A Wittig-type Reaction of Phosphoranes with Carbon Monoxide Coordinated to Palladium. A Synthetic Route to Isocyanide Palladium Complexes

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The reaction of carbon monoxide with triphenyl(phenylimino)phosphorane proceeded at room temperature in the coordination sphere of palladium to give a mixture of phenyl isocyanide and carbonyl complexes of palladium. Triphenyl(*t*-butylimino)phosphorane gave bis(*t*-butyl isocyanide)palladium chloride in a low yield. Benzophenone triphenylphosphazine and triphenyl(*p*-tolylsulfonylimino)phosphorane failed to react with carbon monoxide.

Although phosphoranes (ylides) and carbon monoxide are versatile reagents in organic synthesis, no reaction between them has been recorded. Coordinated carbon monoxide is susceptible to attack by many nucleophiles. For example, an attack by organolithium leads to the formation of aldehydes[1] or metal–carbene complexes.[2] Ylides possess a nucleophilic character and can be expected to react with coordinated carbon monoxide. In fact, Kaska and his co-workers[3] succeeded in applying the Wittig reaction to transition-metal carbonyl. Iminophosphoranes also react with iron carbonyl to form isocyanide-substituted iron carbonyls *via* a Wittig-type reaction.[4] These reactions seem to provide a method of preparing novel organotransition metal complexes.

While no Pd^{2+}-carbonyl with a definite stoichiometry has been characterized, carbonylation by carbon monoxide is generally accepted to occur in the coordination sphere of the Pd^{2+}-ion.[5] A preliminary work of the present study has been published.[6]

This paper will deal with the Pd^{2+}–assisted Wittig-type reaction of carbon monoxide with iminophosphoranes.

Results and Discussion

Triphenyl(phenylimino)phosphorane (I). Triphenyl(phenylimino)phosphorane (I) reacted with carbon monoxide under an atmospheric pressure in the presence of such palladium chloride complexes (hereafter abbreviated as "$PdCl_2$") as $PdCl_2$(COD) (COD=1,5-cyclooctadiene) or $[PdCl_2(\text{styrene})]_2$. The product was revealed by the IR spectrum to be a mixture of

$$2C_6H_5N{=}P(C_6H_5)_3 + \text{"}PdCl_2\text{"} + CO \longrightarrow$$

I

$$-Pd(=O^-)-C(=P^+(C_6H_5)_3)-N(-C_6H_5)- \xrightarrow{-OP(C_6H_5)_3}$$

$$[C_6H_5N{=}P(C_6H_5)_3]PdCl_2(CNC_6H_5) \xrightarrow[-C_6H_5NC]{CO}$$

II

$$[C_6H_5N{=}P(C_6H_5)_3]PdCl_2(CO) \qquad (1)$$

III

Pd^{2+}–isocyanide (II) and –carbonyl (III) complexes. The formation of the isocyanide complex indicates an apparent Wittig-type reaction of the ylide (I) with carbon monoxide coordinated to the palladium. Triphenylphosphine oxide, which is the other typical product of the Wittig reaction, was isolated from the solution.

Complex II is soluble in chloroform and slightly soluble in toluene, while complex III is insoluble in common organic solvents. In dimethyl sulfoxide, III decomposed slowly. The separation of II from III could be achieved by extraction with a mixed solvent of toluene and acetone containing a small amount of chloroform. The analytical data of II and III are in accord with the formula of $PdCl_2$(ylide)L (II, L=C_6H_5NC; III, L=CO). The molecular weight (osmometry in $CHCl_3$) indicates that II is monomeric. The infrared and far infrared spectra of II show strong bands at 2200 and 340 cm^{-1} and a medium absorption at 324 cm^{-1}. Complex III has a strong infrared band at 1900 cm^{-1}. In benzene, III reacted slowly with 2 mol of triphenylphosphine, with the evolution of carbon monoxide, to give $PdCl_2[P(C_6H_5)_3]_2$.

It is noteworthy that $PdCl_2$(COD) itself is inactive to carbon monoxide in benzene.[7] All the systems of "$PdCl_2$" and ylide absorbed carbon monoxide slowly.

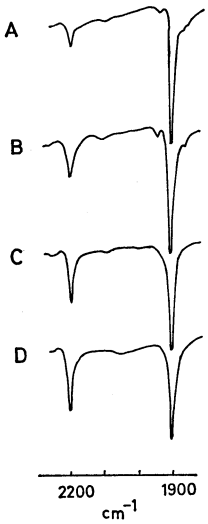

Fig. 1. Typical IR absorptions of ν_{CO} and ν_{CN} of the reaction products obtained from: (A) $PdCl_2$(COD), 27 h; (B) $PdCl_2(C_6H_5CN)_2$, 23 h; (C) $[PdCl_2(\text{styrene})]_2$, 2.5 h. (D) A mixture (1: 1) of II and III.

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The absorption continued for 25—30 h. The ratio of II to III depended upon the reaction time. In the early stages of the reaction a considerable amount of II was detected; it was slowly converted into III. Some typical spectra of the reaction products are shown in Fig. 1.

The reaction of II with carbon monoxide is noteworthy. In a toluene solution, II reacted with carbon monoxide to afford III. In the presence of I (I/II<1), however, the phenyl isocyanide coordinated to palladium reacted with I under an atmosphere of carbon monoxide to afford diphenylcarbodiimide in a moderate yield.[8] The formation of the carbodiimide was shown by the IR absorptions at 2137 and 2104 (sh) cm^{-1} and by isolating diphenylurea after hydrolyzing it with HCl–AcOH.

Triphenyl(t-butylimino)phosphorane (IV). The IV ylide was allowed to react with carbon monoxide under conditions similar to those described above. The product of the Wittig-type reaction in this case was off-white bis(*t*-butyl isocyanide)palladium chloride (V), which was identified with an authentic sample.[9] The infrared

$$2\,t\text{-}C_4H_9N{=}P(C_6H_5)_3 + 2CO + \text{“}PdCl_2\text{”} \longrightarrow$$
$$\text{IV}$$
$$PdCl_2(CNC_4H_9)_2 + 2OP(C_6H_5)_3 \quad (2)$$
$$\text{V}$$

spectrum coincides completely with that of the authentic sample in the 400—4000 cm^{-1} region. The characteristic bands due to ν_{CN} appear at 2240 and 2260 cm^{-1}. The yield after purification was low, because the separation from triphenylphosphine oxide was difficult (see Experimental). The formation of 2 mol of the isocyanide on palladium shows that basic IV reacts with carbon monoxide more smoothly within the coordination sphere of palladium. In this case, however, the reduction of "$PdCl_2$" with IV occurred competitively and a considerable amount of "$PdCl_2$" was reduced to metal.

Besides V, an insoluble carbonyl complex was also formed. However, it could not identified, because its purification was difficult as a result of poor solubility.

Benzophenone Triphenylphosphazine (VI). In the reaction of VI with carbon monoxide, brown "$PdCl_2$" gradually turned to an insoluble yellow solid. The solid was revealed to be a carbonyl–Pd^{2+} complex (VII).

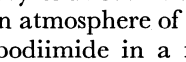
$$(C_6H_5)_2C{=}N{-}N{=}P(C_6H_5)_3 + \text{“}PdCl_2\text{”} + CO$$
$$\text{IV}$$
$$\longrightarrow [(C_6H_5)_2C{=}N{-}N{=}P(C_6H_5)_3]PdCl_2(CO) \quad (3)$$
$$\text{VII}$$

The analytical data are in accord with VII. The yield was quantitative. The infrared spectrum shows a strong band at 1900 cm^{-1}. Neither isocyanide complex (or Wittig-type product derived from VI) nor triphenylphosphine oxide was detected in the reaction system. From these facts, it is concluded that VI fails to react with carbon monoxide at room temperature. Phosphazine VI, whose negative charge is delocalized, may be represented as follows:[10]

$$R_3P{=}N{-}N{=}C\!\!< \longleftrightarrow R_3\overset{+}{P}{-}\overset{-}{N}{-}N{=}C\!\!< \longleftrightarrow R_3\overset{+}{P}{-}N{=}N{-}\overset{-}{C}\!\!<$$

The lack of reactivity toward the coordinated carbon monoxide may be ascribed to this decreased nucleophilicity.

Other Phosphoranes. No reaction of triphenyl(*p*-tolylsulfonylimino)phosphorane (VIII) with carbon monoxide occurred. The lack of reactivity of VIII may be ascribed to its decreased nucleophilicity, caused by electron-withdrawing sulfonyl group.



VIII

$(C_6H_5)_3P{=}C{=}P(C_6H_5)_3$

IX

Hexaphenylcarbodiphosphorane (IX) was allowed to react with carbon monoxide. The brown olefin–palladium complex gradually turned to an insoluble dark green solid which showed infrared bands at 2120 and 1900 cm^{-1}. The former frequency is tentatively assigned to the $\nu_{C\equiv C}$ vibration of $-\overset{|}{\underset{|}{Pd}}-C{\equiv}C-P(C_6H_5)_3$. Triphenylphosphine oxide was isolated from the solution. An analogous reaction has been observed between manganese carbonyl and IX. The absorption band of $Mn(CO)_4Br[C{\equiv}C{-}P(C_6H_5)_3]$ at 2105 cm^{-1} was assigned to the $\nu_{C\equiv C}$ band.[4] The product, which shows the IR band at 2120 cm^{-1}, was relatively stable in the dry state, but exceedingly unstable in solution. All attempts to isolate it in a pure form have been unsuccessful.

Experimental

Materials. The $C_6H_5N{=}P(C_6H_5)_3$[11], $t\text{-}C_4H_9N{=}P(C_6H_5)_3$[12], $(C_6H_5)_2C{=}N{-}N{=}P(C_6H_5)_3$[13], $p\text{-}CH_3C_6H_4SO_2N{=}P(C_6H_5)_3$[14], and $(C_6H_5)_3P{=}C{=}P(C_6H_5)_3$[15] compounds and the palladium complexes were prepared by the known methods. Toluene and benzene were purified by distillation in the presence of benzophenone sodium ketyl and were used under an argon atmosphere. Carbon monoxide (99.5% Matheson Co.) was used without further purification.

General Procedure for the Reactions with Carbon Monoxide. The conventional hydrogenation apparatus under an atmospheric pressure was used. In a round 50-ml flask, ylide, "$PdCl_2$," and toluene (solvent) were placed under an atmosphere of argon. The system was then placed under carbon monoxide by evacuating it by means of an aspirator and by filling it with carbon monoxide several times. Then the flask was shaken under an atmospheric pressure of carbon monoxide at room temperature. After shaking, the resulting solid was filtered off, washed, and dried. Some typical reactions are as follows.

Reaction of I. The ylide (I, 1 mmol) was allowed to react with carbon monoxide in the presence of $[PdCl_2(cyclooctene)]_2$ (0.25 mmol) for 22 h. The solid mass was then extracted with a mixed solvent of toluene, acetone, and chloroform (6:4:1). The subsequent evaporation of the solvent gave II in a 37% yield; mp 99 °C (dec.). Found: C, 58.26; H, 4.27; N, 4.44; P, 4.79%. Calcd for $C_{31}H_{25}N_2PPdCl_2$: C, 58.73; H, 3.95; N, 4.42; P, 4.89%. Complex III (21.6%) remained undissolved; mp 148 °C (dec.). Found: C, 54.20; H, 4.21; N, 2.55; P, 5.30%. Calcd for $C_{25}H_{20}NOPPdCl_2$: C, 53.72; H, 3.58; N, 2.51; P, 5.55%.

Reaction of III with $P(C_6H_5)_3$. III (0.2233 g) was suspended in 2 ml of benzene and was allowed to react with 0.2098 g of $P(C_6H_5)_3$ at a refuxing temperature for 4 h. Filtration gave $PdCl_2[P(C_6H_5)_3]_2$ in a 78% yield (Found: C,

61.65; H, 4.30; P, 8.82%).

Reaction of IV. The reaction of 0.143 g (0.5 mmol) of $PdCl_2(COD)$ with 1 mmol of IV in 10 ml of toluene under carbon monoxide gave gray-green solids after 70 h. After the filtration of the solids, the solution was evaporated to a small volume and ether was added to the concentrated solution. Triphenylphosphine oxide, which was soluble, was removed by this treatment. (In this procedure, a considerable amount of V remained in the solution.) The precipitate, which contained a small amount of the carbonyl compound, was extracted with benzene. The subsequent evaporation of benzene gave pure V; 3 mg (Found: N, 7.23%).

Reaction of VI. The reaction of the VI ylide (1 mmol) with carbon monoxide in the presence of "$PdCl_2$" (1 mmol) for 22 h gave VII in an 80% yield. Found: C, 57.84; H, 3.95; N, 4.46; P, 4.77%. Calcd for $C_{32}H_{25}N_2OPPdCl_2$: C, 58.06; H, 3.78; N, 4.23; P, 4.69.

Reaction of IX. The reaction of ylide IX (1.74 mmol) with "$PdCl_2$" (0.87 mmol) in 10 ml of toluene for 22 h gave 0.436 g of solids, which showed IR absorptions at 2120 and 1900 cm^{-1}.

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