Journal of Organometallic Chemistry, 165 (1979) 391—398

CATIONIC η^3-ALLYL YLIDE AND η^5-CYCLOPENTADIENYL YLIDE COMPLEXES OF PALLADIUM(II)

MITSUYO-FUKUI HIRAI, MITSUNOBU MIYASAKA, KENJI ITOH * and YOSHIO ISHII **

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464 (Japan)

(Received July 18th, 1978)

Summary

The reaction of $(R_3{}^1P^+—\overline{CH}—\overline{CR^2}—\overline{CHR^3})Pd^-Cl_2$ (I; R^1 = Ph or Et; R^2 = H or Me; R^3 = H or Me), or $(R_3{}^1P^+—\overline{CH}—\overline{CR^2}—\overline{CHR^3})_2Pd_2Cl_2(Y^-)_2$ (II; Y = PF_6^-, BF_4^-, or $CF_3SO_3^-$) with silver salts, such as silver hexafluorophosphate, tetrafluoroborate, or trifluoromethanesulfonate, in the presence of a cyclic diolefin (1,5-cyclooctadiene or bicyclo-[2,2,1]-hepta-2,5-diene) afforded cationic (1-phosphonium-η^3-allyl ylide)(diene)palladium(II) complexes. Cationic (triphenylphosphonium-η^5-cyclopentadienyl ylide)(diene)palladium(II) complexes were obtained by the reaction of (diene)$PdCl_2$ with silver tetrafluoroborate followed by an addition of triphenylphosphonium cyclopentadienyl ylide.

Introduction

Cationic allyl complexes of palladium(II), $[(\eta^3\text{-allyl})PdL_2]^+$, have long been known, and most of them involve a supporting Group V Element ligand; L = R_3P, R_3As; L_2 = bipy, diphos, etc. [1]. Cyclic diolefins were also employed as supporting ligands in several cationic η^3-allylic palladium complexes, e.g. $[Pd(\eta^3\text{-allyl})(COD)]^+$ [2,3], $\{[Pd(\eta^3\text{-allyl})]_2(COT)\}^{2+}$ [4] (COD = 1,5-cyclooctadiene; COT = cyclooctatetraene) and a series of $[Pd(\eta^3\text{-allyl})(diene)]^+$ complexes [5]. In this paper, we describe new cationic (η^3-allyl)(diolefin)palladium complexes which include phosphonium allyl ylides as a new class of η^3-allylic ligands.

We have reported an extremely facile preparation of palladate complexes, $(\eta^3\text{-}R_3^1P^+—\overline{CH}—\overline{CR^2}—\overline{CHR^3})Pd^-X_2$ (I; R^1 = Ph or Et; R^2 = H or Me; R^3 = H or Me; X = Cl or Br) [6], or dinuclear neutral palladium complexes ($\eta^3\text{-}R_3^1P^+$—

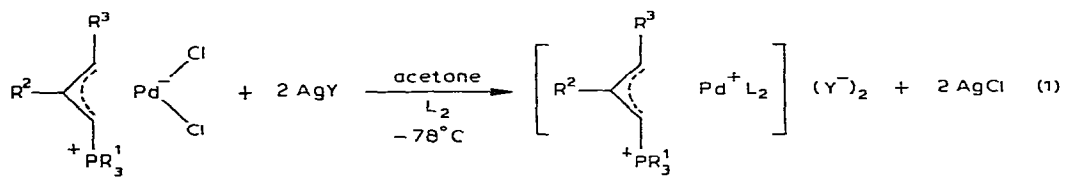
* Present address: Toyohashi University of Technology, School of Materials Science, Tenpaku-cho, Toyohashi 440, Japan.

** Present address; Chubu Institute of Technology, Department of Chemistry, Kasugai 487, Japan.

$\overline{CH—CR^2—CHR^3})_2Pd_2X_2(Y^-)_2$ (II; Y = PF_6^-, BF_4^-, $CF_3SO_3^-$), in which an allyl ylide is coordinated as an η^3-allylic ligand [7]. The latter complexes were readily accessible from I by abstraction of a halogen ligand by Ag^+. The formal charge on the palladium metal in complexes I (—1) increases to zero in II, namely, complexes II are phosphonium salt type η^3-allyl ylide complexes. This paper describes the preparation of (1-phosphonium-η^3-allyl ylide)(diene)palladium(II) complexes III. (Phosphonium-η^3-cyclopentadienyl ylide (diene)palladium(II) complexes IV are prepared in similar fashion from the corresponding (diene)-$PdCl_2$, $AgBF_4$, and triphenylphosphonium cyclopentadienyl ylide. Complexes III and IV are the first η^3-allyl ylide and η^5-cyclopentadienyl ylide cationic palladium complexes with a phosphonium salt structure.

Results and discussion

When η^3-allyl ylide palladate complexes, I, were treated with AgY (Y = PF_6^-, BF_4^-, or $CF_3SO_3^-$) in the presence of a bidentate ligand, such as L_2 = 1,5-cyclooctadiene(COD), bicyclo[2.2.1]hepta-2,5-diene(NBD), or 2,2′-bipyridine (bipy), in acetone at —78°C for 10 min, new cationic complexes, III, which have 1-phosphonium-η^3-allyl ylide and diolefin or bipy as ligands, were obtained (eq. 1) (OTf = trifluoromethanesulfonate).

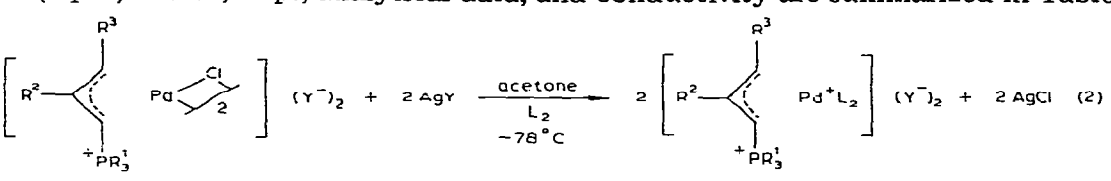


(I) (III)

Complex	R^1	R^2	R^3
Ia	Ph	H	H
Ib	Ph	Me	H
Ic	Ph	H	Me
Id	Et	H	H

Complex	R^1	R^2	R^3	Y^-	L_2	Yield (%)
IIIa	Ph	H	H	PF_6	COD	78
IIIb	Ph	H	H	BF_4	COD	59
IIIc	Ph	H	H	OTf	COD	86
IIId	Ph	Me	H	PF_6	COD	63
IIIe	Ph	H	Me	PF_6	COD	67
IIIf	Et	H	H	PF_6	COD	56
IIIg	Et	H	H	BF_4	COD	81

Cationic complexes, III, also are accessible from dinuclear palladium complexes, II (eq. 2). Color, m.p., analytical data, and conductivity are summarized in Table 1.



(II) (III)

Complex	R^1	R^2	R^3	Y^-
IIa	Ph	H	Me	PF_6
IIb	Ph	H	H	PF_6

Complex	R^1	R^2	R^3	Y^-	L_2	Yield (%)
IIIh	Ph	H	Me	PF_6	NBD	57
IIIi	Ph	H	H	PF_6	bipy	65

TABLE 1

PHYSICAL AND ANALYTICAL DATA FOR THE COMPLEXES III

Complex	Color	M.p., dec. (°C)	Anal. Found (Calcd.) (%)		Conductivity (conc.)[a] (ohm^{-1} cm^2/mol) (mol)
			C	H	
IIIa	pale yellow	174—175	42.95(43.17)	3.75(3.87)	250(6.37×10^{-4})
IIIb	pale yellow	205—212	50.44(50.44)	4.38(4.52)	
IIIc	pale yellow	150—153	45.80(45.68)	4.10(3.83	
IIId	pale yellow	175—177	43.62(43.89)	4.28(4.05)	298(4.54×10^{-4})
IIIe	pale yellow	170—173	44.16(43.89)	4.39(4.05)	273(5.52×10^{-4})
IIIf	yellow	150—152	30.97(30.81)	4.92(4.71)	
IIIg	yellow	167—172	37.42(37.37)	5.42(5.72)	
IIIh	yellow	166—168	43.42(43.28)	3.93(3.63)	
IIIi	yellow	166—174	42.66(43.36)	3.05(3.18)	

[a] In acetone at 20°C.

As a representative example, the NMR spectrum of the allylic protons of complex IIIc is illustrated in Fig. 1, together with those of the corresponding palladate and dinuclear complexes. The variable temperature NMR behavior of $[(Ph_3P^+—\overline{CH^1—CH^2—CH^3H^{3'}})PdBr]_2[PF_6^-]_2$ (V) which is a typical complex with a 1-phosphonium allyl ylide ligand has been studied [7]. The chemical shift of $H^{3,3'}$ protons of complex V was δ 4.27 ppm [d, $J(H^2—H^{3,3'})$ 9.5 Hz] at room temperature. At low temperatures, *syn*($H^{3'}$) and *anti*(H^3) protons definitely separated at δ 4.70 ppm [d, $J(H^2—H^{3'})$ 4.5 Hz] and at δ 3.89 ppm [d, $J(H^2—H^3)$

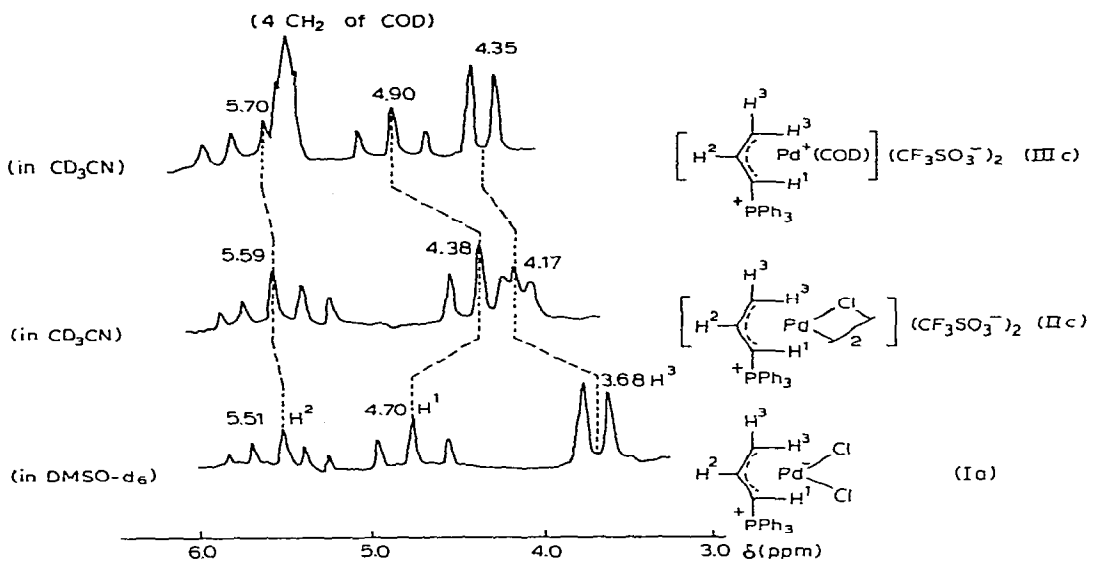
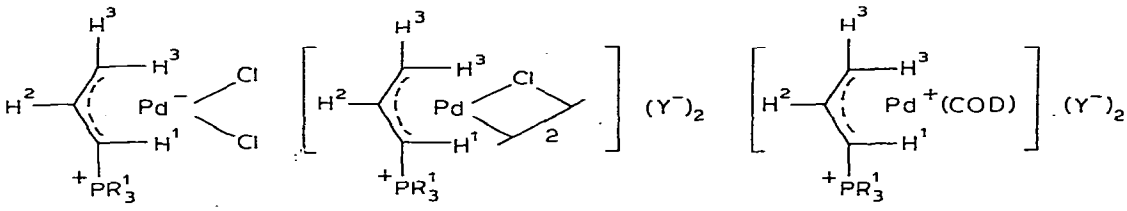


Fig. 1. The allylic proton NMR spectra of complexes Ia, IIc and IIIc. Complexes I were soluble only in DMSO or dimethylformamide, therefore the NMR spectra could not be measured in CD_3CN. All complexes III decomposed in DMSO-d_6. Consequently a comparison of the NMR spectra in the same solvent was impossible.

TABLE 2

THE CHEMICAL SHIFTS OF ALLYLIC PROTONS IN ATE, NEUTRAL, AND CATIONIC COMPLEXES OF PALLADIUM(II)



(I) [a] (II) [b] (III)

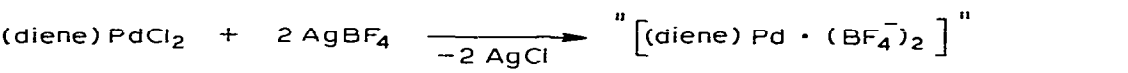
Complex	R^1	Y^-	Formal charge	H^1 ($\Delta\delta H^1$) [c] (ppm)	H^2 ($\Delta\delta H^2$) [c] (ppm)	H^3 ($\Delta\delta H^3$) [c] (ppm)	Solvent
Ia	Ph		−1	4.70	5.51	3.68	DMSO-d_6
IId	Ph	BF_4	0	4.32(−0.38)	5.58(+0.07)	4.13(+0.45)	CD_3CN
IIIb	Ph	BF_4	+1	4.82(+0.12)	5.85(+0.34)	4.36(+0.68)	CD_3CN
IIc	Ph	OTf	0	4.38(−0.32)	5.59(+0.08)	4.17(+0.49)	CD_3CN
IIIc	Ph	OTf	+1	4.90(+0.20)	5.70(+0.19)	4.35(+0.67)	CD_3CN
Id	Et		−1	3.55	5.90	3.67	DMSO-d_6
IIe	Et	BF_4	0	3.32(−0.23)	5.84(−0.06)	4.17(−0.50)	CD_3CN
IIIf	Et	BF_4	+1	3.90(+0.35)	6.15(+0.25)	4.28(+0.61)	CD_3CN

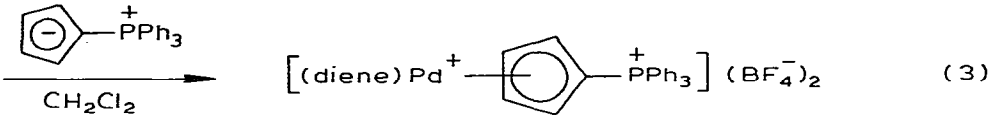
[a] From ref. [6]. [b] From ref. [7]. [c] $\Delta\delta$ is the chemical shift difference from the corresponding ate complex and the positive sign indicates the deshielding effect.

12.0 Hz] (coalescence temperature was 3°C). This is a strong evidence that the 1-phosphonium allyl ylide ligand is coordinated as a dynamic η^3-bonded structure.

In Table 2, chemical shifts of allylic protons are shown in accordance with the formal charge on the palladium atom in typical complexes (−1 → 0 → +1). With respect to the complexes Ia, IIc, and IIIc, the H^2 and H^3 protons are deshielded in the order of an increase of the formal charge (H^2; δ 5.51 → 5.59 → 5.70 ppm and H^3; δ 3.68 → 4.17 → 4.35 ppm). These results definitely suggest that the chemical shift of the H^3 protons is largely influenced by the formal charge variation and that the remote H^2 proton is less affected. In the charge variation from palladate to neutral complexes the H^1 proton is affected by both the phosphonium charge variation and that of the palladium atom, but on going from neutral to cationic complexes, the H^1 proton shows the same tendency as H^3.

Preparation of cationic phosphonium-η^5-cyclopentadienyl ylide complexes is effected by treating the triphenylphosphonium cyclopentadienyl ylide with a coordinatively unsaturated cationic diene—palladium intermediate generated in situ from dichloro(diene)palladium and two molar equivalents of silver tetrafluoroborate (eq. 3).





(3)

(IV, a diene = COD ;
b diene = NBD)

The COD complex IVa was obtained in 53% yield as rose-violet needles which included one mole of dichloromethane of solvation. The NBD complex IVb was synthesized in 64% yield and isolated as a powder. Both complexes are very stable in air and slightly soluble in acetone, benzene, diethyl ether, or less polar solvents. The conductivity of IVa and IVb in dimethylformamide is 172 ohm^{-1}-cm^2/mol (4.39 × 10^{-4} mol) and 170 $ohm^{-1}cm^2$/mol (3.09 × 10^{-4} mol), respectively. These conductivities are smaller than those of cationic 1-phosphonium-η^3-allyl salt type ylide complexes IIIa, IIId, and IIIe. This can be explained in terms of a solvent effect, since the conductivity measurements of IIIa, IIId, and IIIe were performed in the less polar acetone. In polar solvents, the conductivity value of cationic complexes tends toward smaller values than in less polar solvents [8]. This is also supported by an example of the ylide complex [$PhMe_2P^+$—$CH(SiMe_3)PdCl(1,5\text{-}COD)$]($PF_6^-$) which is a one-to-one electrolyte. Its conductivity in acetone (158 $ohm^{-1}cm^2$/mol) was smaller (69.7 $ohm^{-1}cm^2$/mol) in dimethylformamide [9]. Accordingly, the conductivities of IVa and IVb are reasonable for a two-to-two electrolyte.

The chemical shift difference between two pairs of protons at the phosphonium cyclopentadienyl ring is small (in complex IVa, 0.22 ppm and in IVb, zero) [10]. The cyclopentadienyl ylide is coordinated as an η^5-ligand in complexes IVa and IVb to fulfill a stable 18 electron structure.

Experimental

General remarks

IR spectra were measured on a JASCO Model DS-403G spectrometer on KBr disks in air. NMR spectra were recorded on a JEOL C-60HL spectrometer with tetramethylsilane as an internal standard at 25° C. The conductivity was measured with TOA Electronics CM-5B equipment. Dichloromethane was purified by washing with water and sodium carbonate solution, drying over calcium chloride, and fractionally distilling. Diethyl ether was dried with sodium after repeated washing with water. Acetone was dried with Drierite after distillation.

In order to illustrate the synthesis of complexes III, the preparation of IIIa is described as a representative example, and reaction conditions, detailed NMR spectra, and characteristic IR spectra are shown for others. Except for the isolation procedure of triethylphosphonium allyl ylide complexes, all operations are performed under dry, oxygen free nitrogen. Color, analytical data, and m.p. of IIIa—IIIi are summarized in Table 1.

Preparation of (1-triphenylphosphonium-η^3-allyl)(1,5-cyclooctadiene)palladium bis(hexafluorophosphate) (IIIa)

To an acetone (20 ml) suspension of (η^3-allyl ylide)dichloropalladate (Ia [6];

220 mg, 0.45 mmol) and 1,5-cyclooctadiene (0.2 g, 1.8 mmol) was added an acetone (10 ml) solution of $AgPF_6$ (233 mg, 0.92 mmol) at −78° C under nitrogen. The reaction occurred instantaneously, giving a pale yellow solution of IIIa and a gray precipitate of silver chloride. The mixture was stirred at room temperature for 10 min, and filtered quickly through a No. 5C filter paper under nitrogen. The filtrate was evaporated under reduced pressure. The product was recrystallized from acetone or dichloromethane by adding diethyl ether and was isolated in 57% yield. IR (KBr): 836 (νPF_6^-) and 1557 cm^{-1} ($\nu C{=}C$). NMR (in DMSO-d_6): δ 4.51 (m, 1, H^1), 5.73 (m, 1, H^2), 4.50 (m, 2, H^3), 5.48 (m, 4, olefinic), 2.31 (br, m, 4 CH_2 of COD), and 7.5—8.0 ppm (m, 15, Ph).

Preparation of (1-triphenylphosphonium-η^3-allyl)(1,5-cyclooctadiene)palladium bis(tetrafluoroborate) (IIIb)

Complex IIIb was prepared with $(Ph_3P^+\text{-}\overline{CH—CH—CH_2})Pd^-Cl_2$ (Ia [6]; 706 mg, 1.5 mmol), 1.5-COD (0.27 mg, 2.5 mmol), $AgBF_4 \cdot H_2O$ (626 mg, 2.9 mmol) and acetone (50 ml) at −78° C in the same manner to IIIa in 59% yield. IR(KBr): 1050 (νBF_4^-) and 1557 cm^{-1} ($\nu C{=}C$). NMR (in CD_3CN): δ 4.82 (d of d, 1, H^1) [$J(H^1—H^2) = J(H^1—P) = 12.0$ Hz], 5.85 (m, 1, H^2), 4.36 (d, 2, H^3) [$J(H^2—H^3) = 9.3$ Hz], 5.55 (m, 4, olefinic), 2.34 (br, m, 4 CH_2 of COD) and 7.6—8.1 ppm (m, 15, Ph).

Preparation of (1-triphenylphosphonium-η^3-allyl)(1,5-cyclooctadiene)palladium bis(trifluoromethanesulfonate) (IIIc)

The preparation was performed with $(Ph_3P^+—\overline{CH—CH—CH_2})Pd^-Cl_2$ (Ia [6]; 214 mg, 0.45 mmol), 1,5-COD (0.2 g, 1.8 mmol), $AgSO_3CF_3$ (230 mg, 0.90 mmol) and acetone (30 ml) at −78° C for 10 min in 86% yield. IR(KBr): 1265 ($\nu CF_3SO_3^-$) and 1554 cm^{-1} ($\nu C{=}C$). NMR (in CD_3CN): δ 4.90 (d of d, 1, H^1) [$J(H^1—H^2) = J(H^1—P) = 12.0$ Hz], 5.60 (m, 1, H^2), 4.35 (d, 2, H^3) [$J(H^2—H^3) = 9.3$ Hz], 5.51 (br, m, 4, olefinic), 2.33 (m, 4 CH_2 of COD) and 7.5—8.0 ppm (m, 15, Ph).

Preparation of (1-triphenylphosphonium-η^3-methallyl)(1,5-cyclooctadiene)-palladium bis(hexafluorophosphate) (IIId)

A similar procedure to IIIa with $[Ph_3P^+—\overline{CH—C(Me)—CH_2}]Pd^-Cl_2$ (Ib [6]; 178 mg, 0.37 mmol), 1,5-COD (0.2 g, 1.8 mmol), $AgPF_6$ (190 mg, 0.75 mmol) and acetone (30 ml) at −78° C for 10 min gave IIId in 63% yield. IR (KBr): 835 (νPF_6^-) and 1555 cm^{-1} ($\nu C{=}C$). NMR (in DMSO-d_6): δ 4.72 (d, 1, H^1) [$J(H^1—P) = 12.0$ Hz], 3.88 (m, 2, H^3), 1.81 (s, 3, CH_3), 5.42 (br, m, 4, olefinic), 2.23 (m, 4 CH_2 of COD) and 7.4—7.9 ppm (m, 15, Ph).

Preparation of (1-triphenylphosphonium-η^3-crotyl)(1,5-cyclooctadiene)-palladium bis(hexafluorophosphate) (IIIe)

Complex IIIe was prepared with $[Ph_3P^+—\overline{CH—CH—C(Me)H}]Pd^-Cl_2$ (Ic [6]; 127 mg, 0.27 mmol), 1,5-COD (0.1 g, 0.93 mmol), $AgPF_6$ (133 mg, 0.53 mmol) and acetone (20 ml) at −78° C for 10 min in 67% yield. IR(KBr): 835 cm^{-1} (νPF_6^-). NMR (in DMSO-d_6): δ 4.40 (m, 2, H^1 and H^3), 5.83 (m, 1, H^2), 1.23 (d, 3, CH_3) [$J(H^3—CH_3) = 6.0$ Hz], 5.53 (br, m, 4, olefinic), 2.30 (m, 4 CH_2 of COD) and 7.6—8.1 ppm (m, 15, Ph).

Preparation of (1-triethylphosphonium-η^3-allyl)(1,5-cyclooctadiene)palladium bis(hexafluorophosphate) (IIIf)

Complex IIIf was synthesized in an analogous procedure to IIIa with (Et_3P^+—CH—CH—CH_2)Pd^-Cl_2 (Id [6]; 145 mg, 0.43 mmol), 1,5-COD (0.2 g, 1.8 mmol), $AgPF_6$ (216 mg, 0.85 mmol) and acetone (20 ml) at —78°C for 10 min in 56% yield. IR(KBr): 836 (νPF_6^-) and 1557 cm^{-1} ($\nu C{=}C$). NMR (in acetone-d_6): δ 4.80 (m, 1, H^1), 6.50 (m, 1, H^2), 4.82 (d, 2, H^3) [$J(H^2—H^3)$ = 10.0 Hz], 6.57 (br, m, 4, olefinic), 2.68 (m, 4 CH_2 of COD), 2.58 (d of q, 6, P—CH_2) [$J(CH_2—CH_3)$ = 7.0 Hz, $J(CH_2—P)$ = 12.0 Hz] and 1.43 ppm (d of t, 9, P—C—CH_3) [$J(CH_3—P)$ = 18.6 Hz].

Preparation of (1-triethylphosphonium-η^3-allyl)(1,5-cyclooctadiene)palladium bis(tetrafluoroborate) (IIIg)

The preparative reaction was undertaken with (Et_3P^+—CH—CH—CH_2)Pd^-Cl_2 (Id [6]; 466 mg, 1.4 mmol), 1,5-COD (0.3 g, 2.8 mmol), $AgBF_4 \cdot H_2O$ (579 mg, 2.7 mmol), and acetone (50 ml) at —78°C for 10 min in 87% yield. IR(KBr): 1055 (νBF_4^-) and 1557 cm^{-1} ($\nu C{=}C$). NMR (in CD_3CN): δ 3.90 (d of d, 1, H^1) [$J(H^1—H^2) = J(H^1—P)$ = 12.0 Hz], 6.15 (m, 1, H^2), 4.28 (d, 2, H^3) [$J(H^2—H^3)$ = 9.4 Hz], 5.60 (br, m, 4, olefinic), 2.38 (m, 4 CH_2 of COD), 2.27 (d of q, 6, P—CH_3) [$J(CH_2—CH_3)$ = 6.7 Hz, $J(CH_2—P)$ = 13.5 Hz] and 1.29 ppm (d of t, 9, P—C—CH_3) [$J(CH_3—P)$ = 19.5 Hz].

Preparation of (1-triphenylphosphonium-η^3-crotyl)(bicyclo[2.2.1]hepta-2,5-diene)palladium bis(hexafluorophosphate) (IIIh)

Complex IIIh was prepared in accordance with eq. 2 with [Ph_3P^+—CH—CH—C(Me)H]$_2Pd_2Cl_2(PF_6^-)_2$ (IIa [7]; 138 mg, 0.12 mmol), NBD (69 mg, 0.4 mmol), $AgPF_6$ (57 mg, 0.22 mmol) and acetone (20 ml) at —78°C for 10 min. After the reaction was complete, the reaction mixture was treated in the same manner as IIIa in 57% yield. IR (KBr): 837 cm^{-1} (νPF_6^-). NMR (in acetone-d_6): δ 1.10 (d, 3, CH_3) [$J(CH_3—H^3)$ = 6.0 Hz], 3.0—5.0 (m, H^1, H^2, H^3, and bridgehead of NBD), 6.55 (m, 4, olefinic), 1.75 (m, 2, bridge of NBD) and 7.4—7.8 ppm (m, 15, Ph).

Preparation of (1-triphenylphosphonium-η^3-allyl)(2,2'-bipyridine)palladium bis(hexafluorophosphate) (IIIi)

Complex IIIi was prepared by the same method as IIIh with Ph_3P^+—CH—CH—CH_2)$_2Pd_2Cl_2(PF_6^-)_2$ (IIb [7]; 780 mg, 0.66 mmol), bipy (220 mg, 1.4 mmol), $AgPF_6$ (333 mg, 1.31 mmol) and acetone (50 ml) at —78°C for 10 min in 65% yield. IR(KBr): 836 (νPF_6^-). NMR (DMSO-d_6): δ 5.27 (d of d, 1, H^1) [$J(H^1—H^2) = J(H^1—P)$ = 12.0 Hz], 6.35 (m, 1, H^2), 4.82 (d, 2, H^3) [$J(H^3—H^2)$ = 9.7 Hz], 7.5—8.8 (m, 8, bipy ring) and 7.6—8.1 ppm (m, 15, Ph).

Preparation of (triphenylphosphonium-η^5-cyclopentadienyl)(1,5-cyclooctadiene)palladium bis(tetrafluoroborate) (IVa)

To a dichloromethane (20 ml) solution of (1,5-COD)$PdCl_2$ (325 mg, 0.83 mmol) was added a THF (5 ml) solution of $AgBF_4 \cdot H_2O$ (351 mg, 1.65 mmol) at —78°C under nitrogen. After the yellow-colored solution had changed to a milky suspension, a dichloromethane (10 ml) solution of triphenylphosphonium cyclopentadienyl ylide [11] (270 mg, 0.83 mmol) was added. After it

had been stirred for 10 min at room temperature, the reaction mixture was filtered with No. 5C filter paper and a red solution of IVa was obtained. The solution was evaporated in vacuo, and the residue was recrystallized from dichloromethane and diethyl ether to give rose-violet needles of IVa in 53% yield. IR(KBr): 1064 (νBF_4^-) and 1514 cm^{-1} ($\nu C{=}C$). NMR (in acetone-d_6): δ 6.10 (br, m, 4, olefinic), 1.67 (m, 4 CH_2 of COD), 7.18 (m, 2, a pair of cyclopentadienyl ring protons), 6.92 (m, 2, a pair of cyclopentadienyl ring protons), and 7.6—8.3 ppm (m, 15, Ph). Anal.: Found: C, 48.49; H, 3.98. $C_{31}H_{31}B_2F_8PPd \cdot CH_2Cl_2$ calcd.: C, 48.07; H, 4.16%. Conductivity: 172 ohm^{-1} cm^2/mol (4.39 × 10^{-4} mol in dimethylformamide).

Preparation of (triphenylphosphonium-η^5-cyclopentadienyl)(bicyclo[2.2.1]-hepta-2,5-diene)palladium bis(tetrafluoroborate) (IVb)

To a THF (30 ml) suspension of (NBD)$PdCl_2$ (145 mg, 0.54 mmol) was added $AgBF_4 \cdot H_2O$ (230 mg, 1.08 mmol) and triphenylphosphinium cyclopentadienyl ylide (177 mg, 0.54 mmol) under nitrogen at room temperature, and the mixture was stirred for 30 min. The color of the suspension changed from yellow to wine red. The mixture was filtered with No. 5C filter paper and the residue was washed with a large volume of dichloromethane until the mother liquor was colorless. The solution was evaporated under reduced pressure. The product was recrystallized from dichloromethane and diethyl ether to give powder in 64% yield. IR(KBr): 1058 cm^{-1} (νBF_4^-). NMR (in acetone-d_6): δ 5.87 (m, 4, olefinic), 3.95 (br, m, 2, bridgehead of NBD), 1.67 (m, 2, bridge of NBD), 6.75—7.05 (m, 4, cyclopentadienyl ring) and 7.6—8.2 ppm (m, 15, Ph). Anal.: Found: C, 51.56; H, 4.06. $C_{30}H_{27}B_2F_8PPd$ calcd.: C, 51.58; H, 3.90%. Conductivity: 179 ohm^{-1} cm^2/mol (3.09 × 10^{-4} mol in dimethylformamide).

References

1 (a) See, e.g., G. Paiaro and A. Musco, Tetrahedron Lett., (1965) 1583; (b) J. Powell and B.L. Shaw, J. Chem. Soc., A, (1968) 774; (c) R.R. Stevens and G.D. Shier, J. Organometal. Chem., 21 (1970) 774; (d) Y. Takahashi, S. Sakai and Y. Ishii, Inorg. Chem., 11 (1972) 1516; (e) D.J. Mabbott and P.M. Maitlis, J. Chem. Soc. Dalton, (1976) 2156.

2 R.R. Schrock and J.A. Osborn, J. Amer. Chem. Soc., 93 (1971) 3089.

3 D.A. White, Inorg. Syn., 13 (1972) 61.

4 B.F.G. Johnson, J. Lewis and D.A. White, J. Chem. Soc., A, (1970) 1738.

5 D.J. Mabbott, B.E. Mann and P.M. Maitlis, J. Chem. Soc. Dalton, (1977) 294.

6 K. Itoh, H. Nishiyama, T. Ohnishi and Y. Ishii, J. Organometal. Chem., 76 (1974) 401.

7 M.-F. Hirai, M. Miyasaka, K. Itoh and Y. Ishii, J. Organometal. Chem., in press.

8 R. Usón, J. Fornies and S. Gonzalo, J. Organometal. Chem., 104 (1976) 253.

9 K. Itoh, M. Fukui and Y. Ishii, J. Organometal. Chem., 129 (1977) 259.

10 (a) J.C. Kotz and D.G. Pedrotty, J. Organometal. Chem., 22 (1970) 425; (b) V.I. Zdanovitch, A.Zh. Zhakaeva, V.N. Setkina and D.N. Kursanov, J. Organometal. Chem., 64 (1970) C25; (c) D. Cashman and F.J. Lalor, J. Organometal. Chem., 32 (1971) 351; (d) V.I. Zdanovitch, N.E. Kolobova, N.I. Vasyukova, Yu.S. Nekrasov, G.A. Panosyan, P.V. Petrovskii and A.Zh. Zhakaeva, J. Organometal. Chem., 148 (1978) 63.

11 F. Ramirez and S. Levy, J. Amer. Chem. Soc., 79 (1957) 67.