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REACTION OF DI-μ-CHLOROBIS(η^3-4-PHENYL-1,2,3,4-TETRA-P-TOLYL CYCLOBUTENYLPALLADIUM) WITH BUT-2-YNE

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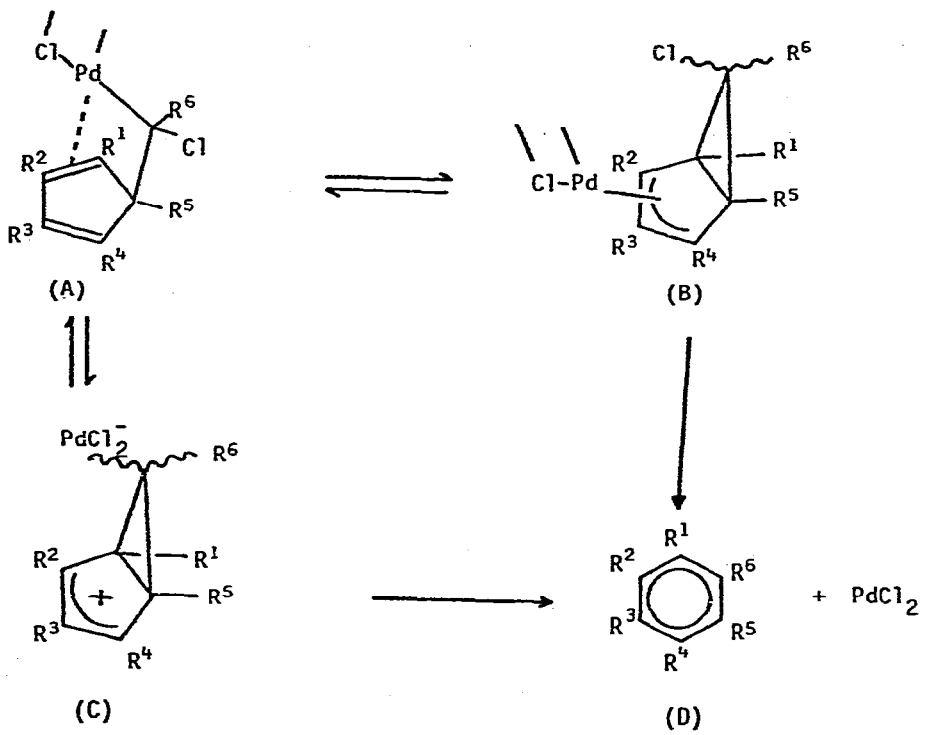
Summary

Reaction of $[Pd(\eta^3\text{-}C_4PhTo_4)Cl]_2$ with MeC≡CMe gave an isomeric mixture of composition $[Pd(\eta^3\text{-}C_6Me_2PhTo_4)Cl]_2$, (II), which was converted into a single compound $[Pd(\eta^3\text{-}C_6Me_2PhTo_4)(acac)]$ (III), on reaction with Tl(acac). Complexes (II) and (III) exhibited dynamic NMR spectra; the low temperature limiting spectra showed that the metal was η^3-bonded to a benzylic group in the molecule. Structures are proposed for (II) and (III) and their relation to the $PdCl_2$ induced cyclotrimerisation of acetylenes is discussed.

In connection with our interest in the reactions of acetylenes with palladium compounds [1] we have now examined the reaction of the η^3-cyclobutenyl complex (I) [2] with but-2-yne. This reaction is of interest since we [2,3] and others [4,5] have found that such η^3-cyclobutenyl complexes are easily converted into σ-(1-η- or 1:3,4-η-)butadienyl complexes and it is known that such compounds react with acetylenes to give acetylene-trimer and -tetramer compounds [6-9].

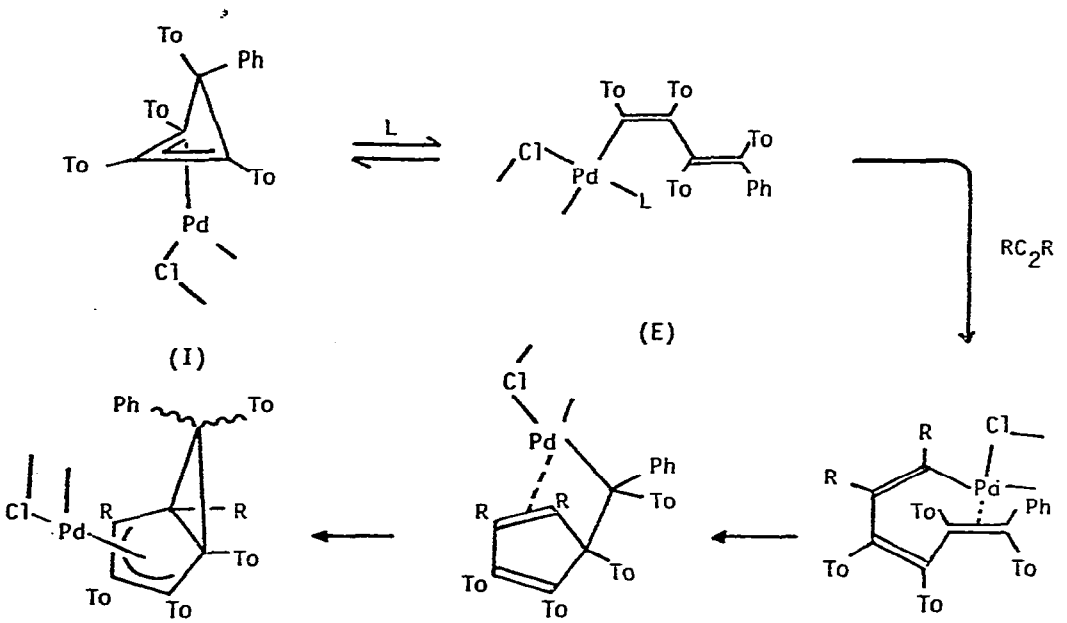
The most common acetylene trimers obtained from reaction of an acetylene with $PdCl_2$ are benzenes and we have shown that their formation occurs via a complex of type (A) [1]. Possible routes from (A) to the benzene (D) are via bicyclo[3.1.0]hexenyl intermediates, the most likely structures for which

are (B) or (C). Both the route via (B), which involves an internal cis-insertion of a coordinated C=C bond into a Pd-C σ-bond, and that via (C), in which there is a Pd-assisted cleavage of the C-Cl bond accompanied by C-C bond formation, have ample precedent (refs. [10] and [11-12] respectively). In order to clarify the question of whether the reaction proceeds by route (A) → (B) → (D) or (A) → (C) → (D) and since the intermediates (B) or (C) are likely to be highly labile, a suitable model system was sought. It was anticipated that this lability could be circumvented if the C-bonded Cl were replaced by poorer leaving group and if the substituents (R^1-R^6) were of such a type that β-elimination processes could not occur.



The penta-arylcyclobutenyl complex (I) is known to isomerise to the η^1-butadienyl (E) [2,3], which may be expected to react with an acetylene, RC_2R, to give a σ-hexatrienyl intermediate (F) which would cyclise to (G). It was anticipated that (G) would not be able to stabilise itself well by

internal coordination of a C=C bond but if the path via (B) were a viable one for (A) → (D) it could cyclise to (H) (or an isomer thereof). On the other hand, if the path via (B) were energetically unfavourable, and if the normal path for (A) → (D) was via (C), then an alternative product with a different skeleton to that of (H) would be expected.



The acetylene but-2-yne was chosen as reactant since this is a small and moderately reactive acetylene the methyl substituents of which have useful NMR characteristics and which also confer greater solubility on the product.

Results and Discussion

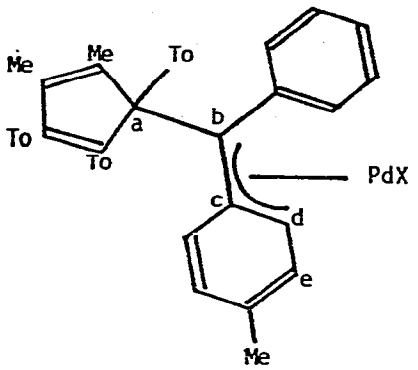
Reaction of (I) with but-2-yne was very slow at +20° but proceeded

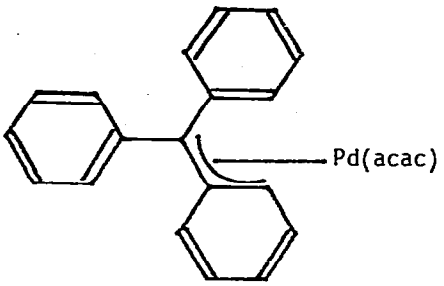
satisfactorily at +60° in a sealed tube. The product (II) analysed, as expected, for $[Pd(C_6Me_2PhTo_4)Cl]_2$ but thin layer chromatography indicated two species to be present which were separated by preparative t.l.c. However, analytical, infrared, and low temperature NMR spectra of the two compounds showed no significant differences and we deduced that the two compounds contained identical organic ligands bound in the same way to Pd but that they were isomeric by virtue of their arrangements about the Pd_2Cl_2 bridge (i.e. they were the dl- and meso-forms). Analogous observations have been made on other systems [10]. Further support for this hypothesis came from the observation that on reaction of either or both compounds with Tl(acac) the same single monomeric complex, $[Pd(C_6Me_2PhTo_4)(acac)]$ (III), was obtained.

Both complexes (II) and (III) exhibited similar dynamic behaviour in solution as shown by their variable temperature NMR spectra; the spectra were more extensively investigated for (III) since this was the more soluble compound. The NMR spectra and the observed dynamic behaviour were not, however, those that would be associated with a complex of type (H) undergoing a series of suprafacial 1,4-sigmatropic shifts. The ^{13}C NMR spectrum of (III) below -20°C showed that one isomer was present to the extent of about 90%. This spectrum also showed a $\gg$C-H at δ 82.6 [90.2 for (II)] while the ^1H spectrum at -20° showed high field aromatic doublets at δ 5.77 and 5.14 [and multiplets at δ 5.94 and 4.91 in (II) at -88°C]. The resonance at δ 5.77 was identified as an ortho-H on a p-tolyl group by a series of selective decoupling experiments. In particular, it was shown to be coupled to a doublet at δ 7.19, which was assigned to the meta-H of the same ring; irradiation at δ 5.77 collapsed the 7.19 resonance to a singlet. If this meta-H were in a phenyl ring it would have been a multiplet which would have collapsed to a doublet on irradiation at δ 5.77.

Such high-field shifted aromatic resonances have been found characteristic of η^3-benzylic complexes, for example, as in (IV) [13].

The absence of any high field resonances in the ^{13}C spectra of (II) and (III) which may be assigned to a fused cyclopropyl ring rules out the





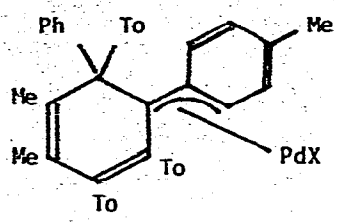
(IV)

(II) X = $Cl_2Pd\{\eta^3\text{-}C_2Me_6PhTo_4\}$

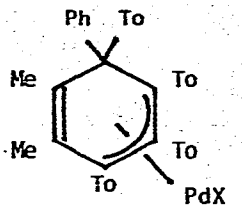
(III) X = acac

possibility that ring closure to an η^3-bicyclo[3.1.0]hexenyl complex has occurred, and the most probable structure for these complexes is based on the ligand shown.

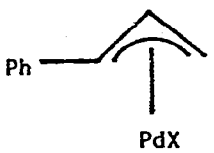
However, the NMR spectra alone cannot exclude the possibility that (II) and (III) contain ligands such as (J, or an isomer thereof) which could arise if the reaction sequence (I) → (H) had proceeded one step further to a monocyclic species. We incline to the view that this has not occurred for two reasons. (i) Powell et al. [9] have shown that the endo-alkoxytetraaryl-cyclobutenylpalladium acetates $[Pd(\eta^3\text{-}C_4Ph_4OMe)(OAc)]_2$ react with acetylenes (RC_2R') in ethanol to give cyclopentadienyl complexes of the form $[\{Pd(C_5Ph_3RR')\}_2(C_2RR')]$. No products containing a C_6 skeleton were observed and this suggests that ring-expansion to a C_6 skeleton does not occur easily in this related system. (ii) The formation of (J) seems rather unlikely since this would necessitate the loss of the resonance stabilisation of one benzene ring which would not occur for an endocyclic allylic isomer, e.g. (K). To support this argument we may also note that complexes derived from the 1-phenylallyl ligand ($PhCHCHCH_2$) bind not benzylically but allylically as shown in (Va). This again suggests that benzylic binding is of higher energy when two alternatives [(Va) or (Vb)] are possible.



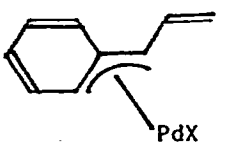
(J)



(K)



(Va)



(Vb)

We suggest therefore that ring closure of (G) has not occurred but that the molecule has stabilised itself as shown in (II) and (III) .

We have previously found [10] that when complexes of the type $[Pd(en\text{-}yl)(cod)]^+$ are generated they undergo ring closure of the en-yl ligand more readily than the parent $[Pd(en\text{-}yl)Cl]_2$ or [Pd(en-yl)(acac)]. Reaction of (II) with $AgPF_6$ in the presence of cod (cycloocta-1,5-diene) gave an unstable solution which rapidly decomposed. However if this solution was immediately reacted with Tl(acac) only the complex (III) was obtained. No ring closure therefore occurs even under such forcing conditions.

We therefore conclude that cyclisation to a bicyclo[3.1.0]hexenyl complex (H) does not occur. Such other evidence as is available [9] also suggests that a C-bonded Cl [as in (A)] is needed before cyclisation can take place and this implies that the ring-expansion (A) → (D) probably occurs by loss of Cl^- via an intermediate of type (C), since if the path were via (B) there is no obvious reason why replacement of Cl by an equivalent group (aryl or alkoxy) should otherwise so markedly affect the course of the rearrangement.

Experimental

$[Pd(\eta^3\text{-}C_6Me_2PhTo_4)Cl]_2$ (II)

A solution of complex $[Pd(\eta^3\text{-}C_4To_4Ph)Cl]_2$ (I) [1] (0.93 g, 0.7 mmol) in chloroform (15 ml) in a Carius tube was cooled to -196°C under vacuum. But-2-yne (140 µl, 1.8 mmol) and chloroform (2 ml) were distilled into the Carius which was then sealed in vacuo and heated (60°C/3 days). The tube was cooled and opened and the solution filtered. Solvent was removed in vacuo and the residue was washed with ether and crystallised from dichloromethane/methanol to give orange crystals of (II). Yield 0.85 g, 89%; m.p. 180-183°C decomp. Found: C, 73.9; H, 6.0; Cl, 5.4. Calc. for $C_{84}H_{78}Cl_2Pd_2$: C, 73.6; H, 5.7; Cl, 5.2.

^1H 100 MHz F/T NMR spectrum at -88°C δ 1.96, 2.19, 2.35 (Me, total 18 H) 4.91 (m,1H), 5.94 (m,2H), 6.35-8.20 (m,18H); at +30°C δ 1.51 (2), 2.02 (5), 2.13 (11), 2.15 (11), 2.31 (5), 6.0 (v.broad), 6.6 (7), 6.8 (3), 7.0 (3), 7.2 (3), 7.3 (1) (relative intensities, arbitrary scale, in parentheses).

^{13}C $\{^1H\}$ NMR spectrum at +30°C: δ, 21.6(Me), 25.0(Me), 67.2[C(a) or C(b)], 70.7[C(b) or C(a)], 90.2[C(d)], 120.5[C(c)], 125.0, 126.2, 128.3, 129.2, 129.8, 130.8, 133.3, 134.0, 136.2, 136.8, 138.5, 139.8, 141.1, 142.0, 151.0, 152.0 (all sp^2 C). Insolubility prevented lower temperature investigations.

Analytical thin layer chromatography showed the presence of two isomers, which were separated by t.l.c. on silica gel using dichloromethane/petroleum ether (b.p. 40-60) (2:3 v/v).

$[Pd(\eta^3\text{-}C_6Me_2PhTo_4)(acac)]$ (III)

Tl(acac) (0.32 g, 1.0 mmol) was added slowly to a stirred suspension of complex (ii) (0.60 g, 0.4 mmol) in dichloromethane (35 ml) at 0°C under nitrogen. Stirring was continued for 15 min after which the solution was filtered to remove TlCl, the filtrate taken to dryness in vacuo and the residue extracted with ether. The ether extract was filtered through a short silica gel column and the eluate evaporated to dryness. The residue was then crystallised from dichloromethane/methanol at 0°C to give yellow crystals of

(III). Yield, 0.49 g, 73%; m.p. 140-143 decomp. [Found: C, 72.6; H, 6.3; Cl, 4.5% mol. wt., 780. Calc. for $C_{47}H_{46}O_2Pd$ (0.5 CH_2Cl_2): C, 72.1; H, 6.0; Cl, 4.5%. mol. wt. 785.] The NMR spectrum showed the presence of dichloromethane of solvation.

^1H NMR spectrum in $CDCl_3$ at +30°C δ, 1.70 (bd.,13), 2.0, 2.05, 2.13(90), 2.27 (18), 2.42 (9) (all Me's) 5.1 (acac CH, 5), 6.58 - 7.2 (m, broad, aromatic, 105) (approximate relative intensities in arbitrary units in parentheses); at -20°C δ 1.74 (3H), 2.02 (3H, acac Me's) 2.14 (6H), 2.16 (6H), 2.31 (3H), 2.42 (3H) (all Me's); 5.14 (1H, bd. acac CH), 5.77 (d, 1H, H(d), J = 7 Hz), 6.10 t, 1H, H(e), J = 7 Hz , 6.60-7.35 (m, 16H), 7.77 (d, 1H, J = 7 Hz), 8.27 (d, 1H, J = 7 Hz).

^{13}C {^1H} NMR spectrum in $CDCl_3$ at -30°C (+30°C spectrum was very broad), δ 15.7, 21.2, 22.3, 23.5 (Me's) 28.4 (acac Me's), 66.1 [C(a) or C(b)], 67.5 [C(b) or C(a)], 82.6 [C(d)], 98.7 (acac CH), 115.7 [C(c)], 123.8, 124.4, 125.6, 126.4, 127.8, 127.9, 128.1, 129.0, 129.3, 129.8, 132.2, 132.8, 133.4, 134.3, 134.6, 135.1, 135.5, 138.5, 138.6, 139.8, 140.7, 150.9, 151.9 (all sp C), 186.0, 187.8 (acac CO's).

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