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PREPARATION OF PHOSPHONIUM SALT TYPE YLIDE PALLADIUM COMPLEXES CONTAINING CYCLIC DIOLEFIN LIGANDS

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Summary

The dimeric η^1-ylide palladium complex, $[\{PhMe_2P^+—CH(SiMe_3)\}Cl_2Pd^-]_2$ (I), prepared in 94% yield from $(PhCN)_2PdCl_2$ and $PhMe_2P{=}CHSiMe_3$, is converted to a new η^1-ylide cyclic diolefin complex; $[\{PhMe_2P^+—CH(SiMe_3)\}Cl(diolefin)Pd]\cdot(PF_6)^-$ (IIa, IIb), by the abstraction of the chloride anion of I with silver hexafluorophosphate in the presence of 1,5-cyclooctadiene or norbornadiene. Complexes IIa and IIb have a neutral palladium(II) moiety and are regarded as palladium(II)-substituted phosphonium salts.

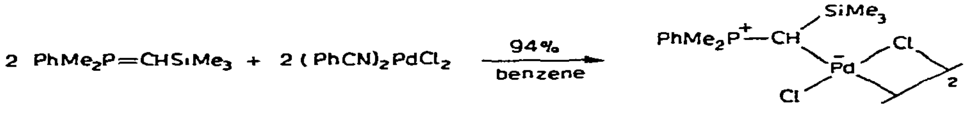
Introduction

The chemistry of transition metal ylide complexes has been actively investigated in recent years [1]. The most common hypothesis of ylide coordination to the transition metal moiety is the formation of a σ-bond with the transition metal atom, resulting in a zwitterionic phosphonium metallate structure in which the transition metal possesses a negative formal charge. There are, however, a few examples of ylide transition metal complexes which have zero formal charge on the metal atom. In this context, Kaska and coworkers reported a η^2-ylide coordination of the particular ylide $Ph_3P{=}C{=}PPh_3$ to zerovalent platinum [2], and Green noted the formation of a tungsten-substituted phosphonium salt by the unusual reaction of tertiary phosphine and a hydridocarbene complex generated as the intermediate [3].

We now report that an α-trimethylsilylphosphonium ylide palladium complex on treatment with silver hexafluorophosphate in the presence of the suitable cyclic diolefin, gives new palladium substituted phosphonium salts in which both ylide and cyclic diolefin are involved as ligands.

Results and discussion

The zwitterionic and dimeric ylide complex, $[\{PhMe_2P^+{-}CH(SiMe_3)\}Cl_2Pd^-]_2$ (I), was prepared in 94% yield by treating dichlorobis(benzonitrile)palladium(II) with a slight excess of $PhMe_2P{=}CHSiMe_3$ [4] in benzene at room temperature.



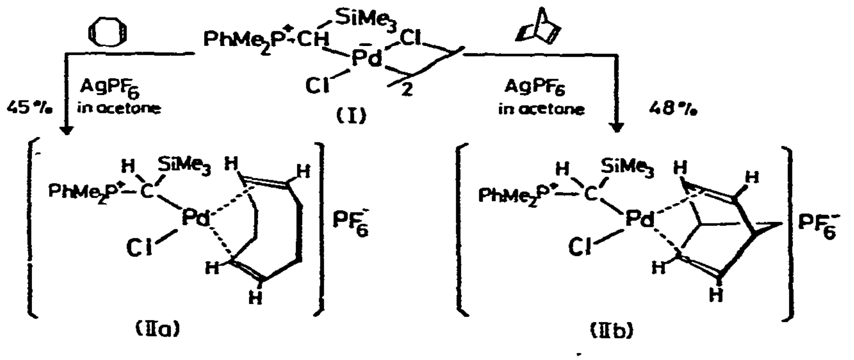
(I)

The ^1H NMR spectrum of I showed proton signals at δ 0.11 (CH_3—Si); 2.55 and 2.88 (doublets, two CH_3—P groups), and at 2.22 ppm (a doublet CH, J(P—H) 12 Hz). The separation of the methyl phosphine signals indicates strongly the presence of a neighboring asymmetric carbon atom, the generation of which from the ylidic carbon atom definitely suggests the formation of a σ-bond between the ylidic center and the palladium atom. The solid state infrared spectrum of I showed both terminal (313 cm^{-1}) and bridging (275 and 240 cm^{-1}) ν(Pd—Cl) frequencies in a similar pattern to the analogous dimeric η^1-ylide palladium complexes reported previously [5], indicative of the dimeric structure of I.

In order to decrease the formal charge of the palladium atom from −1 to zero, namely, to turn the zwitterionic complex into a palladium(II)-substituted phosphonium salt, two chloride anions of the dimeric η^1-ylide complex I should be abstacted by an appropriate cation (e.g. Ag^+) in the presence of a bidentate ligand which can occupy the two coordinative unsaturations thus generated. It was concluded from a number of preliminary experiments that the most suitable supporting ligand was a cyclic diolefin, such as 1,5-cyclooctadiene (COD) or norbornadiene (NBD), and that silver hexafluorophosphate was the best reagent to abstract chloride anions from I.

When an acetone solution of the precursor complex I was treated with silver hexafluorophosphate in the presence of COD, the new palladium-substituted phosphonium hexafluorophosphate of composition $[\{PhMe_2P^+{-}CH(SiMe_3)\}Cl(COD)Pd](PF_6)^-$ (IIa) was obtained in 45% yield. A conductivity measurement of IIa gave a value assignable to an 1 : 1 electrolyte.

The ^1H NMR spectra of IIa in acetone-d_6 for a lower chemical shift region and in methylene chloride for a higher region are shown in Fig. 1. Three kinds of



olefinic proton signals due to the COD ligand appeared in 2 : 1 : 1 intensities at δ 5.90, 5.51, and 5.09 ppm, respectively. The CH_3—P signals of the ylide ligand were observed as two equal-intensity doublets at δ 2.12 and 2.42 ppm. The separation of one kind of olefinic signals and the phosphine methyl protons is explained reasonably in terms of the asymmetric carbon atom of the η^1-ylide ligand which formed a σ-bond to the neutral palladium atom. The two higher field multiplets of the COD ligand (H_b in Fig. 1 at δ 5.51 and 5.09 ppm) may be assigned to two olefinic protons attached to the double bond located *cis* to the asymmetric carbon atom. The influence of the asymmetric carbon atom is too remote to induce a separation of two olefinic protons attached to the double bond located *trans* to the η^1-ylide ligand (H_a in Fig. 1). The appearance of two H_b proton signals (*trans* to chloro ligand) at higher chemical shifts than the H_a protons (*trans* to the η^1-ylide ligand) suggests that the η^1-ylide ligand exhibits a stronger *trans*-influence than the chloro ligand. The solid state infrared spectrum of IIa was also consistent with the proposed structure based on the appearance of the Pd—Cl, CH_3—Si, and P—F frequencies at 279, 1249, and 843 cm^{-1}, respectively. An X-ray structure determination of IIa was recently completed by Pierpont [6], and the depicted structure and the above discussion is unambiguously supported.

An analogous norbornadiene ylide palladium(II) complex, [{$PhMe_2P^+$—CH-($SiMe_3$)}Cl(NBD)Pd]$(PF_6)^-$ (IIb), was prepared in 48% yield from I, silver hexafluorophosphate, and NBD in acetone. Elemental analysis, conductivity and osmomeric molecular weight measurement, as well as the infrared spectrum of IIb were consistent with the depicted structure which was also that of a palladium(II)-substituted phosphonium salt. The ^{1}H NMR spectrum of IIb in acetone-d_6 showed olefinic signals at δ 6.24 (2H), 6.29 (1H), and 5.42 ppm (1H) as well as two bridgehead protons at δ 4.18 and 3.69 ppm (each 1H) for the requisite NBD

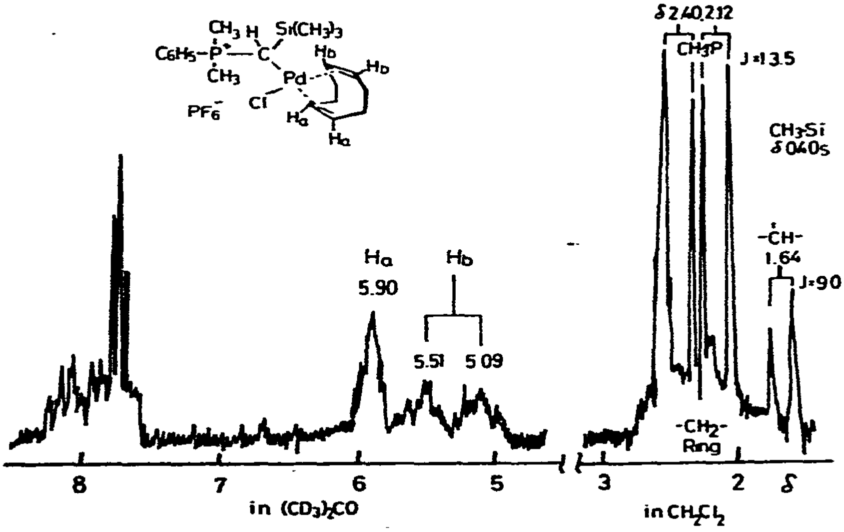


Fig. 1. ^{1}H NMR spectra of [{$PhMe_2P^+$—$CH(SiMe_3)$}Cl(COD)Pd](PF_6) (IIa).

ligand. The separation of the latter two kinds of NBD ligand and that of two phosphine methyl proton signals is ascribed to the presence of the asymmetric carbon atom in a similar manner to the COD analogue (IIa).

The abstraction of the chloride ion from the zwitterionic ylide-palladium complexes by means of silver hexafluorophosphate did not proceed cleanly for other dimeric η^1-ylide palladate dimer complexes containing an electron-withdrawing substituent [5] under similar reaction conditions, and the isolated products were the corresponding protonation products of the free ylide ligand and $(COD)PdCl_2$. The formation of the former product indicates the liberation of free ylide during the reaction. For example, the treatment of $[\{Ph_3P^+—CH(COPh)\}Cl_2Pd^-]_2$ with silver hexafluorophosphate in the presence of COD in acetone gave $(Ph_3P^+—CH_2COPh)Cl$ and $(COD)PdCl_2$, in 69 and 62% yield, respectively.

Experimental

General remarks

All the preparative procedures other than chromatographic separation were undertaken under an atmosphere of argon or nitrogen. The NMR spectra were recorded with JEOL C-60HL spectrometer. The infrared spectra and the conductivity of complexes were measured with a JASCO DS-403G spectrometer, and a TOA Electronics, CM-5B equipment, respectively.

Preparation of $[\{PhMe_2P^+—CH(SiMe_3)\}Cl_2Pd^-]_2$ (I)

A benzene (8 ml) suspension of $(PhCN)_2PdCl_2$ (286.7 mg; 0.7474 mmol) was stirred at room temperature, and $PhMe_2P{=}CHSiMe_3$ [4] (182.9 mg; 0.815 mmol) was added with a syringe. The reaction mixture was stirred for 24 h at room temperature. The orange precipitate was filtered to give the crude product in 94% yield. Recrystallization was achieved with benzene. I: m.p. 135—140°C (dec.); NMR($CDCl_3$): δ 0.11 (s, 9, CH_3—Si), 2.22 (d, 1, J 12 Hz, CH—P), 2.55 (d, 3, CH_3—P, J 13 Hz), 2.58 (d, 3, CH_3—P, J 13 Hz) 7.4—7.8 ppm (m, 5, phenyl); IR(KBr): ν(Pd—Cl) 313s, 275m, and 240m. (Found: C, 36.11; H, 5.09. $C_{12}H_{21}Cl_2PPdSi$ calcd.: C, 35.88; H, 5.27%.)

Preparation of $[\{PhMe_2P^+—CH(SiMe_3)\}Cl(COD)Pd](PF_6)^-$ (IIa)

An acetone (10 ml) solution of $AgPF_6$ (117.7 mg; 0.465 mmol) was added to an acetone (5 ml) solution of I (186.9 mg; 0.232 mmol) and COD (59.2 mg; 0.547 mmol) with stirring at room temperature. The reaction took place rapidly. After 3 h, silver chloride was filtered, and the filtrate was concentrated. The oily residue was purified by column chromatography with silica gel (Merck 7734, ϕ 10 mm × 20 mm) and methylene chloride as eluent. The elute was directly recrystallized from a methylene chloride/ethyl ether mixed solvent (2 : 1 vol.) to yield yellow plates of IIa (45% yield), m.p. 124—126°C (dec.). NMR (acetone-d_6): δ 0.40 (s, 9, CH_3—Si), 5.09 (m, 1, olefinic), 5.51 (m, 1, olefinic), 5.90 (m, 2, olefinic), 7.8—8.2 ppm (m, 5, phenyl). NMR (CH_2Cl_2): δ 1.64 (d, 1, J 9 Hz, CH—P), 2.12 and 2.42 (each d, 3, J 13.5 Hz, CH_3—P), 2.0—2.5 ppm ((br) m, 4, CH_2 of COD). IR(KBr): 1249 (CH_3—Si), 1124 (P—C), 843 (PF_6), 279 (Pd—Cl). Conductivity (acetone): 158 Ω^{-1} cm^2 mol^{-1} (2.09×10^{-3} mol/l) (Found: C, 38.93; H, 5.37. $C_{20}H_{33}ClF_6P_2PdSi$ calcd.: C, 38.78; H, 5.36%.)

Preparation of [{$PhMe_2P^+$—$CH(SiMe_3)$}$Cl(NBD)Pd](PF_6)^-$ (IIb)

An acetone (10 ml) solution of $AgPF_6$ (80.2 mg; 0.317 mmol) was added dropwise to an acetone (5 ml) solution of I (127.4 mg; 0.159 mmol) and NBD (52.0 mg; 0.571 mmol) with stirring at room temperature. Silver chloride was removed by filtration after 3 h, and the residue was chromatographed (similar conditions to those used for IIa.) The product IIb was purified further by recrystallization from a mixed solvent composed of methylene chloride and ether (2 : 1 vol.), to give pure IIb in 48% yield: m.p. 134—136°C (dec.). NMR (acetone-d_6): δ 0.33 (s, 9, CH_3—Si), 1.89 (m, 2, bridge), 2.12 and 2.34 (each, d, 3, J 13.5 Hz, CH_3—P), 3.69 and 4.18 (each m, 1, bridgehead), 5.42 (m, 1, olefinic), 6.24 (m, 1, olefinic), 6.29 (m, 2, olefinic), 7.7—8.3 ppm (m, 5, phenyl), and methine proton signal overlapped with the NBD bridge signals. IR (KBr): 1249 (CH_3—Si), 1124 (P—C), 840 (PF_6) 275 cm^{-1} (Pd—Cl). Conductivity (acetone): 162 Ω^{-1} cm^2 mol^{-1} (1.55 × 10^{-3} mol/l). Mol. wt. (osmometry in chloroform) found 613, calcd. 603. (Found: C, 37.28, H, 5.09. $C_{19}H_{29}ClF_6P_2PdSi$ calcd.: C, 37.83; H, 4.85%).

Reaction of [{Ph_3P^+—$CH(COPh)$}$Cl_2Pd^-]_2$ with $AgPF_6$ in the presence of COD

To a mixture of the title palladate complex (174.2 mg; 0.155 mmol), COD (33.4 mg; 0.310 mmol), and acetone (10 ml) was added an acetone (15 ml) solution of $AgPF_6$ (78.0 mg; 0.310 mmol), at room temperature with stirring. After 1 h at room temperature, silver chloride was filtered. The filtrate was concentrated to a brown oil which was then crystallized from methylene chloride and carefully added ethyl ether to give white plates of (Ph_3P^+—CH_2COPh)Cl (69%) and yellow crystals of (COD)$PdCl_2$ (62%) by fractional crystallization. Both products were characterized unambiguously by comparing the infrared and NMR spectra with those of authentic samples.

Similar results were obtained in the case of [{Ph_3P^+—CH(Z)}$Cl_2Pd^-]_2$, where Z = COMe and COOEt. When silver nitrate was used as a dechlorinating agent, the products were (Ph_3P^+—CH_2Z)$(NO_3)^-$ (Z = COPh, COMe, and COOEt) and (COD)$PdCl_2$.

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