N. Hagihara, J. C. S. Chem. Comm., 54 (1975).
4) Satisfactory elemental analyses were obtained for all compounds described. The structural assignments for compounds (I)-(VI) are based on ^{1}H NMR and IR data.
5) a) F. A. L. Anet, Tetrahedron Letters, 46 3399 (1964) and references therein.
b) R. P. Hughes and J. Powell, J. Organometal. Chem., 30 C45 (1971).

(Received September 24, 1977)