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Preparation and reactions of bis(triphenylphosphine)palladium(0)

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Abstract

The two-coordinate palladium complex, $(Ph_3P)_2Pd$, is successfully prepared by the reaction of $\{(\eta^3\text{-allyl})Pd(PPh_3)_2\}^+ PF_6^-$ with $Ph_2MeSiLi$. The complex has been characterized by IR, ^1H NMR, ^{13}C NMR, ^{31}P NMR, and UV spectroscopy. Oxidative- and coordinative-addition reactions to the two-coordinate palladium(0) complex are also described.

Introduction

Coordinatively unsaturated low valent complexes of transition metals are expected to have high and characteristic reactivities for both coordinative- and oxidative-addition reactions. A few instances of isolable coordinatively unsaturated bisphosphine complexes in a low oxidation state have been reported [1], though it is well known that tetrakisphosphine complexes with d^{10} configuration readily release ligands into the solution to give coordinatively unsaturated species. All of these isolable, coordinatively unsaturated complexes have highly bulky phosphines or isonitriles as ligands, such as $P(t\text{-}Bu)_3$ (cone angle 182°) or PCy_3 (170°), to prevent the approach of a third ligand. Eliminating the steric requirement, Fitton [2] and Osborn [3] have outlined the preparation of bis(triphenylphosphine)palladium(0), $\{(Ph_3P)_2Pd\}_n$. Negishi et al. [4] also reported recently that $(Ph_3P)_2Pd$ species could be generated by the reduction of $(Ph_3P)_2PdX_2$ (X = Cl, Br, or I) with RLi (R = alkyl, vinyl) or $i\text{-}Bu_2AlH$; however, this complex has not been isolated, and requires further characterization because no information other than the IR, and ^1H, ^{31}P NMR spectra was given.

In this paper we present a facile and effective synthesis of bis(triphenylphosphine)palladium(0), $(Ph_3P)_2Pd$, which utilizes diphenylmethylsilyllithium as reduc-

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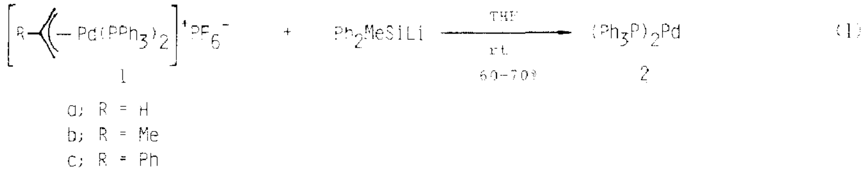
ing agent, and characteristic reactions of the coordinatively unsaturated palladium complex.

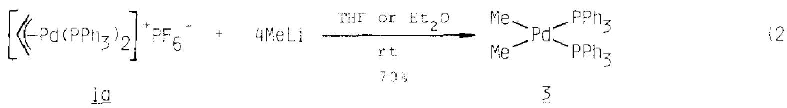
Results and discussion

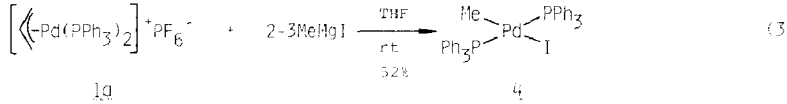
Preparation of bis(triphenylphosphine)palladium(0)

Treatment of η^3-allylbis(triphenylphosphine)palladium(II) hexafluorophosphate (**1a**) with diphenylmethylsilyllithium ($Ph_2MeSiLi$) in tetrahydrofuran at room temperature gave bis(triphenylphosphine)palladium(0) (**2**), which can be isolated as yellow powder, in good yield. Complex **2** was also obtained in similar yields when **1b** and **1c** were used as the starting materials (eq. 1).



In contrast to the results reported by Negishi et al. [4], only the silyllithium reagent was an efficient reducing agent in this reaction. Thus the reaction of **1a** with methyllithium (MeLi) at room temperature afforded *cis*-dimethylbis(triphenylphosphine)palladium(II) (**3**) [5] in 70% yield (eq. 2). When n-butyllithium or t-butyllithium was used as reducing agent, demetallation took place and no palladium complexes were obtained. Complex **1a** gives *trans*-iodomethylbis(triphenylphosphine)palladium(II) (**4**) [6] in good yield at room temperature after reaction with methylmagnesium iodide (eq. 3).





Elemental analysis of complex **2** is consistent with the formulation $\{(Ph_3P)_2Pd\}_n$. The molecular weight of **2** determined by cryoscopy in benzene solution strongly suggests that it is monomeric viz., $(Ph_3P)_2Pd$, which is consistent with the spectroscopic data, such as UV, IR, ^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra. No significant differences between the UV-Vis spectra of complex **2** and those of tetrakis(triphenylphosphine)palladium(0), $(Ph_3P)_4Pd$, were observed.

A possible structure for the product of eq. 1 is the palladium(II) complex, **5** (Fig. 1), which is formed by orthometallation. This structure, however, was excluded on the basis of the IR, ^1H, ^{13}C, and ^{31}P NMR spectra. The IR spectrum, recorded in the solid state in a KBr disk showed only those characteristic of a triphenylphosphine ligand but showed no peaks attributable to Pd–H vibration. Similarly the only signals, even at high field, in the ^1H NMR spectrum were those from the aromatic protons. The $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra clearly show that the two triphenylphosphine ligands in complex **2** are equivalent. From these results, it is

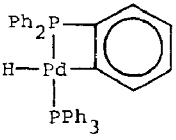


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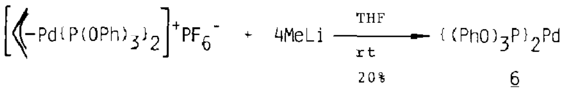
Fig. 1. A possible structure of complex 2.

concluded that complex **2** is monomeric and coordinatively unsaturated, at least in solution.

The synthesis of bis(triphenylphosphite)palladium(0), $\{(PhO)_3P\}_2Pd$ (**6**), was also examined. Treatment of η^3-allylbis(triphenylphosphite)palladium(II) hexafluorophosphate with methyllithium in tetrahydrofuran gave bis(triphenylphosphite)palladium(0) (**6**), $\{\{(PhO)_3P\}_2Pd\}_n$, in 20% yield as colorless prisms (eq. 4). This complex **6** is thermally less stable than $(Ph_3P)_2Pd$ (**2**). Elemental analysis of the complex **6** is consistent with calculated values. The ^1H, ^{13}C, and ^{31}P NMR spectra measured at low temperature under argon suggest that $\{\{(PhO)_3P\}_2Pd\}_n$ is formed. Only one singlet peak is observed at 146 ppm in $^{31}P\{^1H\}$ NMR spectrum, and this indicates that the two phosphite ligands are magnetically equivalent in solution. No reliable molecular weight data have been obtained for **6** because of its instability in solution.



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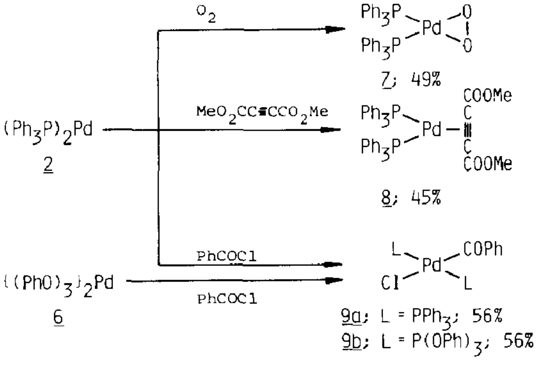
Reaction of two-coordinate palladium(0) complexes

The complexes **2** and **6** show high reactivity towards oxidative and coordinative addition reactions.

Oxidative addition of gaseous oxygen or organic halides to complexes **2** and **6** gave the corresponding oxidative adducts, such as $(Ph_3P)_2PdO_2$ (**7**) [7], $(Ph_3P)_2Pd(MeO_2CC{\equiv}CCO_2Me)$ (**8**) [8], and $(Ph_3P)_2Pd(COPh)Cl$ (**9a**) [9] (eq. 5). During the course of our studies on the oxidative addition reactions of **2**, we obtained some interesting results. The oxidative addition of methyl iodide (1 equiv.)



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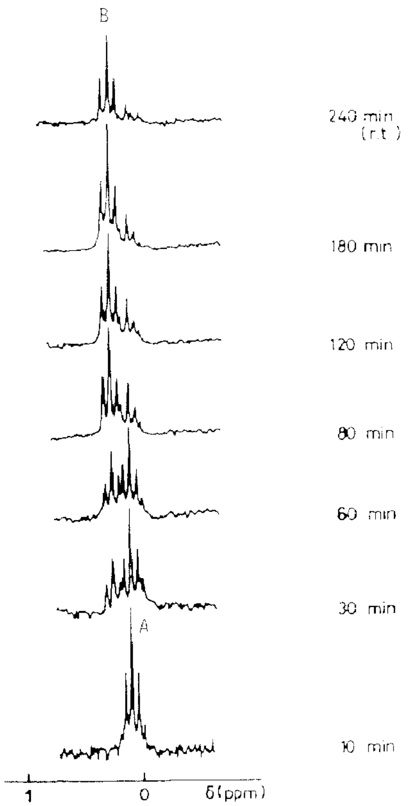

Fig. 2. ^{1}H NMR spectra of the reaction of $(Ph_3P)_2Pd$ with 1 equiv. of MeI. A: Unidentified intermediate δ 0.10 ppm; B: *trans*-**4** δ 0.27 ppm (J 5.85 Hz).

to bis(triphenylphosphine)palladium(0) (**2**) ultimately gave *trans*-iodomethylbis(triphenylphosphine)palladium(II) (**4**) via an unidentified intermediate. The presence of this intermediate was detected by ^{1}H NMR spectroscopy (Fig. 2). The ^{1}H NMR studies have revealed that the intermediate forms rapidly and is gradually converted into the *trans*-adduct (**4**). We could not fully characterize the intermediate by ^{31}P and ^{13}C NMR spectroscopy because of its rapid conversion to the *trans*-adduct during the measurement at room temperature and of its low solubility in toluene-d_8 at low temperature (< -20 °C), but it is likely that the intermediate is the *cis*-isomer of **4*** which forms via a three-centered transition state. In contrast, the reaction of $(Ph_3P)_4Pd$ or $(Ph_3P)_3Pd$ with MeI produces only the *trans*-adduct (**4**) without any intermediates being involved. It is noteworthy that $(Ph_3P)_2Pd$ reacts even with 1 equiv. of MeI with a reasonable reaction rate, whereas an equimolar amount of MeI scarcely adds to $(Ph_3P)_3Pd$ or $(Ph_3P)_4Pd$. An excess amount of organic halide must be used to achieve the desired oxidative addition to $(Ph_3P)_nPd$ ($n = 3, 4$).

The reaction of **2** with 1 equiv. or with excess amounts of triphenylphosphine gave tris(triphenylphosphine)palladium(0) (**10**) and tetrakis(triphenylphosphine)pal-

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* Recently, one of us has reported that *cis*-oxidative adducts were isolated by the oxidative addition reaction of coordinatively saturated palladium(0) complex, $(Ph_3P)_4Pd$, with 1,3-dialkyl-5-fluoro-6-iodouracils and they further isomerized completely to *trans*-ones in solution [10].

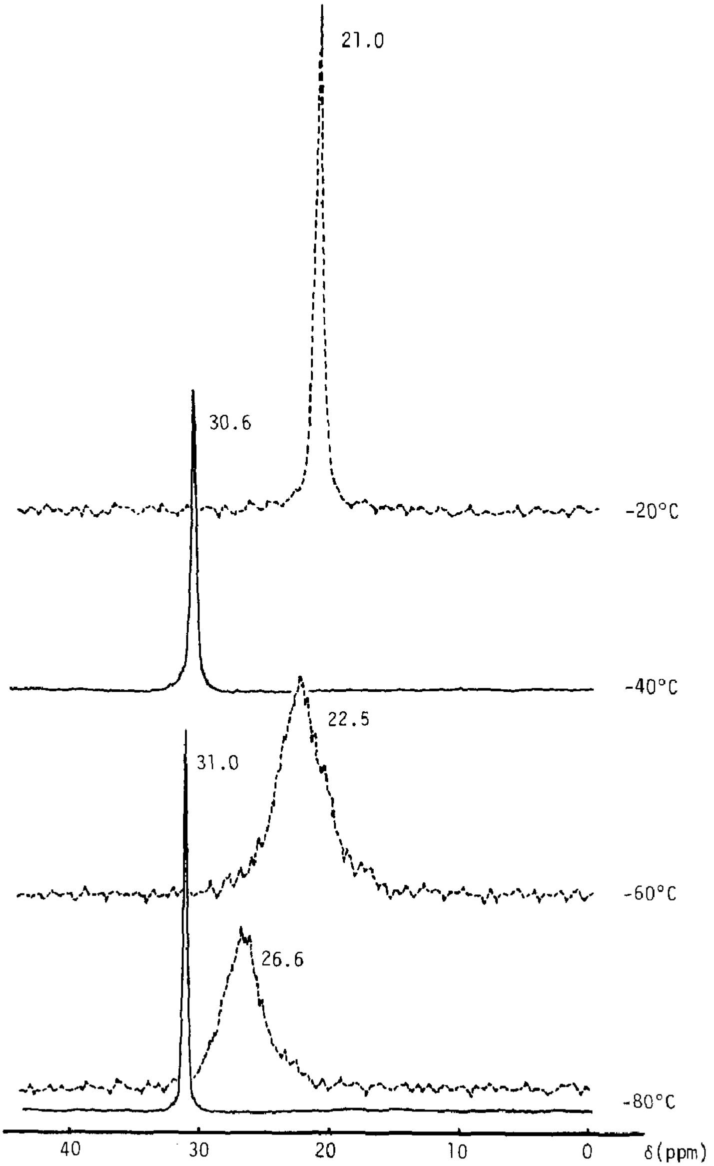


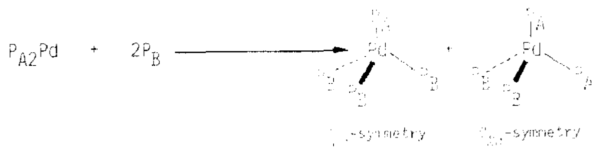
Fig. 3. Variable-temperature $^{31}P\{^1H\}$ NMR spectra of complex **2** (solid line) and $(Ph_3P)_3Pd$ (**10**) (broken line) in toluene-d_8.

ladium(0), respectively, in 40 and 78% yields. The three-coordinate palladium(0) complex (**10**) was also isolated from the reaction of complex **1** and $Ph_2MeSiLi$ in the presence of 1 equiv. of PPh_3 in 73% yield.

The variable-temperature $^{31}P\{^1H\}$ NMR spectrum of complex 2 in toluene-d_8 is shown in Fig. 3 along comparison with that of $(Ph_3P)_3Pd$ (**10**). A sharp singlet peak for **2** shows no equilibration between $(Ph_3P)_2Pd$ and $\{(Ph_3P)Pd + Ph_3P\}$ at least below -40 ° C, whereas ligand exchange (dissociation and coordination) takes place in the case of complex **10** even at -80 ° C in solution.

Coordinative-addition reactions of tertiary phosphines and tertiary phosphites to the two-coordinate palladium(0) complexes (**2** and **6**) have been described elsewhere

[11]. In summary, coordinative-addition reactions to the two-coordinate palladium(0) complexes give four-coordinate palladium(0), $P_AP_{B3}Pd$ and $P_{A2}P_{B2}Pd$ species (eq. 6). Low-temperature $^{31}P\{^1H\}$ NMR studies of these complexes indicate that the complex $P_AP_{B3}Pd$ has C_{3v}-symmetry and the other presumably has C_{2v}-symmetry.



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Experimental

Tetrahydrofuran and pentane were distilled under dry argon from benzophenone ketyl immediately before use. Acetone was distilled from potassium permanganate. Dichloromethane was distilled from phosphorus pentoxide. Ethanol was distilled from magnesium turnings and stored over 4Å molecular sieves. Cationic allylic palladium, $\{(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2\}(PF_6)$, $\{(\eta^3\text{-}CH_2CMeCH_2)Pd(PPh_3)_2\}(PF_6)$, and $\{(\eta^3\text{-}CH_2CPhCH_2)Pd(PPh_3)_2\}(PF_6)$, were prepared by a published procedure [12]. Diphenylmethylsilyllithium, $Ph_2MeSiLi$, was prepared from 1,2-dimethyl-1,1,2,2-tetraphenyldisilane by a standard method [13].

Melting points were determined on a Buchi-510 melting point apparatus in capillaries under argon and are uncorrected. Infrared spectra were recorded as KBr disks on a Hitachi 260-50 spectrometer, and were calibrated against polystyrene film. The UV-Vis spectrum was recorded on a Hitachi-624 digital spectrophotometer. ^1H and ^{13}C NMR spectra were obtained on a JNM FX-100 instrument at 99.54 and 25.00 MHz, respectively, in the solvent indicated. Chemical shifts were reported in ppm downfield from internal tetramethylsilane. ^{31}P NMR spectra were also recorded on a JNM FX-100 instrument at 40.26 MHz. Chemical shifts are positive in ppm downfield from external triphenylphosphine. All the ^{13}C and ^{31}P NMR spectra were obtained in the proton-decoupled mode.

Preparation of bis(triphenylphosphine)palladium(0), $(Ph_3P)_2Pd$ (2)

To a stirred suspension of η^3-allylbis(triphenylphosphine)palladium(II) hexafluorophosphate (**1a**), $\{(\eta^3\text{-}C_3H_5)Pd(PPh_3)_2\}(PF_6)$, (0.82 g, 1 mmol) in 15 ml of dry tetrahydrofuran was added dropwise 4 equiv. of diphenylmethylsilyllithium in tetrahydrofuran solution at room temperature under dry argon. As the lithium reagent was added, an immediate color change of the suspension from white to yellow was observed. Excess lithium reagent was decomposed after 15 min by the addition of ethanol. After the removal of solvent and volatile by-products under reduced pressure, 20 ml of dry ethanol was added to the yellow residual solid. Crude product was collected on a fine frit by filtration and was washed three times with 10 ml of dry ethanol and subsequently with two portions (10 ml) of dry pentane. Drying in vacuo gave 0.44 g (70% based on **1a**) of bis(triphenylphosphine)palladium(0) (**2**) as a yellow powder. Complex **2** was also prepared in much the same yield when $\{(\eta^3\text{-}CH_2CMeCH_2)Pd(PPh_3)_2\}(PF_6)$ (**1b**) and $\{(\eta^3\text{-}CH_2CPhCH_2)Pd(PPh_3)_2\}(PF_6)$ (**1c**) were used as the starting materials. **2**: M.p. 158–162°C (dec). Anal. Found: C, 68.48; H, 4.79. $C_{36}H_{30}P_2Pd$ calcd.: C, 68.53; H, 4.79%. MW (cryoscopy in benzene). Found: 480. $C_{36}H_{30}P_2Pd$ calcd.: 631. UV-Vis spectrum (in CH_2Cl_2, c 3.0×10^{-5} M, 25 °C: λ_{max}/nm (ϵ/M^{-1} cm^{-1}): 340 (8500), 290 (8130). IR (KBr: cm^{-1}): 3050, 1582, 1480, 1437, 1180, 1095, 1025, 740, 700, 510, and 418. ^{1}H NMR (CD_2Cl_2, −40 °C, under Ar) δ 6.67–7.84 (br) ppm. ^{13}C NMR (CD_2Cl_2, −40 °C, under Ar) δ 128,5 (C-3,4,5), 134.2 (C-2,6), and 139.3 (C-1) ppm. ^{31}P NMR (toluene-d_8, −80 °C, under Ar) δ 31.0 (s) ppm.

*Preparation of bis(triphenylphosphite)palladium(0), $\{(PhO)_3P\}_2Pd$ (**6**)*

To the colorless solution of η^3-allylbis(triphenylphosphite)palladium(II) hexafluorophosphate, $\{(\eta^3\text{-}C_3H_5)Pd\{P(OPh)_3\}_2\}(PF_6)$ (1.83 g, 2.00 mmol) in THF (15 ml) was added dropwise 4 equiv. of methyllithium in Et_2O solution (1.18 M, 6.80 ml) at room temperature under Ar. As the lithium reagent was added, a yellow color developed. Excess lithium reagent was decomposed after 30 min by the addition of dry ethanol (2 ml) (20% of propylene was detected by GLC analysis). After removal of the solvent and volatile by-products under reduced pressure, 10 ml of dry ethanol was added to the yellow residual oil and cooled to −78 °C. White precipitates were separated from solvent by a bridge filter. The white solid was first washed twice with 10 ml of dry ethanol, and then with two portions of dry pentane at −78 °C and was dried in vacuo. Recrystallization of the crude white solid from acetone at −30 °C gave bis(triphenylphosphite)palladium(0) (**6**) (0.29 g) in 20% yield as colorless prisms.

6: M.p. 128 °C (dec). Anal. Found: C, 59.36; H, 4.12. $C_{36}H_{30}O_6P_2Pd$ calcd.: C, 59.47; H, 4.13%. IR (KBr: cm^{-1}) 3060, 3045, 1596, 1485, 1186, 1074, 1022, 870, 761, 687, 599, and 500. ^{1}H NMR ($CDCl_3$, −30 °C, under Ar) δ 6.7–7.2 ppm. ^{13}C NMR ($CDCl_3$, −30 °C, under Ar) δ 121.0 (C-3,5), 123.8 (C-4), 129.1 (C-2,6), 151.2 (C-1) ppm. ^{31}P NMR ($CDCl_3$, −30 °C, under Ar) δ 145.3 (s) ppm; (toluene-d_8, −60 °C, under Ar) δ 146.4 (s) ppm.

*Reaction of η^3-allylbis(triphenylphosphine)palladium(II) hexafluorophosphate (**1a**) with methyllithium*

To a white suspension of **1a** (0.64 g, 0.78 mmol) in THF solution (20 ml) was added dropwise 4 equiv. of methyllithium in Et_2O solution (1.08 M, 3.2 ml) at room temperature under argon. The resulting yellow solution was stirred for 1 h. After excess MeLi was decomposed by the addition of dry ethanol (74% of propylene was detected by GLC analysis), the solvent was removed under reduced pressure. EtOH (20 ml) was added to the yellow residual solid and the yellow precipitate was collected on a fine frit by filtration and was first washed twice with 10 ml of EtOH, and then with two portions of 10 ml of dry pentane. Drying in vacuo gave *cis*-dimethylbis(triphenylphosphine)palladium(II) (**3**). Recrystallization of the crude product from THF/pentane at −78 °C gave pure **3** as yellow prisms.

3: M.p. 158–160 °C. Anal. Found: C, 70.25; H, 5.44. $C_{38}H_{36}P_2Pd$ calcd.: C, 69.04; H, 5.49%. ^{1}H NMR (CD_2Cl_2): δ 0.13 (6H, q, J 3.2 Hz), 7.1–7.6 (30H, br) ppm. IR (KBr: cm^{-1}): 2948, 2870 (ν(C–H)), 1135 (δ(C–H)), and 455 (ν(Pd–C)).

*Reaction of η^3-allylbis(triphenylphosphine)palladium(II) hexafluorophosphate (**1a**) with methylmagnesium iodide*

A THF solution (15 ml) of **1a** (0.65 g, 0.79 mmol) was treated with 2 equiv. of MeMgI in Et_2O solution (0.93 M, 1.7 ml) at room temperature under Ar for 30 min gave *trans*-iodomethylbis(triphenylphosphine)palladium(II) (**4**) as yellow needles in 52% yield.

4: M.p. 158–159 °C (dec.). Anal. Found: C, 57.49; H, 4.40; I, 16.67. $C_{37}H_{33}IP_2Pd$ calcd.: C, 57.50; H, 4.30; I, 16.42%. IR (KBr: cm^{-1}): 2980 and 2910 (ν(C–H)). ^1H NMR ($CDCl_3$) δ 0.27 (3H, t, J 6.0 Hz), 7.26–7.33 (18H, m), 7.52–7.69 (12H, m) ppm. ^{13}C NMR ($CDCl_3$); δ 12.82 (t, ^2J(P–C) 31.74 Hz), 127.98 (t, ^3J(P–C) 4.88 Hz), 130.03 (s), 132.22 (t, ^1J(P–C) 22.59 Hz), 135.05 (t, ^2J(P–C) 6.1 Hz) ppm. ^{31}P NMR ($CDCl_3$) δ 36.26 (s) ppm.

Oxidative addition of O_2 to complex ***2***

A solution of **2** (0.25 g, 0.39 mmol) in benzene (15 ml) was stirred at ambient temperature under an atmospheric pressure of O_2 for 2 h. The precipitate was collected on a fine frit by filtration and was washed with benzene (5 ml) and pentane (10 ml). Drying in vacuo gave peroxobis(triphenylphosphine)palladium (**7**, 0.13 g) as a pale-blue powder in 49% yield.

7: M.p. 100 °C (dec). Anal. Found: C, 63.52; H, 4.54. $C_{36}H_{30}O_2P_2Pd$ calcd.: C, 65.22; H, 4.56%. IR (KBr: cm^{-1}): 900 (ν(O–O)).

Reaction of dimethyl acetylenedicarboxylate with complex ***2***

To a solution of dimethyl acetylenedicarboxylate (0.78 g, 5.49 mmol) in THF (10 ml) was added complex **2** (0.85 g, 1.34 mmol) at room temperature under Ar. After the mixture had been stirred for 30 min, the solvent was removed under reduced pressure. Crystallization of the residue from THF/pentane afforded the crude product. Recrystallization from CH_2Cl_2/MeOH gave $(Ph_3P)_2Pd(MeO_2CC{\equiv}CCO_2Me)$ (**8**, 0.47 g) in 45% yield as yellow prisms.

8: M.p. 148–152 °C (dec). IR (KBr: cm^{-1}) 1850 (ν(C≡C)) and 1700 (ν(C=O)). ^1H NMR ($CDCl_3$): δ 3.2 (6H, s), 7.1 (30H, bs) ppm. ^{31}P NMR ($CDCl_3$) δ36.0 (s) ppm.

Oxidative addition of benzoyl chloride to complex ***2***

To a solution of complex **2** (0.70 g, 1.1 mmol) in benzene (10 ml) was added dropwise PhCOCl (0.15 ml, 1.28 mmol) at room temperature under Ar, and the mixture was stirred for 1 h. Dry pentane (40 ml) was added to the mixture, the resulting precipitate was collected on a fine frit by filtration, and washed twice with pentane (10 ml). Drying in vacuo gave crude product. Recrystallization from CH_2Cl_2/pentane gave chlorobenzoylbis(triphenylphosphine)palladium (**9a**, 0.54 g) as yellow prisms in 56% yield.

9a: M.p. 290–292 °C (dec). Anal. Found: C, 60.70; H, 4.16; Cl, 13.93. $C_{44.1}H_{37.2}Cl_{3.2}OP_2Pd$ calcd.: C, 61.24; H, 4.34; Cl, 13.12%. IR (KBr: cm^{-1}) 1650 (ν(C=O)) and 320 (ν(Pd–Cl)). ^1H NMR ($CDCl_3$): δ 5.27 (2.2H, s, CH_2Cl_2), 6.8–7.9 (35H, br) ppm. ^{31}P NMR ($CDCl_3$): δ24.49 (s) ppm.

Oxidative addition of PhCOCl to complex ***6***

To a solution of **6** (0.17 g, 0.24 mmol) in toluene (10 ml) was added dropwise PhCOCl (0.03 ml, 0.24 mmol) at −78 °C under Ar. The reaction mixture was allowed to warm up to room temperature and was stirred for 5 h. After the solvent had been removed under reduced pressure, EtOH (10 ml) was then added. The white powder was collected on a fine frit by filtration and was washed with dry pentane. Drying in vacuo gave chlorobenzoylbis(triphenylphosphite)palladium (**9b**, 0.12 g) in 56% yield.

9b: M.p. 180 °C (dec). Anal. Found: C, 58.20; H, 3.99; Cl, 4.19. $C_{43}H_{35}ClO_7P_2Pd$ calcd.: C, 59.53; H, 4.07; Cl, 4.09%. IR (KBr: cm^{-1}) 1675 (ν(C=O)) and 310 (ν(Pd–Cl)). ^1H NMR ($CDCl_3$): δ 7.0 (35H, bs) ppm. ^{31}P NMR ($CDCl_3$) δ 107.77 (s) ppm.

Oxidative addition of MeI to complex 2

To a solution of complex **2** (0.45 g, 0.71 mmol) in benzene (5.5 ml) was added methyl iodide (0.044 ml, 0.71 mmol) at 20 °C under Ar. The resulting mixture was stirred for 80 min at 20 °C, and 40 ml of Et_2O was then added. The yellow precipitate was collected on a fine frit by filtration. Recrystallization of the yellow powder from CH_2Cl_2/pentane gave *trans*-iodomethylbis(triphenylphosphine)palladium (**4**) in 22% yield as yellow needles.

Coordinative addition of PPh_3 to $(Ph_3P)_2Pd$ (2)

To a solution of $(Ph_3P)_2Pd$ (**2**, 0.24 g, 0.38 mmol) in benzene (10 ml) was added triphenylphosphine (0.10 g, 0.38 mmol) under Ar at room temperature. The mixture was stirred for 10 min, then the solvent was concentrated to ca. 5 ml, and Et_2O was added. The yellow precipitate was collected on a fine frit by filtration and was washed twice with 10 ml of Et_2O. Drying in vacuo gave tris(triphenylphosphine)palladium(0) (**10**, 0.13 g) in 40% yield.

10: M.p. 172–175 °C (dec). Anal. Found: C, 72.30; H, 5.37. $C_{54}H_{45}P_3Pd$ calcd.: C, 72.61; H, 5.08%. ^1H NMR (C_6D_6): δ 6.7–7.63 ppm. ^{31}P NMR (toluene-d_8, under Ar) −80 °C; δ 26.6 ($w_{1/2}$ 136 Hz), −60 °C; 22.5 ($w_{1/2}$ 131 Hz), −40 °C; 21.7 ($w_{1/2}$ 53 Hz), −20 °C; 21.0 ($w_{1/2}$ 32 Hz) ppm.

In situ generation of $(Ph_3P)_3Pd$ (10)

To the white suspension of **1a** (0.63 g, 0.76 mmol) and PPh_3 (0.20 g, 076 mmol) in THF solution (20 ml) was added dropwise 4 equiv. of $Ph_2MeSiLi$ in THF solution (1.18 *M*, 2.0 ml) at room temperature under Ar. Excess silyllithium was decomposed after 15 min by the addition of EtOH (2 ml). The solvent and volatile by-products were removed and 20 ml of EtOH was added to the yellow residual solid. The yellow solid was collected on a fine frit by filtration and was washed with EtOH, Et_2O, and pentane. Drying in vacuo gave $(Ph_3P)_3Pd$ (**10**, 0.50 g) in 73% yield.

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