*Journal of Organometallic Chemistry*, 54 (1973) 345–355



# 2,2′-BI-π-ALLYL COMPLEXES OF PALLADIUM(II)

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(Received September 26th, 1972)

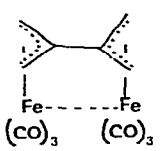
SUMMARY

The preparation and properties of a series of dinuclear palladium(II) complexes containing a bridging 2,2′-bi-π-allyl ligand are described. When the complexes contain bridging carboxylate ligands the bridging 2,2′-bi-π-allyl ligand is asymmetrically distorted. The distortion is different when the carboxylate ligands are replaced by μ-1,3-diphenyltriazene.

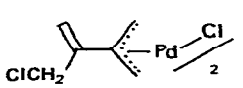
## INTRODUCTION

In the course of an investigation of the insertion of allene into the allyl–palladium bond of acetylacetonato-π-allylpalladium, it was observed that at high allene/Pd ratios a competing reaction occurred, yielding a white crystalline complex, bis(acetylacetonato)-2,2′-bi-π-allyldipalladium(II)[1]. This paper reports the synthesis and spectroscopic properties of a variety of palladium(II) complexes containing the 2,2′-bi-π-allyl ligand.

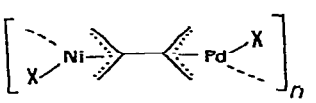
Complexes containing the 2,2′-bi-π-allyl ligand have been reported for only three transition metals. Reaction of allene with $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ yields a complex (I) in which the 2,2′-bi-π-allyl ligand has been reported to undergo a valence tautomerism, as evidenced by $^1H$ NMR spectroscopic studies[2,3]. This same complex (I) has also been prepared from the reaction of (π-2-Cl-$C_3H_4$)$Fe(CO)_3Cl$ with zinc dust[4]. After the commencement of this study, Keim[5] reported that the palladium complex (II), reacted with bis(1,5-cyclooctadiene)nickel(0) to yield the mixed metal complex (III) via an oxidative addition of the allylic chloride function in (II) to the zerovalent nickel species. Reaction of complex (III) with cyclopentadienylsodium was shown to yield complex (IVa) which apparently disproportionated in solution to



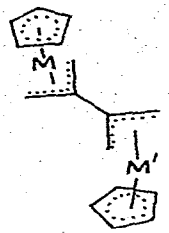
(I)



(II)

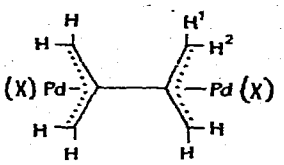


(III)



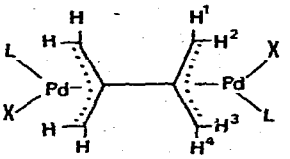
(IV)

(IVa): M = Ni; M′ = Pd
(IVb): M = M′ = Ni



(V)

(Va): X = Cl
(Vb): X = Acac
(Vc): X = Hfacac
(Vd): X = $\pi$-$C_5H_5$



(VI)

(VIa): X = Cl; L = Py
(VIb): X = Cl; L = $PPh_3$
(VIc): X = Cl; L = $AsPh_3$
(VId): X = $O_2CCH_3$; L = Py
(VIe): X = $O_2CCF_3$; L = Py
(VIf): X = $O_2CCCl_3$; L = Py
(VIg): X = $O_2CCF_3$; L = $PPh_3$
(VIh): X = $O_2CCCl_3$; L = $PPh_3$

yield the homonuclear complex (IVb) (M = M′ = Ni) and presumably the dipalladium analogue, although this latter complex could not be isolated[5]. The molecular structure of complex (IVb) (M = M′ = Ni) has recently been determined[6].

## RESULTS

Reaction of a 1/1 mixture of complex (II) and lithium tetrachloropalladate(II) with $CO/H_2O$ in chloroform/methanol solution yielded complex (Va) as an insoluble precipitate in high yield. Reaction of complex (Va) with acetylacetonatothallium(I) in chloroform or benzene precipitated thallium(I) chloride and yielded complex (Vb). This latter complex proved identical in physical and spectroscopic properties to that obtained from the reaction of acetylacetonato-$\pi$-allylpalladium(II) with high concentrations of allene[1]. Treatment of complex (Va) with (hexafluoroacetylacetonato)-thallium(I) yielded complex (Vc). Reaction of complex (Va) with cyclopentadienylsodium in THF solution afforded the analogous $\pi$-cyclopentadienyl derivative (Vd). $^1$H NMR data for complexes (Vb,c,d) are assembled in Table 1. Complex (Va) proved too insoluble in common organic solvents to obtain any $^1$H NMR data.

Complex (Va) reacted readily with basic ligands to yield complexes (VIa–c). The pyridine derivative proved too insoluble for NMR measurements but $^1$H NMR data for the triphenylphosphine and triphenylarsine complexes are presented in Table 2.

TABLE 1

$^1$H NMR DATA FOR COMPLEXES (V)[a]

| *Complex* | *X* | $\tau$ | | |
|---|---|---|---|---|
| | | $H^1$ | $H^2$ | *Other resonances* |
| (Vb) | Acac | 5.99(s) | 7.19(s) | Acac: CH, 4.67(s); $CH_3$, 8.04(s) |
| (Vc) | Hfacac[b] | 6.58(s) | 8.10(s) | Hfacac: CH, 3.80(s) |
| (Vd) | $\pi$-$C_5H_5$ | 6.35(s) | 7.70(s) | $C_5H_5$: 4.22(s) |

[a] 100 MHz; $CDCl_3$; 34°. [b] Spectrum recorded in $C_6D_6$ because of the poor solubility of this complex in $CDCl_3$.

Reaction of complex (Va) with a variety of silver carboxylates in dichloromethane or chloroform yielded complexes (VIIa–e). Refluxing a chloroform solution of complex (VII a) with an excess of trifluoroacetic acid or trichloroacetic acid effected a carboxylate bridge replacement reaction yielding analogous complexes (VII f,g). Similarly, treatment of (VIIa) with 1,3-diphenyltriazene yielded a complex (VIII), with liberation of acetic acid. $^1$H NMR data for complexes (VII) are presented in Table 3. Infrared stretching frequencies for the carboxylate ligands in complexes (VII) are presented in Table 4.

TABLE 2

$^1$H NMR DATA FOR COMPLEXES (VIb) AND (VIc)[a]

| *Complex* | *L* | *Relative intensity of AGMX pattern*[b] | *τ, (multiplicity)*[c]*, J(Hz)* | | | | |
|---|---|---|---|---|---|---|---|
| | | | $H^1$ | $H^2$ | $H^3$ | $H^4$ | *L* |
| (VIb) | $PPh_3$ | 1 | 5.25(dd) $J$(P–H)6 $J_{1,4}$1 | 6.28(d) $J$(P–H)10 | 7.18(s) | 7.05(bs) | |
| | | 2 | 5.51(dd) $J$(P–H)6 $J_{1,4}$1 | 6.43(d) $J$(P–H)10 | 7.18(s) | 6.75(bs) | 2.40(m) |
| (VIc) | $AsPh_3$ | 1 | 5.15(bs) | 6.26(s) | 7.21(s) | 6.59(bs) | 2.40(m) |
| | | 2 | 5.45(bs) | 6.36(s) | 7.21(s) | 6.48(bs) | |

[a] 100 MHz; $CDCl_3$; −40°. [b] Each spectrum consists of two overlapping AGMX patterns. [c] Notation: s, singlet; d, doublet; m, multiplet; b, broad.

TABLE 3

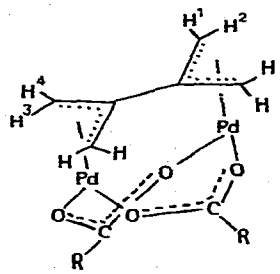
$^1$H NMR DATA FOR COMPLEXES (VII)[a]

| *Complex* | *R* | *τ, (multiplicity)*[b]*, J(Hz)* | | | | |
|---|---|---|---|---|---|---|
| | | $H^1$ | $H^2$ | $H^3$ | $H^4$ | *Other resonances* |
| (VIIa)[c] | $CH_3$ | 5.86(s) | 6.93(s) | 7.33(s) | 6.14(s) | $CH_3$, 7.97(s) |
| (VIIb) | $CH_3CH_2$ | 5.84(s) | 6.90(s) | 7.28(s) | 6.13(s) | $CH_3$, 8.95(t) $CH_2$, 7.70(q) $J$ 7.5 |
| (VIIc) | $(CH_3)_2CH$ | 5.88(s) | 6.92(s) | 7.27(s) | 6.17(s) | CH, 7.48(h) $CH_3$, 8.95(d) 8.96(d)[d] $J$ 7 |
| (VIId) | $C_6H_5$ | 5.68(s) | 6.63(s) | 7.07(s) | 5.98(s) | $C_6H_5$, 2.33(m) |
| (VIIe) | $C_6H_5CH_2$ | 6.01(s) | 7.01(s) | 7.42(s) | 6.27(s) | $C_6H_5$, 2.80(m) $CH_2$, 6.50(s) |

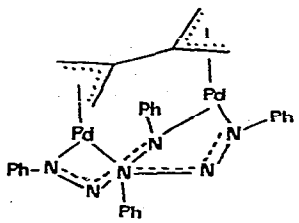
[a] 100 MHz; $CDCl_3$; 27°. [b] Notation: s, singlet; d, doublet; t, triplet; q, quartet; h, heptet; m, multiplet. [c] Spectrum of (VIIa) is temperature independent from −100° to +60°. [d] Methyl groups are diastereotopic due to molecular asymmetry.

The trichloroacetate complex (VIIg) was isolated as red needles which, on heating to 120°, underwent a change to a second yellow form. On cooling to room temperature the yellow form slowly reverted to the original red form. Reflectance infrared studies on both forms indicated them to have identical spectra, with bridging trichloroacetate ligands.

Treatment of complexes (VII) with pyridine or triphenylphosphine resulted in cleavage of the carboxylate bridge to yield complexes (VId–h). Infrared stretching frequencies for the carboxylate ligands in complexes (VId–h) are given in Table 4.

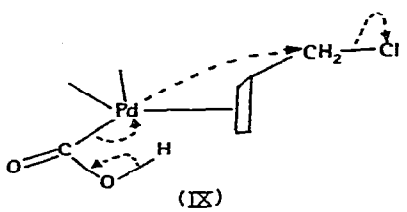



(VII)

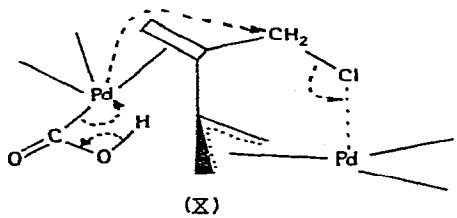



(VIII)

(VIIa): R = $CH_3$
(VIIb): R = $C_2H_5$
(VIIc): R = $(CH_3)_2CH$
(VIId): R = Ph
(VIIe): R = $PhCH_2$
(VIIf): R = $CF_3$
(VIIg): R = $CCl_3$




(IX)




(X)

TABLE 4

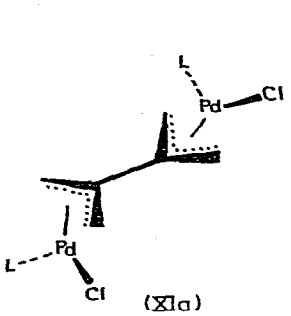
CARBOXYLATE INFRARED STRETCHING FREQUENCIES FOR COMPLEXES (VI) [X = $O_2CR$] AND (VII)[a]

| *Complex* | *L* | *Carboxylate* | $\nu_{asym}$ | $\nu_{sym}$ |
|---|---|---|---|---|
| (VIIa) | | $CH_3CO_2$ | 1570 | 1420 |
| (VIIb) | | $CH_3CH_2CO_2$ | 1570 | 1420 |
| (VIIc) | | $(CH_3)_2CHCO_2$ | 1570 | 1420 |
| (VIId) | | $C_6H_5CO_2$ | 1550 | 1400 |
| (VIIe) | | $C_6H_5CH_2CO_2$ | 1580 | 1400 |
| (VIIf) | | $CF_3CO_2$ | 1665 | 1460 |
| (VIIg) | | $CCl_3CO_2$ | 1635 | 1350 |
| (VId) | Py | $CH_3CO_2$ | 1610 | 1370 |
| (VIe) | Py | $CF_3CO_2$ | 1690 | 1410 |
| (VIf) | Py | $CCl_3CO_2$ | 1680 | 1310 |
| (VIg) | $PPh_3$ | $CF_3CO_2$ | 1690 | 1420 |
| (VIh) | $PPh_3$ | $CCl_3CO_2$ | 1690 | 1315 |

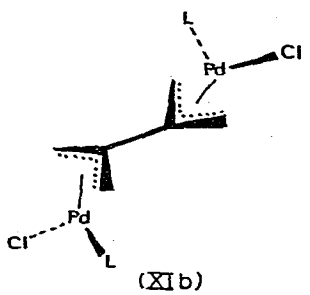
[a] In $cm^{-1}$; measured as Nujol mulls.

## DISCUSSION

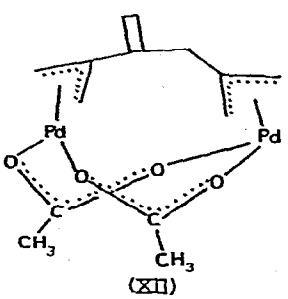
The $CO/H_2O$ reduction of the $PdCl_4^{2-}$ ion in the presence of allylic halides is a common method for the preparation of π-allylic palladium halides[7], via the intermediate (IX)[8]. Utilization of the allylic chloride function present in complex (II), in the same reaction, provides an excellent, high yield synthesis of complex (Va). This reaction is normally carried out in methanol solution[7,8]. Preparation of complex (Va), however requires the use of a chloroform/methanol solvent system, in order to keep both reactant palladium species in solution. A notable feature of formation of complex (Va) by this route is its rapidity compared to a comparable reaction using an organic allyl halide (*e.g.* the reaction is complete within 0.5 min compared to ≈20 min in the preparation of π-allylpalladium chloride dimer). Assuming the same mechanism[8] to be operative, the reaction intermediate may be formulated as (X). If decomposition of (IX) and (X) are rate-determining, the rate enhancement observed for formation of (Va) can be rationalised in terms of palladium assisted cleavage of the carbon–chlorine bond in the allylic halide function, a feature not possible in the monometallic intermediate (IX). An X-ray crystallographic study of complex (II) has shown the allylic chlorine atom to be situated in close proximity to the palladium atom, on the *z*-axis of coordination[9].




(XIa)




(XIb)




(XII)

Complex (Va) undergoes typical reactions involving replacement of chloride ligands as has previously been demonstrated for dimeric π-allylic palladium halides[10,11]. As expected, the $^1H$ NMR spectra of the complexes (Vb, c and d) exhibit two singlet resonances for the protons on the 2,2′-bi-π-allyl ligand. Thus the four *syn*-protons are equivalent as are the four *anti*-protons. The proton-decoupled $^{13}C$ NMR spectrum of complex (Vc) in $C_6D_6$ solution at 34°, shows two carbon resonances for

the 2,2'-bi-$\pi$-allyl unit at 55.4 ppm (terminal C's) and 122.6 ppm (internal C's) downfield from TMS (*cf.* $^{13}$C NMR data for $\pi$-allylic palladium complexes[12]). Two isomers are possible with respect to the disposition of the Pd(X) systems in (V) about the 2,2'-bi-$\pi$-allyl moiety, *i.e.* both palladium atoms may occupy sites on the same face (cisoid) or on opposing faces (transoid) of the 2,2'-bi-$\pi$-allyl system. The $^1$H NMR spectrum of complex (V d) is temperature independent from $-100°$ to $+60°$ implying that if two rotameric forms do exist, they cannot be frozen out within this temperature range. The molecular structure of the nickel analogue of complex (V d) shows it to exist in the transoid form[6] and, on the basis of steric requirements it seems likely that the palladium complexes (Vb–d) would prefer this conformation.

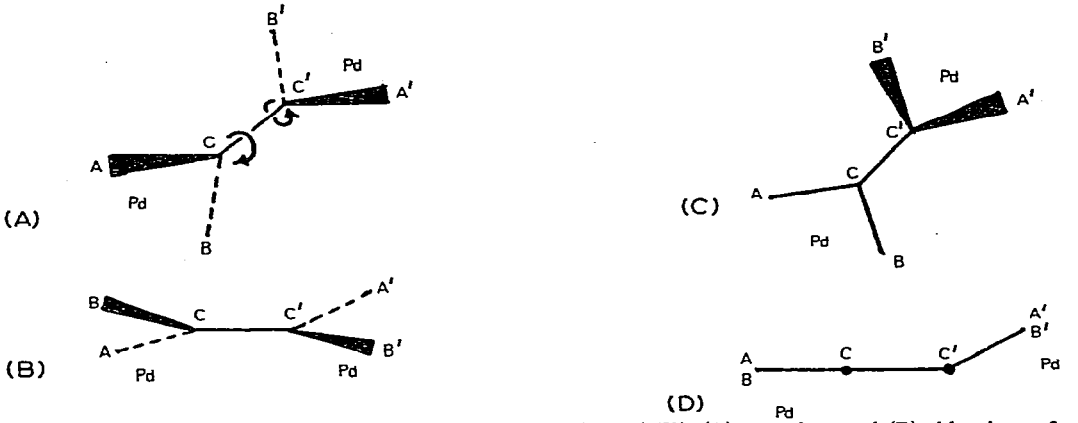
Complex (V a) is presumably polymeric, with bridging chloride ligands, or, by analogy with the structure of allylplatinum chloride[13], may possibly be tetrameric.

Preparation of complexes (VI) is readily achieved by bridge-splitting reactions using the appropriate donor ligand. The pyridine derivative (VI a) proved too insoluble for $^1$H NMR studies. At room temperature the NMR spectra of the $PPh_3$ and $AsPh_3$ derivatives (VIb) and (VIc) were extremely broad, presumably due to rapid exchange process(es) of the type observed in ($\pi$-Allyl)$PdCl(PPh_3)$[14,15]. However, the low temperature ($-40°$) $^1$H NMR spectra (see Table 2) of complexes (VIb) and (VIc) exhibited an interesting feature in that they comprised two overlapping AGMX patterns, in unequal proportions. An AGMX pattern is characteristic for the *syn*- and *anti*-protons of an unsymmetrically bound 2-substituted $\pi$-allylic ligand[14,15] but since the two overlapping patterns are not present in a 1/1 ratio they cannot involve different allylic environments within the same molecule. Two explanations are possible. Firstly, the patterns could arise from unequal proportions of cisoid and transoid isomers, with respect to the 2,2'-bi-$\pi$-allyl plane. This seems to be unlikely since no signs of isomers are observed in complex (V d). A more likely explanation is formation of two sets of diastereoisomeric pairs of unequal population [*e.g.* (XI a) and (XI b)]. One AGMX pattern may thus arise from the *DD,LL* diastereoisomeric pair and the other from the *DL,LD* pair. Since unequal populations are observed, asymmetric induction must affect the relative populations of both pairs.

The bridging carboxylate complexes (VII a–f) containing the 2,2'-bi-$\pi$-allyl ligand are readily prepared. IR data for complexes (VII) (Table 4) are consistent with bridging carboxylate linkages. Molecular weight data for the trichloroacetate complex (VII g) indicated a monomeric structure in chloroform solution, and the mass spectrum of complex (VII a) showed a molecular ion (*m/e* 410). $^1$H NMR data (Table 3) however, indicated four different proton environments within the bi-$\pi$-allyl ligand, indicating some type of distortion within this moiety. Chemical evidence for strain in the 2,2'-bi-$\pi$-allyl ligand in complex (VII a) has been demonstrated by the observation that this complex readily inserts one molecule of allene [ to give complex (XII)] whereas dimeric $\pi$-allyl-palladium acetate does not[16–18]. No further insertion of allene into (XII) was observed, consistent with complex (XII) containing an unstrained organic ligand.

The source of strain in complex (VII) may arise from a rigidity of the acetate bridge system which would impose a fixed distance between the two palladium atoms in the molecule. The Pd–Pd distance in di-$\mu$-acetatodiallyldipalladium(II)[19] is 2.94 Å and that in di-$\mu$-acetatodichlorobis(dimethylphenylphosphine)dipalladium(II)[20] is 2.946 Å. The overall length of the planar 2,2'-bi-$\pi$-allyl ligand in di-$\pi$-cyclopentadienyl-

2,2'-bi-π-allyldinickel(II)[6] is ca. 2.82 Å. Thus the *planar* 2,2'-bi-π-allyl moiety is *too short* to bridge a Pd–Pd separation of 2.94 Å and must distort itself in order to bond effectively to each palladium. Two types of distortion are possible, each of which gives rise to a 2,2'-bi-π-allyl ligand containing four distinct proton environments. Firstly, a torsional twisting about the 2,2'-carbon–carbon bond could accommodate the required Pd–Pd distance [(A) and (B)]. Secondly, an out-of-plane distortion of one allyl unit [(C) and (D)] would have the same effect of increasing the effective bridging capability of the 2,2'-bi-π-allyl unit.




Possible distortions of the 2,2'-bi-π-allyl ligand in complexes (VII). (A) top view and (B) side view, of torsional twisting about the 2,2'-bond; (C) top view and (D) side view of the out-of-plane distortion of one allylic unit.

In terms of the $^1$H NMR spectra the distortion shown in (A) and (B) gives rise to two equivalent unsymmetrically bound allyl palladium bonds whereas the distortion shown in (C) and (D) gives two non-equivalent symmetrically bound allyl palladium bonds. Either case predicts four non-equivalent proton environments. However, (A) and (B) predict only three distinct carbon environments within the 2,2'-bi-π-allyl ligand, namely A=A', B=B', and C=C'. (C) and (D) predict four carbon environments, namely A=B, A'=B', C, and C'(C≠C'). The proton-decoupled $^{13}$C NMR spectrum of (VIIa) exhibits four carbon resonances for the 2,2'-bi-π-allyl ligand; two terminal carbons at 48.0 and 52.7 ppm, and two internal carbons at 118.7 and 122.0 ppm, thus confirming the probable structural distortion as shown in (C) and (D).

The $^1$H NMR spectrum of di-μ-(1,3-diphenyltriazeno)-2,2'-bi-π-allyldipalladium(II), (VIII), in $CDCl_3$ at 34°, in contrast to its di-μ-acetato analogue, shows only two singlet proton peaks attributable to the 2,2'-bi-π-allyl ligand at τ 6.20 (*syn*) and τ 7.16 (*anti*). Evidently the 2,2'-bi-π-allyl ligand in complex (VIII) does not exist under the same conditions of distortion as are imposed on its acetate analogue. X-ray crystallographic determinations on a bridging 1,3-diphenyltriazeno complex of nickel(II) have shown a small Ni–Ni separation (2.38 Å)[21]. This was attributed by the authors to a metal–metal interaction but could conceivably be ascribed to the bridging characteristics of the μ-1,3-diphenyltriazeno linkage, which may force the two metal atoms close together. Thus the palladium–palladium separation imposed

by the bridging ligands in complex (VIII) is probably considerably less than 2.94 Å, allowing the 2,2'-bi-$\pi$-allyl ligand to bridge the two palladium atoms symmetrically.

Complexes (VIIf and g) proved too insoluble for $^1$H NMR measurements. Their IR spectra did exhibit bands characteristic of bridging carboxylate ligands[20] however, and their structure is presumed to be analogous to their acetate analogue.

The change from bridging to monodentate carboxylate groups on going from (VII) to (VI) [X = $O_2$CR] was evidenced by an increase in the value of $\Delta(\nu_{asym} - \nu_{sym})$ in complexes (VI) relative to their precursors[22]. Complexes (VI) [X = $O_2$CR] are considerably more stable than their $\pi$-allyl analogues [($\pi$-Allyl)Pd(OAc)L][23,24] and this is probably a consequence of the strain in complexes (VII). The $^1$H NMR spectra of complexes (VId–h) were very broad at room temperature. At low temperatures spectra were obtained which were similar to those observed for the analogous monomeric $\pi$-allylic systems[25], but no detailed studies of the variable temperature behaviour of complexes (VId–h) were undertaken. No doubling of $^1$H NMR resonance patterns analogous to those observed for complexes (VIb–c), were observed for complexes (VId–h), even on cooling to $-70°$.

## EXPERIMENTAL

$^1$H NMR spectra were run on Varian Associates Model A56/60D, or HA-100 spectrometers. Temperature calibrations were made using a methanol reference sample (Varian 943346-06).

$^{13}$C NMR spectra were run at 25.16 MHz on a Varian Associates Model XL-100-15 spectrometer, operating in the pulsed Fourier Transform mode, and utilising a Varian 620i computer with a 16K memory.

Mass spectra were run on a Bell and Howell Model 21-490 spectrometer at an ionisation energy of 70eV.

Infrared spectra were recorded on a Beckman Model IR 20 spectrometer, and calibrated using a polystyrene reference.

Molecular weights were measured using a Mechrolab Model 301A Vapour Pressure Osmometer.

Melting points were determined on a Kofler hot-stage apparatus and are corrected.

Di-$\mu$-chlorobis-$\pi$-[2-(3-chloro-1-propen-2-yl)allyl]dipalladium(II) was prepared by literature methods[26–29]. (Acetylacetonato)thallium(I), cyclopentadienylsodium, trifluoroacetic acid, trichloroacetic acid, 1,3-diphenyltriazene, and silver acetate were all commercial samples, used without further purification.

Other silver carboxylates were prepared by reaction of the sodium salt of the acid with silver nitrate, in aqueous solution. The precipitated silver salt was filtered at the pump, washed with water and acetone, and dried *in vacuo*.

### *Complexes (V)*

*Complex (Va): di-$\mu$-chloro-2,2'-bi-$\pi$-allyldipalladium(II).* A solution of di-$\mu$-chlorobis-$\pi$-[2-(3-chloro-1-propen-2-yl)allyl]dipalladium(II) (0.654 g) in chloroform (125 ml) was treated with a solution of palladous chloride (0.470 g) and lithium chloride (0.240 g) in a mixture of methanol (65 ml) and water (3 ml). Carbon monoxide was bubbled rapidly through the resultant solution. The initial orange-brown colour faded

rapidly and the product was precipitated as a lemon-yellow, amorphous solid (0.810 g, 88%), dec. 215–220°. (Found: C, 20.12; H, 2.26; Cl, 19.7. $[C_6H_8Cl_2Pd_2]_n$ calcd.: C, 19.81; H, 2.21; Cl, 19.49%.)

*Complex (Vb): bis(acetylacetonato)-2,2'-bi-π-allyldipalladium(II).* A suspension of di-μ-chloro-2,2'-bi-π-allyldipalladium(II) (0.250 g) in chloroform (70 ml) was treated with (acetylacetonato)thallium(I) (0.460 g) and the resultant mixture was shaken vigorously (3 h). Filtration, followed by evaporation of the filtrate to dryness under reduced pressure, and recrystallisation of the residue from a chloroform/petroleum ether (b.p. 30–60°) mixture, yielded the product as colourless needles (0.220 g, 65%), dec. >185°. (Found: C, 39.37; H, 4.61. $C_{16}H_{22}O_4Pd_2$ calcd.: C, 39.12; H, 4.51%.)

An analogous procedure using (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-thallium(I) yielded bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)-2,2'-bi-π-allyldipalladium(II), complex (Vc), as pale yellow needles (81%), dec. 190–195°, after recrystallisation from benzene/petroleum ether (b.p. 30–60°). (Found: C, 27.27; H, 1.36; mol. wt. osmometrically in $C_6H_6$, 705. $C_{16}H_{10}F_{12}O_4Pd_2$ calcd.: C, 27.18; H, 1.43%; mol. wt., 706.)

*Complex (Vd): di-π-cyclopentadienyl-2,2'-bi-π-allyldipalladium(II).* A suspension of di-μ-chloro-2,2'-bi-π-allyldipalladium(II) (0.700 g) in dry tetrahydrofuran (25 ml) was treated with cyclopentadienylsodium (2.20 ml of a 1.96 *M* solution in tetrahydrofuran), under an atmosphere of dry nitrogen. The resultant mixture was filtered. Evaporation of the filtrate to dryness under reduced pressure, and recrystallisation of the residue from petroleum ether (b.p. 60–70°), yielded the product as red needles (0.650 g, 80%), dec. 130–150°. (Found: C, 45.66; H, 4.34; mol. wt. osmometrically in $CHCl_3$, 422. $C_{16}H_{18}Pd_2$ calcd.: C, 45.42; H, 4.29%; mol. wt., 422).

*Complexes (VI)*

*Complex (VIa): dichloro-2,2'-bi-π-allylbis(pyridine)dipalladium(II).* Pyridine (2.0 ml) was added to a suspension of di-μ-chloro-2,2'-bi-π-allyldipalladium(II) (0.045 g) in benzene (10 ml) and the mixture was shaken vigorously (20 h). Benzene (15 ml) was added, the mixture was heated to boiling, and filtered whilst hot. The filtrate was reduced in volume (ca. 10 ml) and petroleum ether (b.p. 30–60°) was added to precipitate the product as a white amorphous powder (0.040 g, 71%), dec. >200°. (Found: C, 37.21; H, 3.65. $C_{16}H_{18}Cl_2N_2Pd_2$ calcd.: C, 36.82; H, 3.47%.)

*Complex (VIb): dichloro-2,2'-bi-π-allylbis(triphenylphosphine)dipalladium(II).* A solution of triphenylphosphine (0.072 g) in benzene (7 ml) was added dropwise, with stirring, to a suspension of di-μ-chloro-2,2'-bi-π-allyldipalladium(II) (0.050 g) in benzene (2 ml). Filtration, followed by addition of petroleum ether (b.p. 30–60°) to the filtrate, precipitated the product as pale yellow prisms (0.080 g, 66%), dec. 223–224°. (Found: C, 57.05; H, 4.22. $C_{42}H_{38}Cl_2P_2Pd_2$ calcd.: C, 56.79; H, 4.31%.)

An identical procedure using triphenylarsine yielded dichloro-2,2'-bi-π-allylbis(triphenylarsine)dipalladium(II), complex (VIc), as yellow needles (70%), dec. 180–190°. Satisfactory microanalytical data could not be obtained for this complex.

*Complexes (VII)*

*Complex (VIIa): di-μ-acetato-2,2'-bi-π-allyldipalladium(II).* A suspension of di-μ-chloro-2,2'-bi-π-allyldipalladium(II) (0.203 g) in chloroform (15 ml) was treated

with silver acetate (0.190 g) and the mixture was shaken vigorously (1 h). Filtration, followed by evaporation of the filtrate under reduced pressure, and recrystallisation of the residue from chloroform/petroleum ether (b.p. 30–60°) yielded the product as yellow prisms (0.203 g, 88%), dec. 133–140°. (Found: C, 29.43; H, 3.68. $C_{10}H_{14}O_4Pd_2$ calcd.: C, 29.22; H, 3.43%.)

Similarly prepared, using the appropriate silver carboxylate, were: di-$\mu$-propionato-2,2'-bi-$\pi$-allyldipalladium(II), complex (VIIb), as yellow prisms (80%), dec. $>130°$. (Found: C, 32.55; H, 4.10. $C_{12}H_{18}O_4Pd_2$ calcd.: C, 32.83; H, 4.13%.) Bis-$\mu$-(phenylacetato)-2,2'-bi-$\pi$-allyldipalladium(II), complex (VIId), as yellow prisms (85%), m.p. 140–145° dec. (Found: C, 46.78; H, 4.07. $C_{22}H_{22}O_4Pd_2$ calcd.: C, 46.92; H, 3.94%.)

*Complex (VIIf): bis-$\mu$-(trifluoroacetato)-2,2'-bi-$\pi$-allyldipalladium(II).* A solution of di-$\mu$-acetato-2,2'-bi-$\pi$-allyldipalladium(II) (0.800 g) in chloroform (25 ml) was treated with trifluoroacetic acid (1.20 ml). The resultant golden-yellow solution was refluxed (2 min), evaporated to dryness under reduced pressure, and the residue dried *in vacuo*. Recrystallisation from chloroform/diethyl ether yielded the product as pale yellow microprisms (0.967 g, 96%), dec. 169–172°. (Found: C, 23.34; H, 1.49. $C_{10}H_8F_6O_4Pd_2$ calcd.: C, 23.13; H, 1.55%.)

*Complex (VIIg): bis-$\mu$-(trichloroacetato)-2,2'-bi-$\pi$-allyldipalladium(II).* A solution of di-$\mu$-acetato-2,2'-bi-$\pi$-allyldipalladium(II) (0.500 g) in chloroform (25 ml) was treated with trichloroacetic acid (1.100 g). The resultant golden-yellow solution was refluxed (5 min), allowed to cool slowly to room temperature, and filtered to give the product as red needles (0.660 g, 88%), dec. 154–160°. (Found: C, 19.43; H, 1.38; Cl, 34.20; mol.wt. osmometrically in $CHCl_3$, 610. $C_{10}H_8Cl_6O_4Pd_2$ calcd.: C, 19.45; H, 1.30; Cl, 34.43%: mol.wt., 617.)

*Complex (VIII): bis-$\mu$-(1,3-diphenyltriazeno)-2,2'-bi-$\pi$-allyldipalladium(II)*

A solution of 1,3-diphenyltriazene (0.216 g) in chloroform (5 ml) was added dropwise to a solution of di-$\mu$-acetato-2,2'-bi-$\pi$-allyldipalladium(II) (0.200 g) in chloroform (3 ml), and the solution set aside for 10 h at 0°. Filtration yielded the product as orange needle-prisms (0.260 g, 78%), dec. 172–178°. (Found: C, 52.45; H, 4.14; N, 12.20. $C_{30}H_{28}N_6Pd_2$ calcd.: C, 52.58; H, 4.12; N, 12.26%.)

*Complexes (VI)*

*Complex (VId): diacetato-2,2'-bi-$\pi$-allylbis(pyridine)dipalladium(II).* Pyridine (80 $\mu$l) was added to a solution of di-$\mu$-acetato-2,2'-bi-$\pi$-allyldipalladium(II) (0.200 g) in chloroform (10 ml). Evaporation of the solution to dryness under reduced pressure, followed by recrystallisation of the residue from chloroform/petroleum ether. (B.p. 30–60°) yielded the product as colourless needles (0.175 g, 63%), dec. 130–140°. (Found: C, 42.53; H, 4.49; mol. wt. osmometrically in $CHCl_3$, 550. $C_{20}H_{24}N_2O_4Pd_2$ calcd.: C, 42.21; H, 4.25%; mol.wt., 569.)

Similarly prepared were: Complex (VIe): bis(trifluoroacetato)-2,2'-bi-$\pi$-allylbis(pyridine)dipalladium(II), as colourless needles (80%), m.p. 149–160° dec. (Found: C, 35.80; H, 2.62. $C_{20}H_{18}F_6N_2O_4Pd_2$ calcd.: C, 35.47; H, 2.68%.) Complex (VIf): bis(trichloroacetato)-2,2'-bi-$\pi$-allylbis(pyridine)dipalladium(II), as colourless needle-prisms (83%), m.p. 95–100° dec. (Found: C, 31.42; H, 2.25. $C_{20}H_{18}Cl_6N_2O_4Pd_2$ calcd.: C, 30.98; H, 2.34%.) Complex (VIg): bis(trifluoroacetato)-2,2'-bi-$\pi$-allylbis-

(triphenylphosphine)dipalladium(II), as colourless prisms (91%), m.p. 123–127° dec. (Found: C, 52.64; H, 4.02. $C_{46}H_{38}F_6O_4P_2Pd_2$ calcd.: C, 52.94; H, 3.67%.) Complex (VIh): bis(trichloroacetato)-2,2'-bi-π-allylbis(triphenylphosphine)dipalladium(II), as colourless prisms (96%), m.p. 100–105° dec. Satisfactory microanalytical data could not be obtained for this complex.

ACKNOWLEDGEMENT

We are grateful to the National Research Council of Canada for financial support of this work and for a Postgraduate Scholarship (to R.P.H.).

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