apparatus and the distillate was examined by analytical GC (175–220 °C depending on sample) and TLC (30% ether/petroleum ether). Ketol 7, when present, appeared at a longer retention time and a smaller $R_f$ than enone 6. The product yields and physical data are recorded in Tables I and II. In some instances analytical samples were obtained by preparative GC or TLC.

**Method B.** To a solution of 4 mmol of alcohol 4 in 6 mL of dry pyridine was added 2 mmol of phosphorus oxychloride, and the solution was refluxed under nitrogen for 2.5 h. The reaction mixture was cooled, 15 mL of water was added, and the cloudy mixture was extracted three times with ether (total volume ~100 mL). The combined organic phases were extracted with cold 6 N HCl until all the pyridine was removed. The ether solution was transferred to a round-bottomed flask, 20 mL of 2 N HCl was added, and the two-phase system was vigorously stirred at room temperature for 18 h to effect hydrolysis of the enol ether moiety. The aqueous phase was separated and extracted three times with ether, and the combined organic phases were extracted once with saturated $NaHCO_3$ solution and once with brine and then dried. After removal of the solvent, the residue was distilled with a Kugelrohr apparatus and analyzed by GC and TLC. Generally a small amount of unhydrolyzed diene 5 was detected and was found to have a shorter retention time and a larger $R_f$ than those for enone 6.[10] The yields of enone 6 for this procedure are reported in Table I.

**Conversion of 4 to Ketol 7.** A solution of 4–5 mmol of crude Grignard product 4 in 100 mL of ether was stirred vigorously for 18 h with 25 mL of 5% $H_2SO_4$. After the aqueous phase was extracted three times with ether, the combined organic phases were extracted once with a saturated $NaHCO_3$ solution and once with brine and then dried with anhydrous $MgSO_4$. Removal of the solvent yielded ketol 7 which exhibited carbonyl absorption at 1720 $cm^{-1}$ in its IR spectrum and a singlet methyl carbinol resonance at $\delta$ 1.3 in its NMR spectrum.

**Acknowledgments.** The authors acknowledge the financial assistance of the National Research Council of Canada.

**Registry No.** **1a**, 2403-57-8; **1b**, 4134-23-0; **1c**, 55023-48-8; **2**, 43042-58-6; **3a**, 42117-32-8; **3b**, 70702-97-5; **3c**, 70702-98-6; **4a**, 70702-99-7; **4b**, 70703-00-3; **4c**, 70703-01-4; **5a**, 70703-02-5; **5b**, 70703-03-6; **5c**, 70703-04-7; **6a**, 42747-41-1; **6b**, 70703-05-8; **6c**, 2244-15-7; **7a**, 70703-06-9; **7b**, 70703-07-0; **7c**, 6756-92-9; **8a**, 1125-99-1; **8b**, 56021-68-2; **9a**, 70703-08-1; **9b**, 70703-09-2; **10a**, 70703-10-5; **10b**, 70703-11-6; **11**, 64889-15-2; **12a**, 70703-12-7; **12b**, 70703-13-8; methyl iodide, 74-88-4.

**Supplementary Material Available:** A table listing the absolute mass determinations of all new compounds reported (1 page). Ordering information is given on any current masthead page.

---

# Preparation of Highly Reactive Metal Powders. Preparation and Reactions of Highly Reactive Palladium and Platinum Metal Slurries

Reuben D. Rieke* and Arunas V. Kavaliunas

*Department of Chemistry, University of Nebraska—Lincoln, Lincoln, Nebraska 68588*

*Received February 6, 1979*

Reduction of compounds of the type $[P(C_2H_5)_3]_2MX_2$ of palladium and platinum with 2 equiv of potassium in ethereal solvents results in highly reactive metal slurries containing insoluble metal and low valent metal phosphine compounds which readily react with a variety of aryl halides to yield the organometallic complexes, *trans*-$[P(C_2H_5)_3]_2M(R)X$ (M = Pd, Pt; R = $C_6H_5$, $C_6F_5$; X = I, Br, Cl, CN). Such a palladium slurry reacts with allyl bromide to yield $P(C_2H_5)_3Pd(C_3H_5)Br$. Reduction of $PdI_2$ with lithium and naphthalene and in the absence of phosphine results in a palladium powder which reacts with $C_6F_5I$ to yield $C_6F_5PdI$, which was isolated as its triethylphosphine adduct.

In 1972, we reported a general procedure for the preparation of highly reactive metal powders.[1] The basic procedure involved the reduction of a metal salt in a hydrocarbon or ethereal solvent.[1-9] We have noted that the reactivities and in some cases products are highly dependent on the reduction conditions, i.e., anion, reducing agent, solvent, temperature, and presence of added alkali salts, Lewis acids, or Lewis bases.[3-9]

In a previous communication,[8] we reported the preparation of highly reactive metal slurries of nickel, palladium, and platinum and the oxidative insertion of these metals into aryl halide bonds to yield the complexes *trans*-$[P(C_2H_5)_3]_2M(R)X$. Organometallic compounds of this type are well known and have been prepared in a variety of ways, most often by alkylating agents such as Grignard and lithium reagents[10,11] and more recently from the zerovalent triethylphosphine complexes of these metals[12] as well as from metals obtained by the metal vaporization technique.[13]

In this paper we describe in detail the preparation of metal slurries of palladium and platinum by alkali metal reduction of the compounds $[P(C_2H_5)_3]_2MX_2$ and the reaction of the resulting metal slurries with a variety of organic halides.

## Experimental Section

**Starting Materials.** Triethylphosphine (Orgmet, Inc.) and the organic halides were used as received. Tetrahydrofuran (THF)

---

(1) R. D. Rieke and P. M. Hudnall, *J. Am. Chem. Soc.*, **94**, 7178 (1972).

(2) R. D. Rieke, P. M. Hudnall, and S. Uhm, *J. Chem. Soc., Chem. Commun.*, 269 (1973).

(3) R. D. Rieke and S. E. Bales, *J. Am. Chem. Soc.*, **96**, 1775 (1974).

(4) R. D. Rieke and L. Chao, *Synth. React. Inorg. Met.-Org. Chem.*, **4**, 101 (1974).

(5) R. D. Rieke, K. Öfele, and E. O. Fischer, *J. Organomet. Chem.*, **76**, C19 (1974).

(6) R. D. Rieke, *Top Curr. Chem.*, **59**, 1 (1975).

(7) R. D. Rieke, *Acc. Chem. Res.*, **10**, 301 (1977).

(8) R. D. Rieke, W. J. Wolf, N. Kujundžić, and A. V. Kavaliunas, *J. Am. Chem. Soc.*, **99**, 4159 (1977).

(9) S. Uhm, Ph.D. Thesis, Unversity of North Carolina—Chapel Hill, 1974.

(10) M. L. H. Green, "Organometallic Compounds", Vol. 2, Methuen, London, 1968, p 224.

(11) G. W. Parshall and J. J. Mrowca, *Adv. Organomet. Chem.*, **7**, 157 (1968).

(12) R. A. Schunn, *Inorg. Chem.*, **15**, 208 (1976).

(13) K. J. Klabunde and J. Y. F. Low, *J. Am. Chem. Soc.*, **96**, 7674 (1974).

0022-3263/79/1944-3069$01.00/0

and 1,2-dimethoxyethane (glyme) were distilled immediately prior to use from the sodium ketyl of benzophenone or from sodium–potassium alloy under argon. Anhydrous metal halides (Ventron or Cerac, Inc.) were used as received. $PdI_2$[14] and the compounds *trans*-$[P(C_2H_5)_3]_2MX_2$[15] were prepared according to published procedures. Potassium was Baker's purified grade. The preparation of metal slurries and their subsequent reaction with organic halides was carried out in an atmosphere of purified argon; however, workup of the organometallic complexes, unless otherwise specified, was done in air.

Analyses were performed by Chemalytics, Inc. and Galbraith Laboratories, Inc.

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)I$.** A 50-mL three-neck flask equipped with a magnetic stirrer and a condenser topped with an argon inlet was charged with 0.959 g (0.00232 mol) of *trans*-$[P(C_2H_5)_3]_2PdCl_2$ and 0.181 g (0.00463 mol) of potassium (freshly cut and cleaned), and then 10 mL of freshly distilled tetrahydrofuran was syringed in. The yellow solution was then refluxed with vigorous stirring for 22 h, after which time a black metal powder existed in a yellow solution. The reaction mixture was allowed to cool to room temperature, 0.26 mL (0.0023 mol) of $C_6H_5I$ was syringed in, and the mixture was stirred for 1 h after which it was filtered, the solids were washed out with dichloromethane, and the solvent was removed from the filtrate under reduced pressure. The crude material was dissolved in hexane, treated with charcoal, and filtered. Slow evaporation of the solvent resulted in large yellow crystals of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)I$; 0.639 g (51%); mp 111–111.5 °C. Very often the crystalline product is obtained somewhat oil covered and the recrystallization must be repeated.

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Br$.** **(A)** A 50-mL three-neck flask, equipped with a magnetic stirrer and a condenser topped with an argon inlet, was charged with 0.840 g (0.00316 mol) of $PdBr_2$. An argon atmosphere was established in the apparatus and 10 mL of freshly distilled glyme was syringed into the flask followed by 0.94 mL (0.0064 mol) of $P(C_2H_5)_3$. Immediately the solution became yellow-orange as *trans*-$[P(C_2H_5)_3]_2PdBr_2$ started forming and after 10 min no $PdBr_2$ was visible in the stirred solution. A piece of potassium (0.247 g, 0.00632 mol) cut and cleaned under hexane was added to the reaction mixture and stirring and heating were started. After 5 h at reflux the mixture contained a black slurry in a yellow solution. To it was added 0.66 mL (0.0064 mol) of $C_6H_5Br$ and reflux was maintained for an additional 14 h. The cooled mixture was filtered, solids were washed out with dichloromethane, and the solvent was removed from the filtrate under reduced pressure. The crude material was dissolved in hot hexane, treated with charcoal, and filtered. Slow evaporation of solvent resulted in large colorless crystals of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Br$: 0.998 g (63%); mp 107–107.5 °C (lit.[12,13] 96–98 °C, 103–104 °C). **(B)** The previously described reaction apparatus was charged with 1.104 g (0.00267 mol) of *trans*-$[P(C_2H_5)_3]_2PdCl_2$, 0.0376 g (0.00542 mol) of freshly cut and cleaned lithium, and 0.0324 g (0.000253 mol) of naphthalene. Glyme (10 mL) was syringed in and the mixture was stirred for 70 h at room temperature, after which time the usual black slurry in a yellow solution was obtained. A sample of 0.57 mL (0.0054 mol) of $C_6H_5Br$ was syringed in and the mixture was refluxed for 21 h. The usual workup yielded 0.612 g (46%) of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Br$.

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)CN$.** A palladium slurry was prepared in the usual manner from 0.247 g (0.00632 mol) of potassium, 0.559 g (0.00315 mol) of $PdCl_2$, and 0.93 mL (0.0063 mol) of $P(C_2H_5)_3$ in 10 mL of glyme. It was then allowed to react at reflux for 37 h with 0.65 mL (0.0063 mol) of $C_6H_5CN$. The mixture was allowed to cool to room temperature and was filtered under argon, and the solvent was removed under vacuum. Several recrystallizations from an 8:1 hexane–THF solvent mixture yielded 0.367 g (26%) of large colorless crystals of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)CN$: mp 112–116 °C to a brown liquid. This is somewhat different from the literature value of 85–90 °C. IR (Nujol) 2125 cm$^{-1}$ $\nu(C{\equiv}N)$, 1568 cm$^{-1}$ $\nu(C{=}C)$ (lit. 2140 and 1580 cm$^{-1}$, respectively).[12] Anal. Calcd for $C_{19}H_{35}NP_2Pd$: C, 51.18; H, 7.91; P, 13.89. Found: C, 51.30; H, 7.88; P, 14.10.

A trace amount of colorless needlelike crystals was also obtained. IR data matched that of *trans*-$[P(C_2H_5)_3]_2Pd(CN)_2$: mp 170–171 °C (lit.[16] 174 °C).

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Cl$.** A slurry obtained by potassium reduction of *trans*-$[P(C_2H_5)_3]_2PdCl_2$ was refluxed for 17 h with 3 equiv of $C_6H_5Cl$ in glyme. The usual workup and recrystallization of the crude material from hexane afforded *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Cl$ as large colorless crystals in 54% yield: mp 98.5–99 °C (lit.[18] 101–102 °C).

In a similar reaction carried out between a palladium slurry and chlorobenzene in refluxing THF for 14 h a yield of only 10% of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Cl$ was obtained. No product was obtained from a reaction of a palladium slurry with chlorobenzene carried out at room temperature.

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)Br$.** Using the standard reaction apparatus a palladium slurry was prepared by reacting 0.530 g (0.0136 mol) of potassium with 1.22 g (0.0069 mol) of $PdCl_2$ and 2.0 mL (0.0014 mol) of $P(C_2H_5)_3$ in 25 mL of THF. The slurry was cooled to −78 °C and 1.70 g (0.0069 mol) of $C_6F_5Br$ was slowly syringed in. The mixture was allowed to warm to room temperature and worked up in the usual manner. Three recrystallizations from methanol yielded 3.08 g (76%) of white needlelike crystals of *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)Br$: mp 125–126 °C (lit.[13] 124–125 °C).

**Preparation of $P(C_2H_5)_3Pd(C_3H_5)Br$.** A palladium slurry was prepared in the usual manner from 0.233 g (0.00597 mol) of potassium and 1.238 g (0.00299 mol) of *trans*-$[P(C_2H_5)_3]_2PdCl_2$ in 10 mL of glyme. It was allowed to cool, 1.45 g (0.0120 mol) of allyl bromide was syringed in, and the mixture was stirred at 40 °C for 70 h, after which time a gray-black slurry existed in a yellow solution. The mixture was filtered, the solids were washed out with dichloromethane, and the solvent was removed from the yellow filtrate under reduced pressure. The product was extracted from the solids with benzene and evaporation of the solvent resulted in a yellow oil. The crude material was recrystallized in the usual manner from cyclohexane to yield 0.786 g (76%) of light yellow crystals of $P(C_2H_5)_3Pd(C_3H_5)Br$: mp 45–48 °C.

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)I$ from $C_6F_5PdI$ and $P(C_2H_5)_3$.** A 50-mL two-neck flask equipped with a magnetic stirrer and a condenser topped with an argon inlet was charged with 0.0412 g (0.00594 mol) of freshly cut lithium, 0.9707 g (0.002695 mol) of $PdI_2$, and 0.0293 g (0.000229 mol) of naphthalene. Glyme (10 mL) was syringed in and stirring at room temperature started. After 20 h a small piece of lithium still remained; the mixture was then stirred at 40 °C for several hours more until only a black powder in a near-colorless solution existed. To this mixture was added 0.65 mL (0.006 mol) of $C_6F_5I$ and the mixture was stirred at ca. 50 °C for 60 h, after which time a dark brown solution existed. The volatiles were removed under vacuum and the product was dissolved in 6 mL of acetone. To this stirred, brown solution was added 0.80 mL (0.0054 mol) of $P(C_2H_5)_3$ and the color immediately became yellow. After 1 min of stirring, the volatiles again were pumped off and the product was extracted with acetone from the unreacted palladium. After removal of the solvent and washing with water, the crude material was dissolved in hot hexane, treated with charcoal, and filtered. Slow evaporation of the solvent yielded yellow prisms, orange plates, and deep red clusters of needles. From the mother liquor a second crop of the former two compounds was obtained. The yield of yellow *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)I$ was 0.745 g (43%): mp 152–154 °C (lit.[13] 154–155 °C). The orange plates were identified by IR as *trans*-$[P(C_2H_5)_3]_2PdI_2$: 0.327 g (20%); mp 134–137 °C (lit.[16] 139 °C). The deep red crystals were recrystallized from acetone to yield 0.050 g (2%) and identified by IR as $[P(C_2H_5)_3]_2Pd_2I_4$: mp 187–191 °C (lit.[18] 191–192 °C).

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)I$.** A 50-mL three-neck flask equipped with a magnetic stirrer and a condenser topped with an argon inlet was charged with 1.406 g (0.00313 mol) of $PtI_2$. THF (8 mL) was syringed in followed by 0.93 mL (0.0063 mol) of $P(C_2H_5)_3$. A clean piece of potassium, 0.245 g (0.00627 mol), was added and stirring and heating were started. After 20

---

(14) S. A. Shchukarev, T. A. Tolmacheva, and Y. L. Pazukhina, *Russ. J. Inorg. Chem.*, **9**, 1354 (1964).

(15) F. R. Hartley, *Organomet. Chem. Rev. A*, **6**, 119 (1970).

(16) P. L. Goggin and R. J. Goodfellow, *J. Chem. Soc. A*, 1462 (1966).

(17) R. J. Cross and R. Wardle, *J. Chem. Soc. A*, 840 (1970).

(18) D. M. Adams and P. Chandler, *J. Chem. Soc. A*, 588 (1969).

min the reduction appeared to be complete; however it was refluxed an additional hour then allowed to cool. A black powder existed in a colorless solution. To it was added 0.35 mL (0.0031 mol) of $C_6H_5I$ and the mixture was stirred for 8 h at room temperature. It was then filtered, solids were washed out with dichloromethane, and the solvent was removed from the filtrate under reduced pressure. Repeated recrystallization from hexane, after treatment with charcoal, resulted in 1.219 g (66%) of very pale yellow crystals of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)I$: mp 120–121 °C (lit.[19] 122 °C).

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Br$.** A platinum slurry was prepared from 0.647 g (0.00243 mol) of $PtCl_2$, 0.72 mL (0.0049 mol) of $P(C_2H_5)_3$, and 0.193 g (0.00494 mol) of potassium in 8 mL of glyme. To it was added 0.52 mL (0.0049 mol) of $C_6H_5Br$ and the mixture was refluxed for 25 h. The usual workup resulted in 0.818 g (57%) of large colorless crystals of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Br$: mp 110–111 °C (lit.[20] 111.0–111.3 °C).

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Cl$.** A platinum slurry was prepared by reducing a mixture of 0.547 g (0.00206 mol) of $PtCl_2$ and 0.60 mL (0.0041 mol) of $P(C_2H_5)_3$ with 0.163 g (0.00416 mol) of potassium in 8 mL of glyme. The reduction was complete in 20 h, after which time 0.84 mL (0.0083 mol) of $C_6H_5Cl$ was syringed in and reflux was continued for 25 h more. The usual workup and recrystallization from hexane resulted in 0.567 g (51%) of colorless crystals of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Cl$: mp 104–106 °C (lit.[21] 105–107 °C).

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)CN$.** A slurry of platinum in glyme was prepared in the usual manner and then was refluxed in glyme for 25 h with a fourfold excess of $C_6H_5CN$. The usual workup and several recrystallizations from hexane resulted in a yield of 15% of *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)CN$: mp 113–119 °C (lit.[20] 127.0–128.0 °C).

**Preparation of *trans*-$[P(C_2H_5)_3]_2Pt(C_6F_5)Br$.** A slurry of platinum was prepared in the usual manner and then was allowed to react for 1 h at room temperature with 1 equiv of $C_6F_5Br$. The usual workup and recrystallization from methanol yielded small colorless needlelike crystals of *trans*-$[P(C_2H_5)_3]_2Pt(C_6F_5)Br$ in 40% yield: mp 129.5–131 °C (lit.[22] 133–134 °C).

## Discussion

**Preparation of Slurries.** Potassium metal reduction of the palladium and platinum compounds $[P(C_2H_5)_3]_2MX_2$ is readily effected in refluxing ethers such as glyme or THF to yield finely divided and highly reactive metal slurries. Equally useful are mixtures of anhydrous metal salts and triethylphosphine; these react in a matter of minutes in ethers to yield the $[P(C_2H_5)_3]_2MX_2$ compounds. Reduction times with potassium vary considerably depending on the compound being reduced; for example, solutions of $[P(C_2H_5)_3]_2PtI_2$ are reduced in about 1 h, whereas some of the others take as long as 20 h. During the early stages of reduction, small amounts of the slurries syringed onto water inflame; the absence of such behavior is assumed to indicate complete reaction of potassium. Reductions involving lithium with naphthalene are easier to judge complete, since the piece of lithium floats and is visible during reduction. Slurries resulting from $[P(C_2H_5)_3]_2MX_2$ are black and in the case of palladium exist in yellow solution which undoubtedly contains the known tris- and tetrakis(triethylphosphine) metal compounds as well as perhaps other substances. In an attempt to determine the insoluble palladium in such a slurry, the powder was separated from the soluble material by centrifugation and careful anaerobic washing of the powder. Analysis of the powder showed that 52% of the starting palladium compound existed as a black, insoluble solid. The removed yellow solution was allowed to react with bromobenzene and yielded 32% of *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Br$, based on the amount of *trans*-$[P(C_2H_5)_3]_2PdCl_2$ used. Thus the organometallic products obtained from these slurries are arising in part from the soluble material present, and in the case of the nitrile derivatives likely arise entirely from them. However, in those reactions where the yields are 60–70% or greater, it is clear that a considerable portion of the product is arising by direct reaction with the palladium metal powder.

Reduction of the phosphine metal halide complexes can also be carried out with other alkali metals. For example, *trans*-$[P(C_2H_5)_3]_2PdCl_2$ was reduced with lithium using a small amount of naphthalene as an electron carrier. However, this procedure offers no particular advantage as the reduction times, reactivity of slurries, and final yields of oxidative insertion products are very similar to the reduction procedure using potassium. It must be pointed out, however, that for the reduction of transition metal halides in the absence of phosphines, the reduction using lithium and naphthalene is far superior to reductions using potassium with regard to reactivity of the resulting metal powders.[23]

**Palladium Compounds.** Palladium slurries react with a variety of aryl halides and result in *trans*-$[P(C_2H_5)_3]_2Pd(R)X$ compounds. The trans geometry for all these compounds was established by NMR spectroscopy.[24] In general, increased temperatures during the reaction of the aryl halide with the slurry results in increased yields of the organopalladium compounds. However, in the case of iodobenzene a reaction with a palladium slurry at elevated temperature resulted in no organopalladium compound, but only biphenyl and *trans*-$[P(C_2H_5)_3]PdI_2$ as well as the ubiquitous palladium metal. This suggests that at elevated temperatures *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)I$ undergoes a reductive elimination reaction of the type observed for analogous nickel compounds.[25] The palladium compounds are stable in the solid state and in solution, although exhibiting some photodecomposition which appears to be accelerated by impurities.

The product of the reaction between allyl bromide and a palladium slurry was not $[P(C_2H_5)_3]_2Pd(C_3H_5)Br$ but $P(C_2H_5)_3Pd(C_3H_5)Br$. The former compound has been obtained in a reaction of $Pd[P(C_2H_5)_3]_3$ with a twofold excess of allyl bromide.[12] $P(C_2H_5)_3Pd(C_3H_5)Br$ was obtained by allowing a palladium slurry to react with a fourfold excess of allyl bromide. A similar effect of excess allylic halide has been noted in a reaction between $Pd[P(C_6H_5)_3]_4$ and a large excess of 2-methallyl chloride, which yielded $P(C_6H_5)_3Pd[CH_2C(CH_3)CH_2]Cl$.[26]

Reduction of $PdI_2$ with lithium in the presence of a catalytic amount of naphthalene and in the absence of triethylphosphine results in a palladium powder which reacts with $C_6F_5I$ to give a deep brown solution of $C_6F_5PdI$. This compound in acetone immediately reacted with triethylphosphine and was isolated as *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)I$ in 44% yield. The palladium slurry prepared in this manner does not react under these conditions with triethylphosphine; thus it can be ruled out that the product aries via a zerovalent triethylphosphine compound of palladium. From this same reaction mixture was isolated a 20% yield of *trans*-$[P(C_2H_5)_3]_2PdI_2$ as well as a 2% yield of $[P(C_2H_5)_3]_2Pd_2I_4$. The former compound was also obtained as a byproduct during a metal atom

---

(19) G. Booth and J. Chatt, *J. Chem. Soc. A*, 634 (1966).

(20) D. R. Coulson, *J. Am. Chem. Soc.*, **98**, 3111 (1976).

(21) J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 4020 (1959).

(22) D. T. Rosevear and F. G. A. Stone, *J. Chem. Soc.*, 5275 (1965).

(23) R. D. Rieke, A. V. Kavaliunas, L. D. Rhyne, and D. J. J. Fraser, *J. Am. Chem. Soc.*, **101**, 246 (1979).

(24) J. M. Jenkins and B. L. Shaw, *Proc. Chem. Soc., London*, 279 (1963).

(25) G. W. Parshall, *J. Am. Chem. Soc.*, **96**, 2360 (1974).

(26) J. Powell and B. L. Shaw, *J. Chem. Soc. A*, 774 (1968).

reaction of palladium with $C_6F_5I$ followed by trapping the product with triethylphosphine.[13] The analogous compound, $C_6F_5PdBr$, has also been prepared electrochemically from the metal.[27]

**Platinum Compounds.** Platinum slurries, obtained by potassium reduction of $[P(C_2H_5)_3]_2PtX_2$ in ethereal solvents, exhibit similar reactivities with aryl halides to those of palladium. The yields of products are, as in the case of palladium, varied with the highest being for the more reactive aryl halides. The compounds possess the trans geometry as determined by NMR spectroscopy[24] and in contrast to the palladium compounds exhibit no photosensitivity.

## Summary

Highly reactive slurries of palladium and platinum have been prepared by alkali metal reduction of compounds $[P(C_2H_5)_3]_2MX_2$ in ethers using simple apparatus and procedures. These metals undergo oxidative insertion into carbon–halogen bonds of aryl halides and yield compounds of the type *trans*-$[P(C_2H_5)_3]_2M(R)X$.

Metal slurries prepared in the presence of triethylphosphine contain, besides the black insoluble metal powder, compounds of the metals in low oxidation states, most likely the known tris and tetrakis phosphine metal compounds which are known to react with organic halides, and contribute to the yields of the products obtained here.

Highly reactive transition metal powders have been prepared in the absence of stabilizing ligands and the chemistry of these metals is being studied. The ability to prepare with simple apparatus metal powders which undergo oxidative insertion reactions as well as reactions with neutral ligands is of great importance not only to synthetic organic, organometallic, and inorganic chemistry but also to catalysis and surface chemistry.

**Acknowledgment.** We gratefully acknowledge support of this work by the U.S. Army Research Office. We thank Matthey Bishop, Inc., for a generous loan of platinum and palladium salts.

**Registry No.** *trans*-$[P(C_2H_5)_3]_2PdCl_2$, 15642-19-0; $C_6H_5I$, 591-50-4; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)I$, 70774-40-2; $PdBr_2$, 13444-94-5; $P(C_2H_5)_3$, 554-70-1; *trans*-$[P(C_2H_5)_3]_2PdBr_2$, 15638-55-8; $C_6H_5Br$, 108-86-1; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Br$, 52230-30-5; $PdCl_2$, 7647-10-1; $C_6H_5CN$, 100-47-0; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)CN$, 70774-41-3; *trans*-$[P(C_2H_5)_3]_2Pd(CN)_2$, 15638-57-0; $C_6H_5Cl$, 108-90-7; *trans*-$[P(C_2H_5)_3]_2Pd(C_6H_5)Cl$, 15697-59-3; $C_6F_5Br$, 344-04-7; *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)Br$, 54071-54-4; *trans*-$[P(C_2H_5)_3]_2Pd(C_3H_5)Br$, 70774-42-4; $PdI_2$, 7790-38-7; $C_6F_5I$, 827-15-6; *trans*-$[P(C_2H_5)_3]_2Pd(C_6F_5)I$, 54071-55-5; *trans*-$[P(C_2H_5)_3]_2PdI_2$, 15638-56-9; $[P(C_2H_5)_3]_2Pd_2I_4$, 22180-56-9; $PtI_2$, 7790-39-8; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)I$, 15559-63-4; $PtCl_2$, 10025-65-7; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Br$, 13964-98-2; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)Cl$, 13938-93-7; *trans*-$[P(C_2H_5)_3]_2Pt(C_6H_5)CN$, 33914-65-7; *trans*-$[P(C_2H_5)_3]_2Pt(C_6F_5)Br$, 14494-01-0; allyl bromide, 106-95-6; $[C_6F_5PdI]_n$, 70728-62-0.

---

[27] J. J. Habeeb and D. G. Tuck, *J. Organomet. Chem.*, **139**, C17 (1977).

---

# Photolysis of *N*,*N*-Diethyldiazoacetamide. Participation of a Noncarbenic Process in Intramolecular Carbon–Hydrogen Insertion[1]

Hideo Tomioka,* Hirohisa Kitagawa, and Yasuji Izawa

*Chemistry Department of Industry and Resources, Faculty of Engineering, Mie University, Tsu, Mie 514, Japan*

*Received March 23, 1979*

The mechanistic details of the photochemical process of *N*,*N*-diethyldiazoacetamide (1) have been investigated in order to elucidate the relation of intramolecular C–H insertion selectivity with the reacting state. The examination of the effects of sensitizer and quenchers on the product distributions showed that singlet carbene is involved in the formation of the $\gamma$-lactam whereas the singlet excited state of 1 is the most likely intermediate leading to the $\beta$-lactam. The nearly equal participation of the carbene and rearrangement processes in the excited state is in marked contrast with the result of diazoacetone and is interpreted in terms of the influence of the equilibrium ratio of the *Z* and *E* forms of 1. The reaction patterns of each reacting state are suggested to be affected by a conformational effect, i.e., the closest approach distance to the carbene center, for the carbene process, and an electronic one, i.e., stabilization in the transition state, for the excited 1 reaction.

There have been many reactions which demonstrate that singlet and triplet carbenes are chemically distinguishable and, hence, that some of them can be widely used as a diagnostic for the spin state of the reacting carbene.[2] Among the many studies on the establishment of the reactivity patterns in the singlet and triplet states, little has been reported on the mechanistic details of intramolecular C–H insertion selectivity. Gutsche et al.[3] have shown that the intramolecular reaction product ratio in the photolysis of (2-*n*-butylphenyl)diazomethane is the same whether the irradiation is effected directly or via photosensitization: the results are interpreted in terms of an equilibrium between the singlet and triplet species of the aryl carbene. One might easily expect that the spin multiplicity of the reacting carbene should be an important factor in controlling the intramolecular C–H insertion selectivity since both closest approach distances between the carbene center and C–H centers and the insertion mechanism (e.g., concerted or stepwise) are closely related to the electronic structure of the reacting carbene, i.e., angle, energy, and electronic properties.

In order to elucidate these problems we have examined the mechanistic details of the photodecomposition[4] of *N*,*N*-diethyldiazoacetamide leading to lactams and found that not only singlet carbene but, unexpectedly, the singlet

---

[1] Presented in part at the Symposium on Photochemistry, Kyoto, Japan, November 19–21, 1977; Abstract 1A16.

[2] For reviews, see: (a) W. Kirmse, "Carbene Chemistry", 2nd ed, Academic Press, New York, N.Y., 1971; (b) R. A. Moss and M. Jones, Jr., Ed., "Carbenes", Vol. I, Wiley, New York, N.Y., 1974; Vol. II, 1975.

[3] (a) T. A. Baer and C. D. Gutsche, *J. Am. Chem. Soc.*, **93**, 5180 (1971); (b) C. D. Gutsche, G. L. Bachman, W. Udell, and S. Bäuerlein, *ibid.*, **93**, 5172 (1971).

[4] R. Rando, *J. Am. Chem. Soc.*, **92**, 6706 (1970); **94**, 1629 (1972).

0022-3263/79/1944-3072$01.00/0