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DIMERIC PALLADIUM(I) COMPLEXES CONTAINING THE BRIDGING CYCLOPENTADIENYL GROUP

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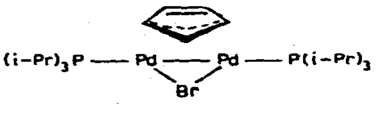
Summary

Dimeric palladium(I) complexes of the type $[\mu\text{-}(\eta^3\text{-}C_5H_5)\text{-}\mu\text{-}XPd_2(PR_3)_2]$ (X = Br, R = i-Pr, Ph, Cy; X = Cl, I, R = i-Pr) have been prepared by reduction of the complexes $[(\eta^5\text{-}C_5H_5)(PR_3)PdX]$ with a variety of reducing agents (Mg, Na/Hg, $LiAlH(t\text{-}BuO)_3$, $LiAlH_4$, $NaBH_4$, n-BuMgBr). PMR and IR data and some properties of the new complexes are reported.

Introduction

Few complexes containing palladium(I) have previously been reported [1—5] and only two series of these complexes contain the bridging cyclopentadienyl group [1,2]. In an earlier communication [1] we briefly described the reduction of the palladium(II) complexes Ia—c by magnesium metal in THF to give the dimeric palladium(I) complexes IVa—c. The crystal structure of IVa showed a short Pd—Pd distance (2.609 Å), with the two palladium atoms bridged by the bromine atom and the C_5H_5 ring, which has unequal C—C distances. The C_5H_5 ring can be regarded as an allyl plus alkene group, as shown in the diagram.



(IVa)

We now report details of this and other, more convenient, methods of preparation of these and other palladium(I) complexes, together with their PMR and IR data and some reactions.

The properties and spectroscopic data of the new complexes are similar to those of the complex IVa and it is concluded that all possess dimeric structures analogous to that shown.

TABLE 1

PREPARATIVE METHODS, MELTING POINTS, PMR AND ANALYTICAL DATA FOR THE COMPLEXES $[\mu\text{-}(\eta^3\text{-}C_5H_5)\text{-}\mu\text{-}XPd_2(PR_3)_2]$

Complex	PR_3	X	Method of preparation [a] (yield (%))	M.p. [b] (°C)	PMR [c] $\tau(C_5H_5)$	Analysis: Found (calcd.) (%)
IVa	$P(i\text{-}Pr)_3$	Br	1 (82); 2 (48); 3*i* (80); 3*iii* (26); 4 (90) [e]	148	4.67	C, 41.29 (40.73); H, 6.84 (6.98); Br, 12.80 (11.78); P, 8.95 (9.13)
IVb	PPh_3	Br	1 (57); 3*i* (90); 4 (91)	180—192	5.02	C, 55.59 (55.81); H, 3.90 (4.00); Br, 8.96 (9.06)
IVc	PCy_3	Br	1 (59); 3*i* (83); 3*ii* (83)	~180 [d]	4.77	C, 53.59 (53.60); H, 7.75 (7.79); Br, 8.97 (8.70)
Va	$P(i\text{-}Pr)_3$	Cl	1 (10); 3*i* (19)	120—128	4.66	C, 43.50 (43.58); H, 7.30 (7.47); Cl, 5.80 (5.59)
VIa	$P(i\text{-}Pr)_3$	I	1 (10)	126—130	4.53	C, 38.50 (38.09); H, 6.44 (6.53); I, 18.19 (17.50)
XIa	$P(i\text{-}Pr)_3$	SPh	a (87)	116—120	4.50	C, 48.98 (49.23); H, 7.17 (7.41); S, 5.13 (4.53)
XIb	PPh_3	SPh	a (68)	182—188	4.91	C, 61.64 (61.92); H, 4.38 (4.42); S, 3.51 (3.52)

[a] See Experimental section. [b] Capillary tube, in air. All complexes decomposed at the m.p. [c] $CDCl_3$ solution, TMS internal reference. [d] Did not melt, but darkened above 180°C. [e] After 10 days at 25°C in THF.

Results and discussion

The dimeric palladium(I) complexes IV—VI have been prepared from the reaction of the complexes I—III [6] with various reducing agents according to eqn. 1.

$$2[(\eta^5\text{-}C_5H_5)(PR_3)PdX] \xrightarrow[\text{agent}]{\text{reducing}} [\mu\text{-}(\eta^3\text{-}C_5H_5)\text{-}\mu\text{-}XPd_2(PR_3)_2] \qquad (1)$$

$$\text{(I—III)} \qquad\qquad\qquad\qquad \text{(IV—VI)}$$

I, IV: X = Br; II, V: X = Cl; III, VI: X = I; a: R = i-Pr; b: R = Ph; c: R = Cy (Cy = Cyclohexyl)

The preferred method of preparation of the dimeric complexes is that using $LiAlH_4$ or $LiAlH(t\text{-}BuO)_3$, since high yields of pure products were obtained. Reduction with magnesium metal or sodium amalgam was difficult to control and gave varying amounts of starting material, dimer and palladium metal, depending on reaction time and conditions.

The complexes IV—VI were isolated as red crystals. Complexes IVa, Va and VIa are readily soluble in THF, $CHCl_3$ or toluene; IVb and IVc are less soluble. The solids are indefinitely stable in air at room temperature, but solutions decompose slowly even under nitrogen, depositing palladium metal.

The IR spectra of the dimeric complexes IV—VI and XI show absorptions due to the C_5H_5 group at frequencies similar to those observed for IVa (see Experimental Section), having three characteristic weak absorptions in the region 3020 to 3100 cm^{-1}, as found for monomeric η^3-C_5H_5 complexes of aluminium and gallium [7].

The PMR spectra of all the dimeric complexes IV—VI and XI (in $CDCl_3$) showed a 1 : 2 : 1 triplet in the region τ 4.50—5.02, due to the five equivalent protons of the C_5H_5 group which are coupled to the two equivalent phosphorus nuclei, (J(P—H) = 2 Hz). The C_5H_5 ring must therefore be fluxional in solution.

The similarity between the IR and PMR data for the complexes IV—VI and XI and those of complex IVa indicates that all the dimeric complexes have structures analogous to that of IVa shown.

Preparative methods, yields, melting points, PMR, and analytical data for the complexes IV—VI and XI are presented in Table 1.

Methods of preparation

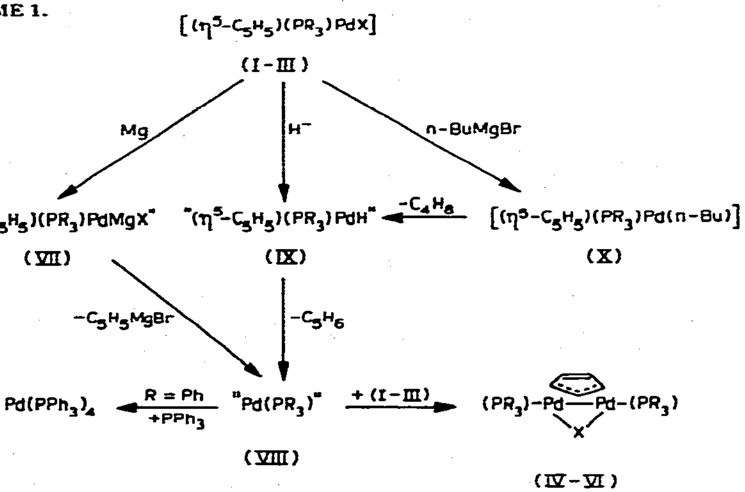
Method 1: reduction with magnesium

The complexes I—III were reduced by magnesium in THF to give the dimeric complexes IV—VI. The reaction of magnesium with the bromide Ia in THF was followed by PMR spectroscopy. When reaction of Ia was complete a triplet at τ 4.75 (J(P—H) = 2 Hz), due to the C_5H_5 protons of IVa, and a sharp singlet at τ 4.01, apparently due to C_5H_5MgBr, (lit.: τ 4.06 [8]) were observed. The addition of one drop of water caused this singlet to disappear and a multiplet centred at τ 3.56 was observed due to the vinyl protons of cyclopentadiene.

The reaction probably proceeds via initial insertion of magnesium into the Pd—X bond to give the "inorgano-Grignard" species VII. It has been shown that the analogous complexes $[(\eta^5\text{-}C_5H_5)(PPh_3)NiBr]$ and $[(\eta^5\text{-}C_5H_5)(Ph_2PCH_2CH_2\text{-}$

PPh_2)FeBr] react with magnesium under the same conditions to give "inorgano-Grignard" reagents [9,10]. The presumed intermediates VII may then undergo loss of C_5H_5MgX to give the palladium(0) species VIII, which then react with I—III to give the dimers IV—VI, as shown in Scheme 1.

SCHEME 1.



Method 2: reaction with sodium amalgam

The reaction of Ia with sodium amalgam in THF was followed by PMR spectroscopy. A singlet at τ 4.30 was observed in the PMR spectrum of the reaction mixture, presumably due to C_5H_5Na (lit.: τ 4.48 [11]). This singlet disappeared on adding water and a signal at τ 3.58, due to cyclopentadiene, was observed.

Method 3: reduction with $LiAlH(t\text{-}BuO)_3$, $LiAlH_4$ or $NaBH_4$

Reaction of the complexes I—III with these hydridic reducing agents probably proceeds via initial formation of the as yet unreported hydrido complexes IX as unstable intermediates, which then decompose by elimination of cyclopentadiene (observed in the PMR spectra of products) to give VIII as further intermediates. These palladium(0) species may then react with the complexes I—III to give the dimers IV—VI, as shown in Scheme 1.

The stoichiometric reaction, in THF, of $LiAlH(t\text{-}BuO)_3$ with the bromide Ib in the presence of excess PPh_3 gave the palladium(0) complex $Pd(PPh_3)_4$. In the absence of PPh_3 palladium metal was formed.

Method 4: reduction with n-BuMgBr

Reaction of Ib with n-BuMgBr proceeds by initial formation of the unstable but isolable n-butyl complex Xb [12] which decomposes at 25°C, presumably by β-hydrogen elimination from the n-butyl group, to give but-1-ene and the unstable hydrido-intermediate IXb which would lead to the dimeric complex IVb as shown in Scheme 1.

The reaction of an equimolar mixture of Ib and Xb in C_6D_6 was followed by PMR spectroscopy. The products were but-1-ene, cyclopentadiene and, quantitatively, IVb.

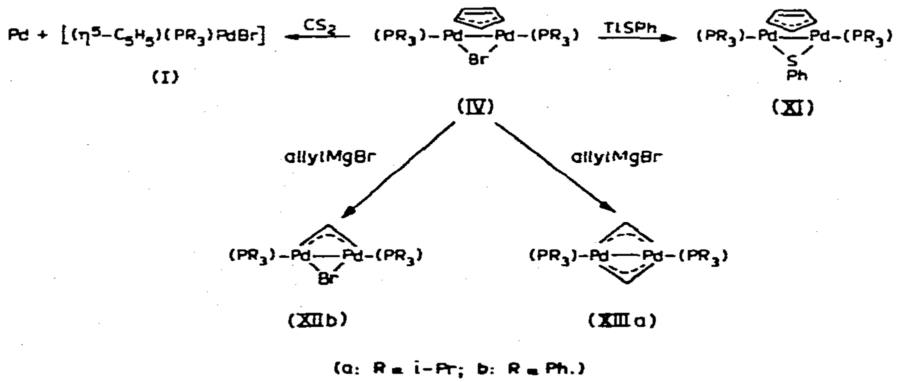
The n-butyl complex Xb decomposed in benzene in the presence of excess PPh_3 to give cyclopentadiene, but-1-ene and $Pd(PPh_3)_4$.

All the proposed mechanisms for the reduction of the palladium(II) complexes I—III to give the dimeric complexes IV—VI involve the highly electron deficient palladium(0) species "$Pd(PR_3)$", VIII. The formation of such a zerovalent palladium species is supported by the fact that the 1 : 1 reaction of $LiAlH(t\text{-}BuO)_3$ with Ib in THF in the presence of excess PPh_3 gave $Pd(PPh_3)_4$. Also the decomposition of the n-butyl complex X in the presence of excess PPh_3 gave but-1-ene, cyclopentadiene and $Pd(PPh_3)_4$.

Reactions

Some reactions of the dimeric complexes IV are summarised in Scheme 2.

SCHEME 2.



The reaction of one equivalent of CS_2 with IVa and IVb in C_6D_6 gave the monomeric complexes Ia and Ib respectively, together with palladium metal. Both IVa and IVb react with TlSPh in C_6D_6 to give the corresponding bridging thiophenolato complexes XIa and XIb.

AllylMgBr reacts with IVb in THF replacing the C_5H_5 group to give the bridging allyl complex XIIb, similar to that reported previously [13]. Reaction of XIIb with excess allylMgBr at 25°C failed to replace the bromine atom. In contrast to this the 1 : 1 reaction of allylMgBr with IVa gave a mixture of the bis(μ-allyl) complex XIIIa and IVa (and probably some XIIa). Two equivalents of allylMgBr react with IVa to give a high yield of XIIIa.

Attempts to replace the bridging bromine atom of the complexes IVa or IVb with other potentially bridging groups (using TlOCOPh, TlSCN, TlS_2CNEt_2, TlC_5H_5) led to decomposition and deposition of palladium metal.

Experimental

All experiments were carried out under dry, purified nitrogen, using dried, degassed solvents. THF was distilled from $LiAlH_4$ immediately before use; other solvents were dried by standard methods. IR spectra were recorded on a Perkin—Elmer 257 spectrometer, and PMR spectra with a Perkin—Elmer R12B spectrometer, operating at 35°C and 60 MHz.

TABLE 2

MELTING POINTS, PMR AND ANALYTICAL DATA FOR THE COMPLEXES η^5-CYCLOPENTADIENYL-TERTIARY PHOSPHINE PALLADIUM HALIDE, I—III

Compound	PR_3	X	M.p. [a] (°C)	PMR of C_5H_5 group [b]		Analysis: Found (calcd) (%)
				τ	J(P—H) (Hz)	
Ia	P(i-Pr)$_3$	Br	111—112	4.19	2.5	ref. 6
Ib	PPh$_3$	Br	132—133 (dec.)	4.36	2.5	ref. 6
Ic [c]	PCy$_3$	Br	188—190 (dec.)	4.24	2.5	C; 51.79 (51.94); H, 7.09 (7.20); Br, 14.38 (15.03)
II [c]	P(i-Pr)$_3$	Cl	93—94 (dec.)	4.21	3.0	C, 46.16 (45.79); H, 6.98 (7.14); Cl, 9.41 (9.66)
III [c]	P(i-Pr)$_3$	I	92—94	4.12	3.0	C, 36.88 (36.66); H, 5.60 (5.71); I, 28.73 (27.67)

[a] Capillary tubes, in air; dec. = decomposed. [b] $CDCl_3$ solution, TMS internal reference. [c] New compounds.

The complexes I—III were prepared by literature methods [6], and their melting points, PMR and analytical data are presented in Table 2.

In several preparations of the complexes Ib and Ic the products were contaminated with up to 30% of the dimeric complexes IVb and IVc. Pure samples of Ib and Ic were therefore obtained by chromatography or fractional crystallisation.

Preparation of complexes of the type [μ-(η^3-C_5H_5)-μ-$XPd_2(PR_3)_2$]

Methods of preparation and yields of the complexes IV—VI are summarised in Table 1. Only one example of each method is given below.

Method 1. Reduction with Mg. 15 ml THF were distilled onto 0.904 g (2.2 mmol) of complex Ia and 0.5 g magnesium turnings (excess) in a Schlenk tube. The mixture was warmed to 25°C and stirred for 2 h. The colour turned from green to dark red. The solution was then filtered and the THF removed under reduced pressure, leaving a red-black solid which was extracted with toluene (2 × 5 ml). The resulting clear, deep-red solution was concentrated to 2 ml, 30 ml pentane were added and the solution was cooled to —30°C for 24 h. Dark red crystals of μ-(η^3-cyclopentadienyl)-μ-bromo-bis(triisopropylphosphine palladium), IVa, were filtered off. Yield 0.750 g (82%). IR (nujol): 3100w, 3075w, 3030w, 1239m, 1156m (br), 1092m, 1057m, 1024m, 922w (br), 880s, 797m, 764m—s, 717m—s, 655s cm^{-1}.

Method 2. Reduction with Na/Hg. To a stirred solution of 0.510 g of complex Ia (1.24 mmol) in 25 ml THF was added excess Na/Hg (1.2% w/w). The solution, which quickly turned black, was decanted from excess Na/Hg and filtered through 2 cm Al_2O_3. The solvent was removed to give a red-black solid. Work-up of this solid, as described above, gave 0.200 g IVa (48%).

Method 3. Reduction with metal hydrides. (i): LiAlH(t-BuO)$_3$. 3.4 ml of a THF solution of LiAlH(t-BuO)$_3$ (0.15 *M*, 0.51 mmol) were added slowly, with stirring, to a solution of 0.532 g of Ic (1.00 mmol) in 15 ml THF. The colour changed immediately from green to red. The THF was removed under reduced pressure and the resulting solid extracted with 3 × 5 ml toluene. The red toluene solution was concentrated to ca. 5 ml, 15 ml hexane were added, and the solution was cooled to $-30°$C for 24 h. The red powdery complex μ-(η^3-cyclopentadienyl)-μ-bromo-bis(tricyclohexylphosphine palladium), IVc, was filtered off, washed with pentane and air-dried. Yield 0.383 g (83%). Recrystallisation from toluene/hexane at $-30°$C gave an analytically pure sample. (*ii*): $LiAlH_4$. 0.10 g $LiAlH_4$ (2.6 mmol) in 15 ml THF was added slowly to 0.87 g of Ic (1.65 mmol) in 15 ml THF. The solution became red-black immediately. 1 ml EtOH was added to destroy the excess $LiAlH_4$ and the solvents were removed under reduced pressure leaving a grey-red solid. Work up, as described in 3(i) gave red needles of IVc. Yield 0.62 g (83%). (*iii*): $NaBH_4$. Reaction of Ia with solid $NaBH_4$ in THF gave 26% IVa after 15 days.

Method 4. Reduction with n-BuMgBr. 0.4 ml of an Et_2O solution of n-BuMgBr (1.3 *M*, 0.52 mmol) was added dropwise, with stirring, to 0.513 g Ib (1.0 mmol) in 15 ml THF at $-78°$C. The solution was allowed to warm to $-40°$C, and became dark-red after 45 min. The solution was then warmed to 25°C, filtered through a 2 cm column of Al_2O_3, 4 ml toluene were added, and the volume reduced to ca. 4 ml under reduced pressure. Addition of 20 ml pentane gave a red-brown precipitate of μ-(η^3-cyclopentadienyl)-μ-bromo-bis(triphenylphosphine palladium), IVb, which was filtered off, washed with pentane and dried in vacuum. Yield 0.40 g (91%). The product was recrystallised by dissolving in 20 ml CH_2Cl_2, adding 5 ml toluene, and reducing the volume to ca. 5 ml.

Reaction of (IVa) with CS_2

3.2 μl of CS_2 (0.053 mmol) were added to 36 mg IVa (0.053 mmol) in 0.6 ml C_6D_6. In the PMR spectrum the resonance due to the C_5H_5 group of IVa disappeared and was replaced by a doublet of equal intensity at τ 4.37, J(P—H) = 2.5 Hz, due to the C_5H_5 group of Ia. Palladium metal was deposited on the sides of the tube.

A similar experiment with IVb and CS_2 gave Ib and palladium metal.

Reaction of IVa with TlSPh

To 43 mg of complex IVa (0.064 mmol) in 0.6 ml C_6D_6 were added 20 mg TlSPh (0.064 mmol). The mixture was shaken for 5 min and the precipitated TlBr centrifuged to the stoppered end of the PMR tube. The PMR spectrum showed resonances due to μ-(η^3-cyclopentadienyl)-μ-thiophenolato-bis(tri-isopropylphosphine palladium), XIa, (C_6H_5: τ 2.5—3.2 (m), C_5H_5: τ 4.2 (t) J(P—H) = 2 Hz; i-Pr: τ 7.8—9.2 (m)). Removal of solvent and crystallisation from pentane at $-30°$C gave pure product in 87% yield.

μ-(η^3-cyclopentadienyl)-μ-thiophenolato-bis(triphenylphosphine palladium), XIb, was prepared similarly from IVb and TlSPh and recrystallised from toluene/pentane.

Reaction of IVa with allylMgBr

7.1 ml of an Et_2O solution of allylMgBr (0.68 *M*, 4.83 mmol) were added to 0.655 g IVa (0.996 mmol) in 20 ml THF (25°C). Yellow crystals of bis-[μ-(η^3-allyl)tri-isopropylphosphine palladium], XIIIa, were deposited after 10 min and were washed with H_2O, EtOH, and Et_2O. Yield 0.381 g (64%). Anal. Found: C, 46.40; H, 8.23; calcd.: C, 46.84; H, 8.52%.

Reaction of IVb with allylMgBr

To 0.729 g IVb (0.827 mmol) in 15 ml THF was added 1.4 ml of allylMgBr solution (0.68 *M*, 0.95 mmol). The resulting orange solution was hydrolysed (NH_4Cl, aq.) and dried ($MgSO_4$). Removal of solvent left a yellow solid which was recrystallised from CH_2Cl_2/toluene to give μ-(η^3-allyl)-μ-bromo-bis(triphenylphosphine palladium), XIIb. Yield 0.60 g (85%). Anal. Found: C, 54.60; H, 4.20; Br, 9.41. calcd.: C, 54.57; H, 4.11; Br, 9.31%.

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