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THE PHENYLATION OF DICHLORO-η^4-NORBORNADIENE-PALLADIUM AND -PLATINUM

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Summary Phenylation of dichloro-η^4-norbornadienepalladium either with diphenylmercury or, more conveniently, with sodium tetraphenylborate gave di-μ-chlorobis(2 5,6-η-3-endo-phenylnorbornen-2-yl-endo-palladium) (IV) This reaction provides the first definitive evidence for a cis addition of Pd-R to a coordinated double bond. By contrast phenylation of dichloro-η^4-norbornadieneplatinum gave first [Pt(Ph)(Cl)(nor-C_7H_8)] and then [PtPh$_2$(nor-C_7H_8)] and no phenylation of the norbornadiene could be induced Complex (IV) underwent a reversible ring-closure to give the nortricyclenyl complex (VI), [PdCl(py)$_2$(C_7H_8)], on reaction with pyridine. In the solid state (IV) is bonded in a σ,π-form but the homoallylic form for (IV) and for related complexes is probably easily accessible.

Nucleophilic attack at a double bond coordinated to Pd(II) or Pt(II) generally occurs exo- with respect to the metal [1], but it has recently become widely accepted that the direction of attack is very much a function of the nature and state (for example, of solvation) of the nucleophile and its relative affinity for carbon compared to other electrophilic centres in the molecule such as the metal. Prior to the work reported here on the phenylation of coordinated dienes, a Communication on which has appeared [3], no fully authenticated example of endo-attack on a double bond coordinated to Pd(II) had been observed but in a number of cases mechanistic arguments led to the conclusion that endo-attack was occurring [2].

RESULTS

Attempts to phenylate diene-palladium chloride complexes using PhMgBr all failed, only biphenyl and decomposition products could be isolated. Other arylating agents were investigated and of these diphenylmercury was found to have good reactivity towards Pd-Cl and Pt-Cl bonds Purification of the product was, however, sometimes difficult and tedious and as an alternative phenylating agent for Pd-Cl bonds, sodium tetraphenylborate in acetone was employed. This was the reagent of choice here since it gave clean reactions and the product was easily isolated and purified

Reaction of dichloro(norbornadiene)platinum (Ib) with two equivalents of diphenylmercury gave the known diphenyl(η^4-norbornadiene)platinum (III) [4]. The intermediate in this reaction, chloro(phenyl)(η^4-norbornadiene)-platinum (IIb) could be obtained in 58% yield by treatment of (Ib) with a deficiency of diphenylmercury or alternatively by mixing equimolar solutions of (Ib) and (III).

When the reaction conditions used to prepare (III) were applied to the palladium analogue (Ia) the only product obtained was di-μ-chlorobis(2.5,6-η^3-3-endo-phenylnorbornen-2-yl-endo-palladium) (IV). Initial n m r spectroscopic investigations indicated that the phenyl was attached to the ligand and the question of whether the phenyl was endo- or exo- to the metal was resolved by an X-ray structure determination [3] which showed the endo-phenyl geometry indicated, subsequent n m r. spectroscopic measurements (Table 1 and Experimental) supported this assignment.

The arylation of (Ia) also proceeded in acetone using sodium tetraphenylborate and gave a 79% yield of the analytically pure complex

The presumed intermediate, (IIa), in the formation of (IV) could not be isolated or detected; furthermore all attempts to cause the chloro(phenyl)-platinum analogue (IIb) to rearrange to give an analogue of (IV) were quite unsuccessful. There was no detectable reaction on heating (IIb) in chloroform or tetrahydrofuran either alone or in the presence of LiBr, $SnCl_2$, or hexamethylphosphoramide $[(Me_2N)_3P{=}O]$. Triphenylphosphine or dimethyl sulphoxide displaced the norbornadiene.

The palladium σ,π-complex (IV) also underwent a further rearrangement to the σ-nortricyclenyl complex (VI) on reaction with an excess of pyridine (py). This complex was identified by its n.m.r. spectra which showed the absence of olefinic carbons and hydrogens. ^{1}H n.m.r.* δ at 0.54, 1.15 [H(6),H(2)], 0 96[H(1)], 1.02, 2.16, 2.60[H(4),H(3),H(5)], 1.24[H(7)], and 7.0-9.0 [phenyl and pyridine]. ^{13}C {^{1}H} δ at 12.0[C(1)], 15.9 17.4[C(2),C(6)], 35.1[C(7)], 39.0, 43.9, 50.2[C(3),C(4),C(5)], 124.3, 125.0[py,β-C], 137.2, 137.6[py,γ-C], 152.5, 153.1[py,α-C], 126.3, 128.1, 129.1, 143.3 [phenyl]. The observation that the pyridine resonances in

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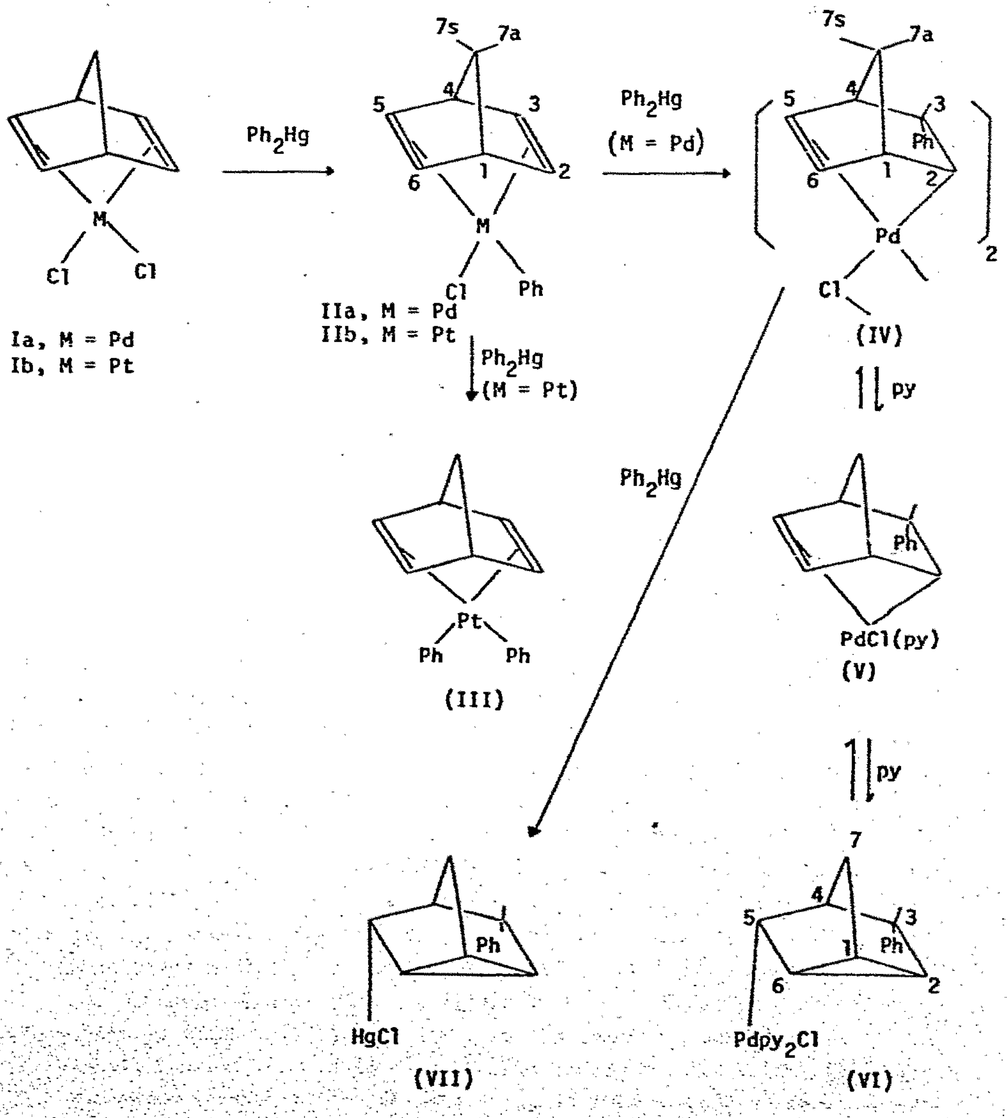
* All resonances were multiplets except H(3) and H(5) which were singlets; the resonances were assigned by selective decoupling of the ^{13}C spectrum.

the ^{13}C n.m.r. spectrum were doubled suggested that the two pyridines were inequivalent and hence cis- to each other.



If the norbornenyl complex was reacted with only 2 equivalents of pyridine per dimer (IV) then a very unstable material could be obtained the ^{1}H n.m.r. spectrum of which was different from that of (IV) or (VI), in particular in the olefinic region around δ 6.0, and to which is tentatively ascribed the structure (V).

A similar spectrum could also be generated by mixing together equimolar solutions of (IV) and (VI) and this suggested that the norbornenyl-nortricycleny rearrangement was reversible. This was also indicated by the identification of (IV) from a reaction of (VI) and dichlorobis(benzonitrile)palladium in chloroform,

$$\underset{(VI)}{Pd(C_7H_8Ph)py_2Cl} + Pd(PhCN)_2Cl_2 \rightarrow \tfrac{1}{2}\underset{(IV)}{[Pd(C_7H_8Ph)Cl]_2} + Pdpy_2Cl_2$$

When (Ia) was treated with a large excess of diphenylmercury, the phenylnortricyclenylmercury compound (VII), was formed. In separate experiments it was shown that this derived from (IV).

DISCUSSION

The use of diphenylmercury (or phenylmercuric chloride) as a reagent for the preparation of phenyl-metal compounds is well-known and the use of phenylmercury as an *in situ* phenylating agent for double-bonds in the presence of palladium(II) is also well-established as in the reactions discovered by Heck [6]

$$Ph_2Hg + PdCl_2 \rightarrow \text{"PhPdCl"} + PhHgCl$$

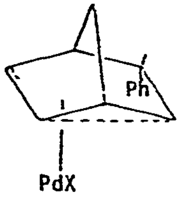
$$\text{"PhPdCl"} + RCH{=}CH_2 \rightarrow RCH(PdCl)CH_2Ph \rightarrow RCH{=}CHPh + Pd^\circ + HCl$$

However, definitive proof of *cis*-addition to a double-bond was lacking until it was shown in the work described here that, in the product (IV) of phenylation of dichloro(norbornadiene)palladium, Ph ...Pd had effectively added across a double bond It was not possible to isolate or to obtain evidence for the expected intermediate phenyl-palladium complex (IIa), but the platinum analogue (IIb) could be made, both directly by the phenylation of (Ib) and indirectly by a redistribution reaction of (Ib) and (III).

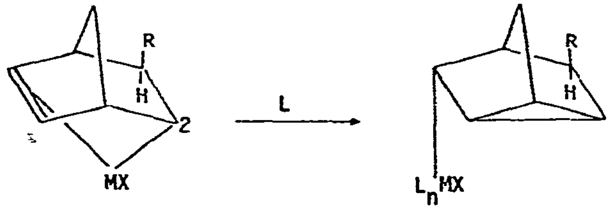
However, neither the phenyl-platinum complex (IIb) nor (III) showed any tendency to cis-insert to give the platinum analogue of (IV) under a variety of conditions. It is interesting also to note that there is no evidence for the combination of a phenyl and a C_7 fragment even in the mass-spectra of the platinum complexes (IIb) or (III). Whereas (VII), and even (IV), which did not show a molcular ion peak, gave clear indications of the presence of C_{13} units (e.g. at m/e 169 or 167 corresponding to $C_{13}H_{13}^+$ or $C_{13}H_{11}^+$) in the break-down, such peaks were conspicuously absent in the mass-spectra of (IIb) and (III) and indicated that even under the forcing conditions of a mass-spectrometer C_7-phenyl bond formation did not occur. The strongest peak in the spectrum for both (IIb) and (III) was at m/e 154, corresponding to $C_{12}H_{10}^+$ (i.e. diphenyl), which must arise from the coupling together of two phenyl groups.

The fact that the norbornenyl-palladium complex (IV) is formed even more conveniently and in rather better yield by reaction of (Ia) with sodium tetraphenylborate suggests that the intermediate (IIa), though not necessarily the reaction path to it, are common to both These reactions are still under investigation [7]

In connection with our identification of (IV) as the endo-phenyl isomer by an X-ray determination [3], it is also pertinent to comment on the evidence in favour of the homoallylic form (A) Such a structure has been postulated for the exo-substituted complexes of type (VIII, M = Pd, Pt, R = alkoxide, acetate, X = Cl, diketonate, etc) [9] in order to account for the ease with which they undergo ring-closure to give the nortricyclenyl complexes (IX) [9-13]



(A)



(VIII) (IX)

The arguments for the homoallylic form have been summarised and extended by Hughes and Powell [14], who have interpreted their ^{13}C and ^{1}H n.m r. data in terms of a distortion of the ligand away from the σ,π bonded and towards the homoallylic form. Their argument, which rests particularly on the application of the Karplus relation to J(H-H), and on the values of J(C-Pt) (in particular to C(2)) in the platinum complex (VIII, R = acetate, MX = Pt(hfac)), unfortunately does not constitute final proof because the application of the Karplus relation to strained organic systems is very difficult [15], and because so little is still understood of the variation of chemical shift and coupling constant in ligands complexed to metals.

We have analysed both the ^{1}H and ^{13}C n.m.r. data for complex (IV) in the same manner as Hughes and Powell. The most interesting feature of the comparison (Table 1) is that the ^{1}H chemical shifts and the values of J(H-H) are very similar in (IV) and (VIII, R = acetoxy, MX = Pd(hfac)), with the exception of course of H(3) which is exo and attached to a carbon bearing phenyl in (IV) and is endo and attached to a carbon bearing acetoxy in (VIII).

It is clear from these data that (IV) and (VIII) have the same basic structure of the ligand in solution, and by implication therefore any

Table 1

^{1}H n.m.r. spectra of (IV) and (VIII, R = acetoxy, MX = Pd(hfac))

	H(1)	H(2)	H(3)	H(4)
(IV)	3.43[*J*(1-2)=4.2; *J*(1-5)=1.8; *J*(1-6)=3.4]	2.84[*J*(2-3)=3.8, *J*(2-4)=2.2]	2.57	3.05[*J*(4-5)=3.4]
(VIII)	3.23[*J*(1-2)=4.4; *J*(1-5)=1.9, *J*(1-6)=3.8]	2.87[*J*(2-3)=0, *J*(2-4)=2.3]	2.10	3.03[*J*(4-5)=4.2]

	H(5)	H(6)	H(7a)	H(7s)
(IV)	6.33[*J*(5-6)=4.2]	5.84	1.87[*J*(7a-7s)=9.4]	1.72
(VIII)	6.09[*J*(5-6)=3.8]	6.23	2.10[*J*(7a-7s)=10.5]	1.78

arguments supporting the homoallylic form which are adduced to (VIII) must apply to (IV). This is confirmed by the ease with which (IV) cyclises to the nortricyclenyl form (VI).

The X-ray structure determination of (IV) allows the following unequivocal statements concerning the solid-state structure of one norbornenyl ligand in (IV) [3][†]:

(i) The metal is bonded to three carbon atoms [Pd-C(2) 2.04(2), Pd-C(5) 2.25(2), Pd-C(6) 2.14(2)Å] and is closest to C(2).

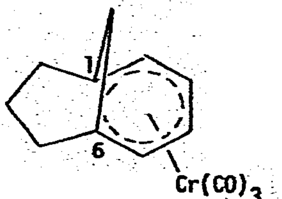
(ii) The coordination plane of the metal does not bisect the C(5)-C(6) bond but is closer to C(6) [0.51Å] than to C(5) [0.9Å].

(iii) The non-bonded carbons C(3) and C(5) are 2.57Å apart and the angle ∠C(3)C(4)C(5) is 109° whereas the distance C(2)-C(6) is 2.35Å and ∠C(2)C(1)C(6) is 98°.

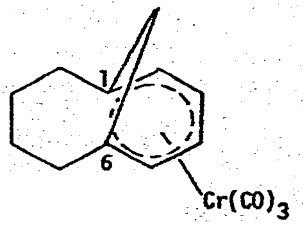
The crystal structure therefore shows that the metal is more strongly bonded to C(2) than to C(6) and particularly C(5), as would be expected for an asymmetric σ,π-bonding situation. This bonding would not be expected for a homoallylically bonded C(2)C(6)C(5) moiety where (based on the analogy to allylic-palladium complexes) one would expect C(2) and C(5) to be at comparable distances from the metal and C(6) to be if anything a little closer.

While the closing of the angle at the bridgehead carbons from 109° for C(3)C(4)C(5) to 98° for C(2)C(1)C(6) is consistent with a deformation to a homoallylic form, it is also to be expected for a σ,π-form since C(2) and C(5)C(6) act as the two ends of a chelate, and in particular as the coordination plane cuts C(5)-C(6) about one third of the way along.

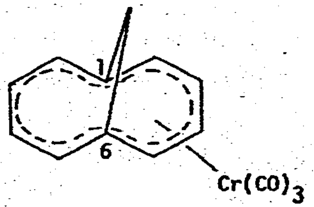
In our view the most compelling argument against a homoallylic form for the ligand in solid (IV) is the distance (2.35Å) separating C(2) and C(6). Some data on the lengths of C-C bonds of bond order less than one are available from the homoaromatic methano-annulene systems (IX-XI)



(IX)



(X)



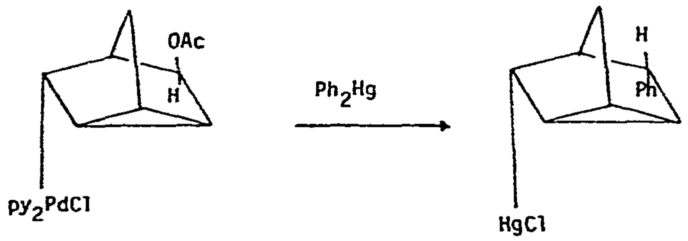
(XI)

[†] A disorder problem makes the accurate determination of bond lengths in the other norbornenyl unit of the dimer (IV) difficult; however, all indications are that the structure of this ligand is the same as the one for which accurate data are available.

The transannular separations C(1)-C(6) in these molecules are 1.65Å (IX) [16], 1.72Å (X) [17] and 2.14Å (XI) [18], clearly showing the homoaromaticity in (IX) and (X) and the lack of it in (XI). Particularly interesting is the fact that the parent hydrocarbon of (X) is a triene and does not show any evidence for homoaromaticity.

We therefore conclude that in the solid (IV) the separation C(2)-C(6) is too large for there to be any significant bonding between these atoms. However, this does not rule out the existence of the homoallylic form as an intermediate or transition state in the potential energy surface linking the norbornenyl and the nortricyclenyl forms. It is even possible that in solution (IV) moves significantly closer to the homoallylic form.

The formation of the nortricyclenylmercury complex (VII) had already been observed to occur on reaction of the exo-acetoxynortricyclenylpalladium complex (XII) with diphenylmercury [19], and similar reactions occur with other organomercury compounds.



(XII) (VII)

The mechanism of the formation of (VII) from (XII) is not clear but it may well occur via (i) a reversal to the norbornenyl form followed (ii) by loss of acetate and (iii) attack by phenylmercury on a norbornadiene-palladium species in the manner described here. The further steps would then be (iv) ring closure in the manner of (IV)→(VI) (but without the pyridine) and (v) Hg-Pd exchange. The evidence presented here certainly supports such a mechanism.

EXPERIMENTAL

Dichloro(norbornadiene)-palladium and -platinum complexes were prepared by literature methods [20]. All reactions were carried out under nitrogen except where indicated.

Chloro(η^1-phenyl)(η^4-norbornadiene)platinum (IIb)

Diphenylmercury (0.36 g, 1 mmol) dissolved in dichloromethane (10 ml) was added with stirring to a suspension of dichloronorbornadieneplatinum (Ib) (0.72 g, 2 mmol) in dichloromethane (25 ml), and stirring was continued for 1 hr at 20°C. The solution was filtered to remove unreacted (Ib) (0.23 g) and then cooled to -30°C for 4 h. Mercuric chloride (0.25 g, 90%) was filtered off, the solvent was removed in vacuo and the residue was crystallised from benzene-diethyl ether to yield colourless needles [0.27 g, 58%, based on reacted (Ib)] of complex (IIb). mp. 128-129°C (dec.) Found: C, 39.1; H, 3.4; Cl, 8.8%. *M* (mass-spectroscopic) 398, 399, 400, 401, 402. $C_{13}H_{13}ClPt$ requires C, 39.1; H, 3.3; Cl, 8.9% *M*, 398, 399, 400, 401, 402. ^{1}H n.m.r. δ 1.74, 1.76 [H(7a,7s)], 4.05 [H(1,4)], 4.86 [t, H(2,3), *J*{H(2,3)-H(1,4)} = 2.5 Hz, *J*{H(2,3) - Pt} = 78 Hz], 5.67 [t, H(5,6), *J*{H(5,6)-H(1,4)} = 2.5 Hz, *J*{H(5,6) - Pt} = 31 Hz], 7.1 [m, phenyl].

Diphenyl(η^4-norbornadiene)platinum (III)

Diphenylmercury (1.42 g, 4 mmol) dissolved in dichloromethane (25 ml) was added to a suspension of complex (Ib) (0.72 g, 2 mmol) in dichloromethane (25 ml) over 5 min. The solution turned yellow and a white solid (phenylmercury chloride, 1.02 g) was precipitated which was filtered off after 10 min. The filtrate was evaporated to dryness and the residue was chromatographed on Florisil in dichloromethane to remove diphenyl and phenylmercury chloride; complex (III) was obtained as colourless crystals (0.38 g, 44%) mp. 149-150°C; lit. [5b] 146-152°. Found: C, 51.7; H, 4.3%, *M* (mass-spectroscopic) 440, 441, 442. $C_{19}H_{18}Pt$ requires C, 51.7, H, 4.1%, *M*, 440, 441, 442. ^{1}H n.m.r. δ at 1.71 [bd.s. H(7)], 4.13 [bd. H(1,4)], 5.51 [t, H(2,3,5,6) = 2 Hz, J(H-Pt) = 38 Hz], 7.01 [s, phenyl].

Di-μ-chlorobis[2:5,6-η^3-3-*endo*-phenylnorbornen-2-yl-*endo*-palladium] (IV)

(i) A solution of diphenylmercury (1.1 g, 3.2 mmol) in dichloromethane (5 ml) was added dropwise over 30 min. to a suspension of dichloro(norbornadiene)-palladium (Ia) (0.87 g, 3.2 mmol) in dichloromethane (5 ml) at -10°C. The solution was filtered to remove phenylmercuric chloride, and the filtrate was chromatographed on Florisil in dichloromethane to remove more PhHgCl and diphenyl. The complex (IV) crystallised from dichloromethane-pentane in yellow needles (0.5 g, 50%), m.p. 190° decomp. Found: C, 50.4; H, 4.5; Cl, 11.1%; *M*, 622. $C_{26}H_{26}Cl_2Pd_2$ requires C, 50.2; H, 4.2; Cl, 11.4%; *M*, 595. ν(Pd-Cl) 217 (vs), 246 (s), 274 cm^{-1}. ^{13}C {^{1}H} NMR δ, 31.6 {C(2)}, 45.7 {C(4)}, 50.8{C(1)}, 58.2{C(7)}, 61.0{C(3)}, 71.1{C(6)}, 112.5{C(5)}, 126.5, 128.2, 128.5 and 142.0 (phenyl).

(ii) A better preparation, which can easily be scaled up, is as follows: Sodium tetraphenylborate (3.8 g, 11.1 mmol) dissolved in acetone (10 ml) was slowly added to a suspension of complex (Ia) (3.0 g, 11.1 mmol) in acetone (300 ml) with vigorous stirring. The reaction mixture darkened; after the addition was complete the volume of solvent was reduced to 20 ml on a rotary evaporator and the solution was kept at 0°C for 1 hr. The crude complex (IV) [3.5 g] crystallised and was filtered off. It was purified by chromatography on silica gel in dichloromethane and crystallised in orange yellow needles [2.72 g, 79%] from dichloromethane-methanol; m.p. 190° (decomp).

Chlorobis(pyridine)-η^1-endo-3-phenylnortricyclen-5-yl-endo-palladium (VI)

Pyridine (0.26 ml, 3.2 mmol) dissolved in dichloromethane (1 ml) was added slowly to a solution of complex (IV) (0.50 g, 0.08 mmol) in dichloromethane (5 ml). The mixture was stirred (30 min) at 20°C, the volume was then reduced (to 1 ml) on a rotary evaporator and methanol (5 ml) was added. Pale yellow crystals of (VI) (0.50 g, 66%, m.p. 150-152° decomp.) were obtained on cooling the solution to 0°C. Found: C, 57.9; H, 5.2; Cl, 7.8; N, 5.9%. $C_{23}H_{23}ClN_2Pd$. 0.5 H_2O requires C, 57.8; H, 5.1; Cl, 7.4; N, 5.9%. The presence of water was confirmed by the observation of a weak band at 3450 cm^{-1} in the i.r. spectrum. Far i.r.: ν(Pd-Cl) 222 (vs), 237 (s) cm^{-1}.

Chloro(endo-3-phenyl-endo-5-nortricyclenyl)mercury (VII)

A solution of diphenylmercury (2.30 g, 6.5 mmol) in dichloromethane (60 ml) was added dropwise over 1 hr. to a suspension of dichloro(norbornadiene)-palladium (Ia) (0.87 g, 3.2 mmol) in dichloromethane at -10°C. The black solid was then filtered off and the colourless solution was chromatographed on Florisil. This gave the mercury complex (VII) (0.55 g, 42%), m.p. 145°, of identical n.m.r. spectrum to that reported [19]. Found: C, 38.0; H, 3.3%, *M* (mass-spectroscopic) 404, 406. $C_{13}H_{13}HgCl$ requires: C, 38.5, H, 3.2%, *M*, 404, 406.

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