Preparation and Nuclear Magnetic Resonance Spectra of Bis(η^3-allyl ylide)-, (η^3-Allyl)(η^3-allyl ylide)-, (η^3-Allyl ylide)(η^5-cyclopentadienyl ylide)-, and (η^3-Allyl)(η^5-cyclopentadienyl ylide)-palladium(II) Complexes

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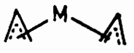
Bis(η^3-allyl ylide)palladium complexes with general formula $[Pd\{\eta^3-(R^1{}_3P)CHCR^2CHR^3\}\{\eta^3-(Ph_3P)CHCHCH_2\}]Y_2$ (1; R^1 = Ph or Et; R^2 = H; R^3 = H or Me; Y = BF_4 or O_3SCF_3) are prepared by treating $[Pd\{\eta^3-(R^1{}_3P)CHCR^2CHR^3\}Cl_2]$ with AgY followed by addition of $Ph_3P{=}CH{-}CH{=}CH_2$. (η^3-Allyl)(η^3-allyl ylide)palladium complexes, $[Pd(\eta^3-CH_2CRCH_2)\{\eta^3-(Ph_3P)CHCHCH_2\}]Y$ (2: R = H or Me; Y = BF_4 or O_3SCF_3) are obtained similarly from the allylchloropalladium dimer. The series $[Pd\{\eta^3-(R^1{}_3P)CHCHCHR^2\}\{\eta^5-(Ph_3P)C_5H_4\}][BF_4]_2$ (3: R^1 = Ph or Et; R^2 = H or Me) is prepared by the reaction of $[Pd\{\eta^3-(R^1{}_3P)CHCHCHR^2\}Cl_2]$ with $Ag[BF_4]$ and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$. Treatment of $[\{Pd(\eta^3-CH_2CR^1CR^2R^3)Cl\}_2]$ (R^1 = H or Me; R^2 = H or Me; R^3 = H) with AgY (Y = BF_4 or O_3SCF_3) and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ gives $[Pd(\eta^3-CH_2CR^1CR^2R^3)\{\eta^5-(Ph_3P)C_5H_4\}]Y$ (4). The ^1H n.m.r. spectra of these new η^3-allyl ylide and η^5-cyclopentadienyl ylide palladium complexes are discussed.

BIS(η-ALLYL)TRANSITION-METAL complexes are frequently key intermediates in various homogeneous catalyses or transition-metal-mediated reactions. In particular, the chemistry of $[Ni(\eta-C_3H_5)_2]$ is well studied in connection with the oligomerization of dienes.[1,2] The bis(η-allyl)palladium complex was first prepared by Wilke *et al.*[1] from allylmagnesium chloride and anhydrous palladium(II) chloride. Beconsall *et al.*[3,4] investigated the variable-temperature n.m.r. spectra of isoleptic π-allyl complexes and concluded that $[Pd(\eta-C_3H_5)_2]$ existed in solution as a mixture of two dynamic forms, depicted above, between which a rapid exchange occurred over the n.m.r. time scale by way of σ–π interconversion. The relative intensity of the resonances due to the two sandwich structures was temperature independent, irrespective of repeated recrystallization from pentane and of the preparative solvents used. The temperature independency of the equilibrium in $[Pd(C_3H_5)_2]$ is quite different from that involving $[Ni(C_3H_5)_2]$ where the interconversion also occurs in the n.m.r. time scale. Dietrich and Uttech[5] suggested that $[Ni(CH_2CMeCH_2)_2]$ is present exclusively in the solid state as a *trans* structure (from *X*-ray analysis), and Chenskaya *et al.*[6] concluded from vibrational spectroscopy that $[Pd(C_3H_5)_2]$ should have a C_{2h} *trans* conformation in a solid state.

trans (A)



cis (B)

For some years, we have studied palladium(II) complexes with 1-phosphonioallyl ylides as a new class of η^3-allyl ligands. Zwitterionic or neutral palladium(II) complexes ligating such ylides were previously reported.[7–9] The preparation of bis(η-allyl)palladium complexes such as bis(1—3-η-1-phosphoniopropenide)palladium(II) and (η-allyl)(1—3-η-1-phosphoniopropenide)palladium(II) is described in this paper. The variable-temperature n.m.r. spectra of $[Pd\{\eta^3-(Ph_3P)CHCHCH_2\}_2][BF_4]_2$ indicate that the ratio of the *trans* and *cis* components changes from 2.1 to 1.2 : 1 over the range −30 to 30 °C. This temperature dependence differs from that of homoleptic $[Pd(C_3H_5)_2]$ which did not show any change in the *cis* : *trans* ratio. (1—3-η-1-Phosphoniopropenide)(η-triphenylphosphoniocyclopentadienide)palladium(II) and (η-allyl)(η-triphenylphosphoniocyclopentadienide)palladium(II) complexes having similar structures to phosphonium salts are also described. The present complexes do not induce an allyl coupling reaction which is the most typical reaction of bis(η-allyl)transition-metal complexes; therefore, these ylide complexes are more stable than $[Pd(C_3H_5)_2]$.[1–4]

RESULTS AND DISCUSSION

Bis(1—3-η-*phosphoniopropenide*)*palladium*(II) *and* (η-*Allyl*)(1—3-η-*phosphoniopropenide*)*palladium*(II) *Complexes*.—When a dichloromethane solution of $[Pd\{\eta^3-(R^1{}_3P)CHCR^2CHR^3\}Cl_2]$[8] ($R^1$ = Ph or Et; R^2 = H or Me; R^3 = H) was treated with a tetrahydrofuran (thf) solution of 2 mol equivalents of AgY (Y = BF_4 or O_3SCF_3) followed by $Ph_3P{=}CH{-}CH{=}CH_2$, prepared separately in thf, the corresponding complexes $[Pd\{\eta^3-(R^1{}_3P)CHCR^2CHR^3\}\{\eta^3-(Ph_3P)CHCHCH_2\}]Y_2$ (1) were obtained in fairly good yields [equation (1)]. A similar treatment of $[\{Pd(\eta^3-CH_2CR^1CR^2R^3)Cl\}_2]$ (R^1 = H or Me; R^2 = H or Me; R^3 = H) with 2AgY (Y = BF_4 or O_3SCF_3) followed by the addition of $Ph_3P{=}CH{-}CH{=}CH_2$ gave $[Pd(\eta^3-CH_2CR^1CR^2R^3)\{\eta^3-(Ph_3P)CHCHCH_2\}]Y$ [equation (2)]. Yields, analytical data, m.p.s, and conductivities of complexes (1) and (2) are summarized in Table 1. In the solid state the complexes are stable in air for a few hours at room temperature and for a few days under an inert atmosphere.

Proton n.m.r. data for complexes (1) and (2) are given in Supplementary Publication No. SUP 22491 (3 pp.).† Typical ^1H n.m.r. data are given in the Experimental section. The spectra of complex (1a) in $(CD_3)_2CO$ solution at −30 and 30 °C are illustrated in Figure 1. Assignment of the chemical shifts was made by com-

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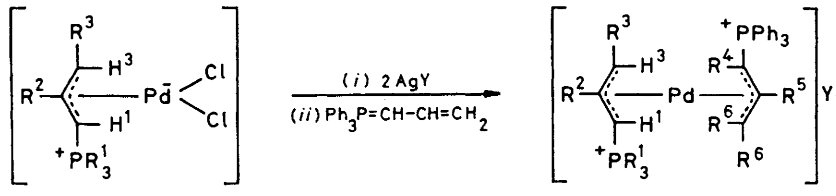
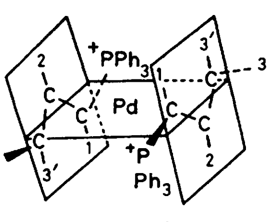
† For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

parison with n.m.r. spectra of $[Pd(C_3H_5)_2]$.[4] For the latter complex, the central and *syn* protons of the *trans* structure (A) were observed at lower field than that of the *cis* (B) [central δ 5.60(A), 4.03(B); *syn* δ 4.11(A), 3.90(B)]. This trend is not exhibited by the H^1 and H^3 protons of the typical complex $[Pd\{\eta^3\text{-}(Ph_3P)CH^1CH^2CH^3{}_2\}_2][BF_4]_2$ (1a) because their chemical shifts are characteristic of η^3-allyl ylide ligand.[9] Since the H^2 proton is generally unaffected compared with the terminal protons in η^3-allyl ylide palladium complexes, the H^2 proton of *trans* structure (A) was assigned to a signal at δ 5.66 at lower field and that of *cis* structure (B) to a signal at δ 5.52. The spectrum at −30 °C (Figure 1) apparently shows that the *trans* structure is predominant. Chemical shifts of the H^1, H^2, and H^3 protons of the *trans* structure are assigned to signals at δ 4.60, 5.66, and 4.05, and of the *cis* to those at δ 4.97, 5.52, and 3.96, respectively. The ratio of the two components (A) and (B) (as measured by the relative peak intensity of the most upfield peaks assignable to H^3 protons) changes from *ca.* 2.1 : 1 at −30 °C to 1.2 : 1 at 30 °C.

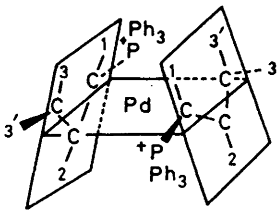


(1)

(1a) $R^1 = Ph, R^2 = R^5 = H^2, R^3 = R^6 = H^3, R^4 = H^1, Y = BF_4$
(1b) $R^1 = Ph, R^2 = R^5 = H^2, R^3 = R^6 = H^6, R^4 = H^1, Y = O_3SCF_3$
(1c) $R^1 = Ph, R^2 = H^2, R^3 = Me, R^4 = H^4, R^5 = H^5, R^6 = H^6, Y = BF_4$
(1d) $R^1 = Ph, R^2 = H^2, R^3 = Me, R^4 = H^4, R^5 = H^5, R^6 = H^6, Y = O_3SCF_3$
(1e) $R^1 = Et, R^2 = H^2, R^3 = H^3, R^4 = H^4, R^5 = H^5, R^6 = H^6, Y = BF_4$



trans (A)



cis (B)

Beconsall *et al.*[4] have reported a change of equilibrium constant of the two components for $[Ni(C_3H_5)_2]$ by a fast σ–π interconversion. Although they could not observe the temperature dependence of the n.m.r. spectra of $[Pd(C_3H_5)_2]$, the ratio of the two components was unchanged after six recrystallizations from pentane and when the preparation was undertaken in dimethoxymethane instead of diethyl ether. This fact is explained by assuming that there is a fast equilibrium over the n.m.r. time scale. The temperature dependence of the *trans–cis* equilibrium in the present complex (1a) is quite different from that of typical bis(η-allyl)palladium complexes. A plausible equilibrium scheme is shown in Figure 2. Path (a) is a σ–π interconversion through a vinylphosphonium intermediate [having Pd–C(3) bonding]. Path (b) is a σ–π interconversion by way of an allylphosphonium intermediate [having Pd–C(1) bonding]. The participation of a vinylphosphonium intermediate is strongly supported by the large coupling constant *J*(2P) 26.1 Hz in the 1-triphenylphosphonioallyl ylide ligand.[10] On the other hand, path (b) is

TABLE 1

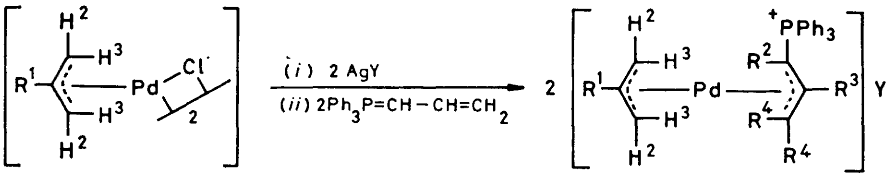
Yields, analytical data, m.p.s, and conductivities obtained for the new palladium complexes (1) and (2)

Complex	Yield (%)	Analysis (%) Calc. C	Analysis (%) Calc. H	Analysis (%) Found C	Analysis (%) Found H	M.p. (θ_c/°C) (decomp.)	Λ[a] / S cm² mol⁻¹
$[Pd\{\eta^3\text{-}(R^1{}_3P)CHCR^2CHR^3\}\{\eta^3\text{-}(Ph_3P)CHCHCH_2\}]Y_2$							
(1a) $R^1 = Ph, R^2 = R^3 = H, Y = BF_4$	53	54.8	4.60[b]	55.05	4.35	118—123	258 (6.47)
(1b) $R^1 = Ph, R^2 = R^3 = H, Y = O_3SCF_3$	55	52.35	3.80	51.8	3.95	144—149	291 (2.26)
(1c) $R^1 = Ph, R^2 = H, R^3 = Me, Y = BF_4$	74	55.25	4.75[b]	54.7	4.55	125—129	242 (3.08)
(1d) $R^1 = Ph, R^2 = H, R^3 = Me, Y = O_3SCF_3$	78	52.8	3.85	52.1	4.50	115—120	262 (3.53)
(1e) $R^1 = Et, R^2 = R^3 = H, Y = BF_4$	49	48.65	5.15	48.65	5.40	64—69	201 (2.92)
$[Pd(\eta^3\text{-}CH_2CR^1CH_2)\{\eta^3\text{-}(Ph_3P)CHCHCH_2\}]Y$							
(2a) $R^1 = H, Y = BF_4$	45	53.7	4.50	54.2	4.65	87—90	154 (4.86)
(2b) $R^1 = H, Y = O_3SCF_3$	17	48.65	4.25[c]	48.8	4.05	98—100	154 (12.6)
(2c) $R^1 = Me, Y = BF_4$	60	52.8	4.95	52.85	4.80	85—87	125 (39.2)
(2d) $R^1 = Me, Y = O_3SCF_3$	38	50.95	4.30	50.5	4.10	105—107	176 (10.8)

[a] In acetone at 20 °C; 10^4 concentration/mol dm⁻³ given in parentheses. [b] Calculated for $2H_2O$ adduct. [c] Calculated for H_2O adduct.

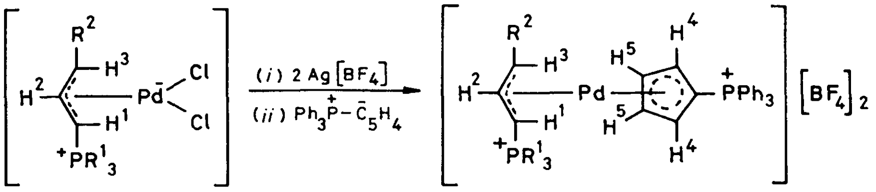
rejected, since the bulky triphenylphosphonium group cannot take an *anti* position, based on a consideration of a molecular model.

The spectrum of complex (2a) is shown in Figure 3. The assignments were also made by comparison with the n.m.r. spectra of $[Pd(C_3H_5)_2]$ [4] and $[Pd\{\eta^3\text{-}(Ph_3P)CH^1CH^2CH^3_2\}_2][BF_4]_2$. From these results, in complex (2a) the H^2 and H^6 protons of the *trans* structure should appear at lower fields than the *cis* structure. The H^2, H^3, H^4, and H^6 protons of the *trans* structure are assigned to signals at δ 4.62, 2.64, 3.58, and 3.76, and of the *cis* to those at δ 3.99, 2.77, 4.28, and 3.08; the H^1 and H^5 protons could not be assigned because of their complexity.



(2)

(2a) $R^1 = H^1, R^2 = H^4, R^3 = H^5, R^4 = H^6, Y = BF_4$
(2b) $R^1 = H^1, R^2 = H^4, R^3 = H^5, R^4 = H^6, Y = O_3SCF_3$
(2c) $R^1 = Me, R^2 = H^4, R^3 = H^5, R^4 = H^6, Y = BF_4$
(2d) $R^1 = Me, R^2 = H^4, R^3 = H^5, R^4 = H^6, Y = O_3SCF_3$



(3)

(3a) $R^1 = Ph, R^2 = H^3$
(3b) $R^1 = Ph, R^2 = Me$
(3c) $R^1 = Et, R^2 = H^3$

(1—3-η-Phosphoniopropenide)(η-triphenylphosphoniocyclopentadienide)palladium(II) *and* (*η-Allyl*)(*η-triphenylphosphoniocyclopentadienide*)*palladium*(II) *Complexes.*—Treatment of $[Pd\{\eta^3\text{-}(R^1_3P)CHCHR^2\}Cl_2]$ (R^1 = Ph or Et; R^2 = H or Me) in acetone with an acetone solution of $Ag[BF_4]$ and $Ph_3\overset{+}{P}-\overset{-}{C}_5H_4$ in dichloromethane gave $[Pd\{\eta^3\text{-}(R^1_3P)CHCHCHR^2\}\{\eta^5\text{-}(Ph_3P)C_5H_4\}][BF_4]$ (3) [equation (3)]. A similar procedure with $[\{Pd(\eta^3\text{-}CH_2CR^1CR^2R^3)Cl\}_2]$ (R^1 = H or Me; R^2 = H or Me; R^3 = H) in dichloromethane, a thf solution of AgY (Y = BF_4 or O_3SCF_3), and $Ph_3\overset{+}{P}-\overset{-}{C}_5H_4$ in dichloromethane gave $[Pd(\eta^3\text{-}CH_2CR^1CR^2R^3)\{\eta^5\text{-}(Ph_3P)C_5H_4\}]Y$ (4) [equation (4)]. These complexes are very stable in the solid state under an inert atmosphere at room temperature, but decompose in moist air. Yields, analytical data, and physical properties of complexes (3) and (4) are summarized in Table 2 and ^1H n.m.r. spectral results in SUP 22491. Data for complexes (3a) and (4a) are given as representative examples in the Experimental section. The protons of the cyclopentadienyl ylide ligand in complex (3a) are assigned at δ 6.05 (H^4) and 5.60 and

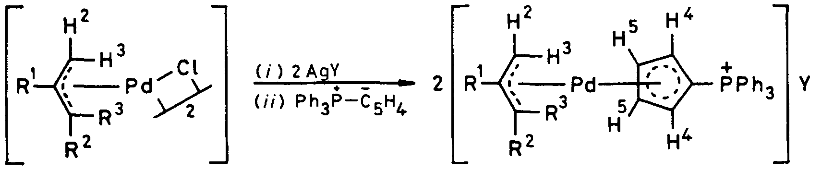
TABLE 2

Yields, analytical data, m.p.s, and conductivities obtained for the new palladium complexes (3) and (4)

		Analysis (%)					
		Calc.		Found			
Complex	Yield (%)	C	H	C	H	M.p. (θ_c/°C) (decomp.)	Λ [a] S cm² mol⁻¹
$[Pd\{\eta^3\text{-}(R^1_3P)CHCHCHR^2\}\{\eta^5\text{-}(Ph_3P)C_5H_4\}][BF_4]_2$							
(3a) R^1 = Ph, R^2 = H	74	57.0	4.35 [b]	56.85	4.20	141—145	240 (3.25)
(3b) R^1 = Ph, R^2 = Me	76	57.45	4.50 [b]	57.65	4.70	137—140	262 (3.20)
(3c) R^1 = Et, R^2 = H	79	50.25	5.00	50.5	5.25	95—100	200 (3.34)
$[Pd(\eta^3\text{-}CH_2CR^1CR^2R^3)\{\eta^5\text{-}(Ph_3P)C_5H_4\}]Y$							
(4a) R^1 = H, R^2 = R^3 = H, Y = BF_4	67	55.7	4.30	55.35	4.55	82—87	156 (18.0
(4b) R^1 = H, R^2 = R^3 = H, Y = O_3SCF_3	53	52.05	3.90	52.3	3.80	80—83	157 (14.9)
(4c) R^1 = Me, R^2 = R^3 = H, Y = BF_4	79	56.45	4.55	55.75	4.75	95—100	151 (16.5)
(4d) R^1 = Me, R^2 = R^3 = H, Y = O_3SCF_3	53	52.8	4.10	52.9	4.05	103—105	161 (9.73)
(4e) R^1 = H, R^2 = Me, R^3 = H, Y = BF_4	70	56.45	4.55	56.25	4.85	120—123	180 (10.8)
(4f) R^1 = H, R^2 = Me, R^3 = H, Y = O_3SCF_3	56	52.8	4.10	52.1	4.15	112—114	154 (9.95)

[a] In acetone at 20 °C; 10^4 concentration/mol dm^{-3} given in parentheses. [b] Calculated for H_2O adduct.

5.76 (H^5), respectively. On the other hand, in complex (4a) the resonances of the H^4 and H^5 protons were not split at all. This magnetic non-equivalence of the cyclopentadienyl ring protons in complex (3a) is due to an anisotropy of the phenyl rings on the triphenylphosphonium allyl ylide ligand. A small chemical-shift difference between α and β protons of the cyclopentadienyl ylide ligand [0.37 in (3a) and zero in (4a)] indicates that the triphenylphosphonium cyclopentadienyl ylide in complexes (3) and (4) is co-ordinated as a η^5-ligand.[11–14] The *syn*, *anti*, and C^2 protons of the η^3-allyl ligand in $[Pd(C_3H_5)(C_5H_5)]$ appeared at δ 3.40, 2.10, and 4.57.[15,16]



(4)

(4a) $R^1 = H^1$, $R^2 = H^2$, $R^3 = H^3$, $Y = BF_4$
(4b) $R^1 = H^1$, $R^2 = H^2$, $R^3 = H^3$, $Y = O_3SCF_3$
(4c) $R^1 = Me$, $R^2 = H^2$, $R^3 = H^3$, $Y = BF_4$
(4d) $R^1 = Me$, $R^2 = H^2$, $R^3 = H^3$, $Y = O_3SCF_3$
(4e) $R^1 = H^1$, $R^2 = Me$, $R^3 = H^{3'}$, $Y = BF_4$
(4f) $R^1 = H^1$, $R^2 = Me$, $R^3 = H^{3'}$, $Y = O_3SCF_3$

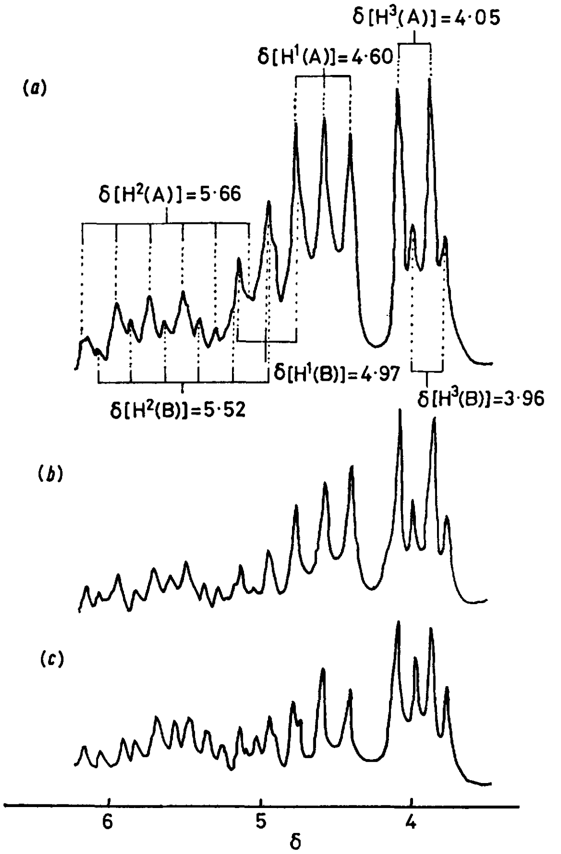


FIGURE 1 Proton n.m.r. spectra of complex (1a) in $(CD_3)_2CO$ at temperature (*a*) −30, (*b*) 0, and (*c*) 30 °C

The corresponding signals of complex (4a) are observed at lower field, at δ 4.02, 2.58, and 4.50. This downfield shift of the η^3-allyl resonance suggests that the triphenylphosphonium cyclopentadienyl ylide is more electron-withdrawing than cyclopentadienyl. No appreciable change in the spectrum of complex (3a) was observed within the range −75 to 65 °C.

EXPERIMENTAL

Hydrogen-1 n.m.r. spectra were recorded on a JEOL C-60HL spectrometer, i.r. spectra on a JASCO model 403G spectrophotometer. Conductivity was measured on a TOA Electronics CM-5B instrument.

The preparation of complexes (1)—(4) is illustrated by (1a), (2a), (3a), and (4a) and reaction conditions are shown for the other complexes.

Bis(1—3-*η*-*triphenylphosphoniopropenide*)*palladium Bis*(*tetrafluoroborate*)(1a).—To a cationic complex generated *in situ* by treatment of $[Pd\{\eta^3\text{-}(Ph_3P)CHCHCH_2\}Cl_2]$ (496 mg, 1.04 mmol) with $Ag[BF_4]\cdot H_2O$ (439 mg, 2.06 mmol) in dichloromethane (14 cm³) and thf (35 cm³) was added a thf (15 cm³) solution of $Ph_3P{=}CH{-}CH{=}CH_2$ prepared from $[Ph_3P{-}CH_2{-}CH{=}CH_2]Br$ (400 mg, 1.04 mmol) and excess of $Na[NH_2]$ in thf (10 cm³) at −78 °C under an atmosphere of nitrogen. The reaction occurred instantaneously to give a yellow solution of $[Pd\{\eta^3\text{-}(Ph_3P)CHCHCH_2\}_2][BF_4]_2$ (1a). The mixture was stirred for 20 min, and filtered in an atmosphere of nitrogen as quickly as possible. The solution was evaporated under reduced pressure. The product was recrystallized from chloroform by adding a large volume of diethyl ether, and filtered off in an atmosphere of nitrogen to give a yellow hygroscopic powder (0.67 mg, 70%). N.m.r. in $(CD_3)_2CO$: *trans*(A), δ 4.60 (d of d, 1, H^1), 5.66 (m, 1, H^2), and 4.05 (d, 2, H^3); *cis*(B), δ 4.97 (d of d, 1, H^1), 5.52 (m, 1, H^2), and 3.96 (d, 2, H^3); $J(H^1\text{–}H^2) = J(H^1\text{–}P)$ 13.5, $J(H^2\text{–}H^3)$ 10.5, and $J(H^2\text{–}P)$ 26.1 Hz. Ratio of the components (A) and (B): 2.1 : 1 at −30 °C, 1.7 : 1 at 0 °C, and 1.2 : 1 at 30 °C.

The following complexes were prepared similarly: *bis*(1—3-*η*-1-*triphenylphosphoniopropenide*)*palladium bis*(*trifluoromethylsulphate*) (1b), from $[Pd\{\eta^3\text{-}(Ph_3P)CHCHCH_2\}Cl_2]$ (182 mg, 0.83 mmol), $Ag[O_3SCF_3]$ (196 mg, 0.76 mmol), and $Ph_3P{=}CH{-}CH{=}CH_2$ (0.38 mmol) in dichloromethane-thf (10 cm³ : 20 cm³) at −78 °C for 20 min, in 55% (210 mg) yield; (1—3-*η*-1-*triphenylphosphoniobutenide*)(1—3-*η*-1-*triphenylphosphoniopropenide*)*palladium bis*(*tetrafluoroborate*) (1c), from $[Pd\{\eta^3\text{-}(Ph_3P)CHCHCH(Me)\}Cl_2]$ (498 mg, 1.00 mmol), $Ag[BF_4]\cdot H_2O$ (423 mg, 2.00 mmol), and $Ph_3P{=}$

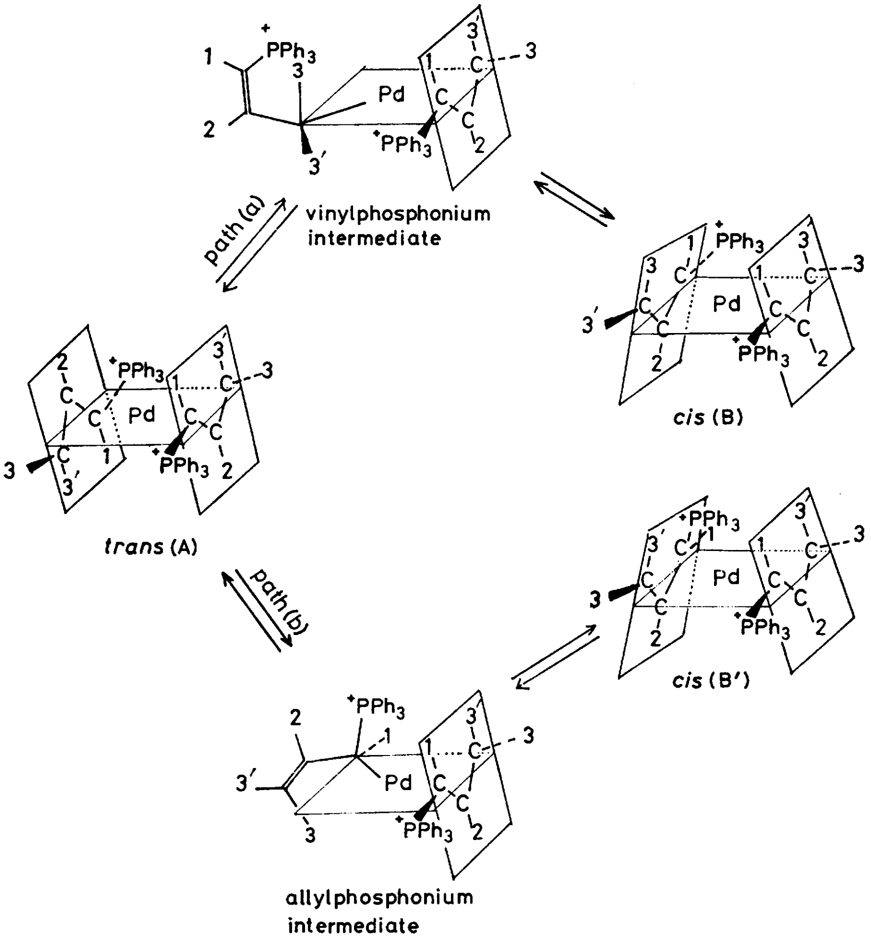


FIGURE 2 Equilibrium scheme between *trans*(A) and *cis*(B)

CH–CH=CH$_2$ (1.00 mmol) in dichloromethane–thf (15 cm^3 : 35 cm^3) at −78 °C for 20 min, in 74% (665 mg) yield; (1—3-η-1-*triphenylphosphoniobutenide*)(1—3-η-1-*triphenylphosphoniopropenide*)*palladium bis(trifluoromethylsulphate)* (1d), from [Pd{η^3-(Ph$_3$P)CHCHCH(Me)}Cl$_2$] (163 mg, 0.33 mmol), Ag[O$_3$SCF$_3$] (170 mg, 0.66 mmol), and Ph$_3$P=CH–CH=CH$_2$ (0.33 mmol) in dichloromethane–thf (10 cm^3 : 20 cm^3) at −78 °C for 20 min, in 78% (691 mg) yield; (1—3-η-*triethylphosphoniopropenide*)(1—3-η-1-*triphenylphosphoniopropenide*)*palladium bis(tetrafluoroborate)*(1e), from [Pd{η^3-(Et$_3$P)CHCHCH$_2$}Cl$_2$] (104 mg, 0.31 mmol), Ag[BF$_4$]·H$_2$O (131 mg, 0.62 mmol), and Ph$_3$P=CH–CH=CH$_2$ (0.31 mmol) in dichloromethane–thf (10 cm^3 : 20 cm^3) at −78 °C for 20 min, in 49% (112 mg) yield.

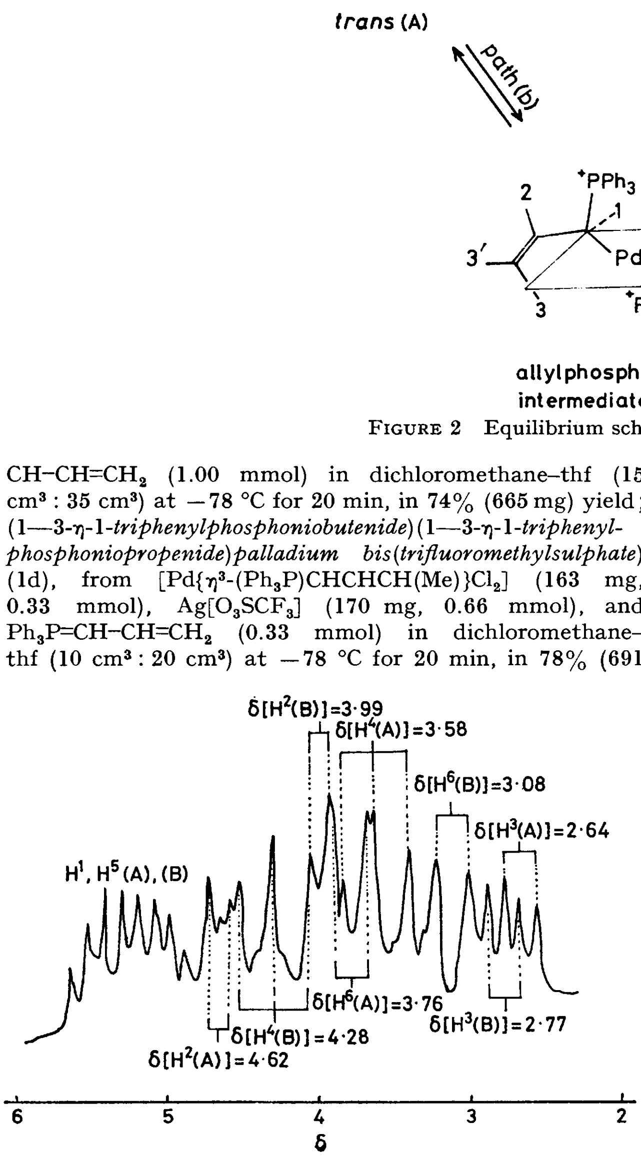


FIGURE 3 Proton n.m.r. spectrum of complex (2a) in CDCl$_3$

(η-*Allyl*)(1—3-η-1-*triphenylphosphoniopropenide*)*palladium Tetrafluoroborate* (2a). To the cationic complex which was generated *in situ* in dichloromethane (10 cm^3) by the reaction of [{Pd(η^3-CH$_2$CHCH$_2$)Cl}$_2$] (176 mg, 0.48 mmol) with Ag[BF$_4$]·H$_2$O (202 mg, 0.95 mmol) was added a thf (30 cm^3) solution of Ph$_3$P=CH–CH=CH$_2$ prepared from [Ph$_3$P–CH$_2$–CH=CH$_2$]Br (367 mg, 0.96 mmol) and Na[NH$_2$] (100 mg, 2.6 mmol) in thf (30 cm^3) at −78 °C, stirred for 1 h, and quickly filtered under an atmosphere of nitrogen. The solution was evaporated *in vacuo* and the residue recrystallized from chloroform by adding a large volume of diethyl ether, then filtered off in an atmosphere of nitrogen. The complex (2a) was obtained as a very hygroscopic yellow powder (232 mg, 45%). N.m.r. in CDCl$_3$: *trans*(A), δ 5.8—4.8 (m, 2, H^1 and H^5), 4.62 (d, 2, H^2), 2.60 (d, 2, H^3), 3.67 (d of d, 1, H^4), and 3.80 (d, 2, H^6); *cis*(B), δ 5.8—4.8 (m, 2, H^1 and H^5), 4.00 (d, 2, H^2), 2.62 (d, 2, H^3), 4.56 (d of d, 1, H^4), and 3.10 (d, 2, H^6); J(H^1–H^2) 7.5, J(H^1–H^3) 13.0, and J(H^4–H^5) = J(H^4–P) = J(H^5–H^6) 14.0 Hz. Ratio of the components (A) and (B): 1.0 : 1 at room temperature.

The following complexes were prepared similarly: (η-

allyl)(1—3-η-1-*triphenylphosphoniopropenide*)*palladium trifluoromethylsulphate* (2b), from [{Pd(η^3-CH_2CHCH_2)Cl}$_2$] (183 mg, 0.50 mmol), Ag[O_3SCF_3] (257 mg, 1.0 mmol), and $Ph_3P{=}CH{-}CH{=}CH_2$ (1.0 mmol) in dichloromethane-thf (20 cm^3 : 30 cm^3) at −78 °C for 1 h, in 17% (120 mg) yield; (η-2-*methylallyl*)(1—3-η-*triphenylphosphoniopropenide*)-*palladium tetrafluoroborate* (2c), from [{Pd(η^3-CH_2CMeCH_2)-Cl}$_2$] (490 mg, 1.24 mmol), Ag[BF_4]·H_2O (529 mg, 2.49 mmol), and $Ph_3P{=}CH{-}CH{=}CH_2$ (2.48 mmol) in dichloromethane–thf (25 cm^3 : 40 cm^3) at −78 °C for 1 h, in 60% (822 mg) yield; (η-2-*methylallyl*)(1—3-η-1-*triphenylphosphoniopropenide*)*palladium trifluoromethylsulphate* (2d), from [{Pd(η^3-CH_2CMeCH_2)Cl}$_2$] (168 mg, 0.43 mmol), Ag[O_3SCF_3] (219 mg, 0.86 mmol), and $Ph_3P{=}CH{-}CH{=}CH_2$ (0.86 mmol) in dichloromethane–thf (10 cm^3 : 15 cm^3) at −78 °C for 1 h, in 38% (199 mg) yield.

(*Triphenylphosphoniocyclopentadienide*)(1—3-η-1-*triphenylphosphoniopropenide*)*palladium Bis*(*tetrafluoroborate*) (3a).—To the cationic complex generated *in situ* in acetone (20 cm^3) by treatment of [Pd{η^3-(Ph_3P)CHCHCH$_2$}-Cl$_2$] (166 mg, 0.35 mmol) with Ag[BF_4]·H_2O (140 mg, 0.66 mmol) was added a dichloromethane solution (5 cm^3) of $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (108 mg, 0.33 mmol) in an atmosphere of nitrogen. The mixture was stirred at room temperature for 20 min, then filtered under an inert atmosphere. The solution was evaporated under reduced pressure and the product recrystallized from dichloromethane by adding a large volume of diethyl ether to give a deep red powder (235 mg, 74%). N.m.r. in $CDCl_3$: δ 3.88 (d of d, 1, H^1), 4.78 (m, 1, H^2), 3.07 (d, 2, H^3), 6.05 (m, 2, H^4), and 5.60 and 5.75 (each m, 2, H^5); J(H^1–H^2) = J(H^1–P) 6.0, J(H^2–H^3) 10.5, and J(H^2–P) 21.0 Hz.

The following complexes were prepared similarly: (1—3-η-1-*triphenylphosphoniobutenide*)(*triphenyphosphoniocyclopentadienide*)*palladium bis*(*tetrafluoroborate*) (3b), from [Pd{η^3-(Ph_3P)CHCHCH(Me)}Cl$_2$] (410 mg, 0.83 mmol), Ag[BF_4]·H_2O (354 mg, 1.66 mmol), and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (272 mg, 0.83 mmol) in acetone–dichloromethane (30 cm^3 : 10 cm^3) at room temperature for 30 min, in 76% (590 mg) yield; (1—3-η-1-*triethylphosphoniopropenide*)(*triphenylphosphoniocyclopentadienide*)*palladium bis*(*tetrafluoroborate*) (3c), from [Pd{η^3-(Et_3P)CHCHCH$_2$}Cl$_2$] (107 mg, 0.33 mmol), Ag[BF_4]·H_2O (140 mg, 0.66 mmol), and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (108 mg, 0.33 mmol) in acetone–dichloromethane (20 cm^3 : 10 cm^3) at room temperature for 20 min, in 79% (199 mg) yield.

(η-*Allyl*)(*triphenylphosphoniocyclopentadienide*)*palladium Tetrafluoroborate* (4a).—To the cationic complex prepared *in situ* in dichloromethane (20 cm^3) by treating [{Pd(η^3-CH_2CHCH_2)Cl}$_2$] (188 mg, 0.51 mmol) with Ag[BF_4]·H_2O (212 mg, 1.03 mmol) was added a dichloromethane solution (5 cm^3) of $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (336 mg, 1.03 mmol) at room temperature under an atmosphere of nitrogen. The mixture was stirred for 30 min, AgCl quickly filtered off in air, and the orange-red filtrate evaporated to dryness. The residue was recrystallized from dichloromethane–diethyl ether to give ochre-orange needles (388 mg, 67%). N.m.r. in $CDCl_3$: δ 4.60 (m, 1, H^1), 4.02 (d, 2, H^2), 2.58 (d, 2, H^3), and 6.33 (m, 4, H^4 and H^5); J(H^1–H^2) 6.6, J(H^1–H^3) 11.3, and J(H^2–H^3) 0 Hz.

The following complexes were prepared similarly: (η-*allyl*)(*triphenylphosphoniocyclopentadienide*)*palladium trifluoromethylsulphate* (4b), from [{Pd(η^3-CH_2CHCH_2)-Cl}$_2$] (106 mg, 0.29 mmol), Ag[O_3SCF_3] (148 mg, 0.58 mmol), and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (188 mg, 0.58 mmol) in dichloromethane (20 cm^3) at room temperature for 30 min, in 53% (190 mg) yield; (η-2-*methylallyl*)(*triphenylphosphoniocyclopentadienide*)*palladium tetrafluoroborate* (4c), from [{Pd(η^3-CH_2-$CMeCH_2$)Cl}$_2$] (197 mg, 0.50 mmol), Ag[BF_4]·H_2O (212 mg, 1.00 mmol), and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (326 mg, 1.00 mmol) in dichloromethane (30 cm^3) at room temperature for 30 min, in 79% (495 mg) yield; (η-2-*methylallyl*)(*triphenylphosphoniocyclopentadienide*)*palladium trifluoromethylsulphate* (4d), from [{Pd(η^3-CH_2CMeCH_2)Cl}$_2$] (81 mg, 0.21 mmol), Ag-[O_3SCF_3] (106 mg, 0.41 mmol), and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (135 mg, 0.41 mmol) in dichloromethane–thf (15 cm^3 : 5 cm^3) at room temperature for 30 min, in 53% (193 mg) yield; (η-1-*methylallyl*)(*triphenylphosphoniocyclopentadienide*)*palladium tetrafluoroborate* (4e), from [{Pd(η^3-$CH_2CHCHMe$)Cl}$_2$] (260 mg, 0.66 mmol), Ag[BF_4]·H_2O (281 mg, 1.32 mmol), and $Ph_3\overset{+}{P}{-}\overset{-}{C}_5H_4$ (431 mg, 1.32 mmol) in thf (35 cm^3) at room temperature for 30 min, recrystallized needles being obtained in 70% (529 mg) yield; (η-1-*methylallyl*)(*triphenylphosphoniocyclopentadienide*)*palladium trifluoromethylsulphate* (4f), from [{Pd(η^3-$CH_2CHCHMe$)Cl}$_2$] (191 mg, 0.48 mmol) in thf (30 cm^3) at room temperature for 30 min, ochre-orange needles being obtained in 56% (347 mg) yield.

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