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INTERMEDIATES IN THE PALLADIUM-CATALYSED REACTIONS OF 1,3-DIENES

IV *. THE REACTIONS OF η^1,η^3-OCTADIENEDIYL-PALLADIUM COMPLEXES WITH ALKYNES AND ACTIVATED ALKENES

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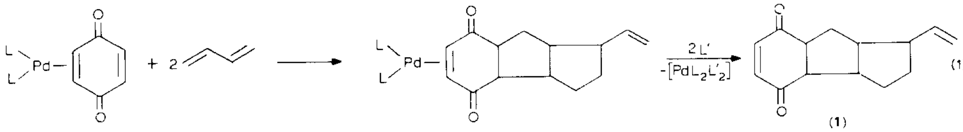
Summary

The reactions of $[Pd(PR_3)(\eta^1,\eta^3\text{-}C_8H_{12})]$ complexes with the dimethyl ester of acetylene dicarboxylic acid involves an unusual 1,3-addition of the alkyne to an allyl fragment to give cyclopentene-substituted η^3-allylpalladium complexes. *p*-Benzoquinone and 5-hydroxynaphthoquinone react similarly.

Introduction

Ten years ago its was reported that palladium-bonded *p*-benzoquinone undergoes a stoichiometric reaction with butadiene to give a complex containing the tricyclic system **1** (eq. 1). [2]. We report here results which suggest that this unusual reaction proceeds by attack of the quinone on an η^1,η^3-octadienediylpalladium species.



(1)

(1)

Results

This work originated in investigations of the role played by η^1-η^3-octadienediylpalladium-ligand complexes (**2**) in the palladium catalysed transformations of 1,3-dienes [1]. The extension to reactions with alkynes was expected to lead to complexes

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* For part III see ref. 1.

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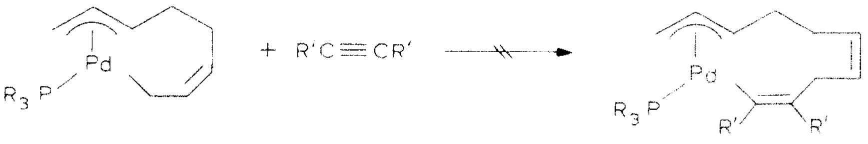
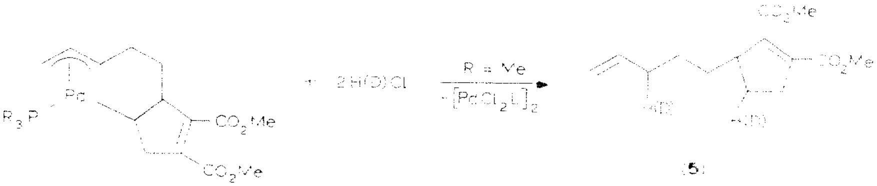
similar to **3** as the result of insertion into the Pd–η^1-allyl bond (eq. 2), related behaviour having previously been observed in the reaction of $[\mathrm{Ni(PPh_3)}(\eta^3,\eta^3\text{-}\mathrm{C_8H_{12}})]$ with alkynes [3].



(2)

(**2**) (**3**)

Complex **2** (R = Me, NMe$_2$, Ph) reacts readily with the dimethyl ester of acetylenedicarboxylic acid at −30°C to give pale yellow compounds stable at room temperature. The absence of signals in the olefinic region of the ^{1}H NMR spectrum rules out structures related to **3**, and this and the ^{13}C NMR spectrum indicate that an unusual 1,3-addition of the alkyne to an allyl fragment has occurred, to give **4**. Confirmation of the structure comes from the further reaction of **4** (R = Me) with HCl (or DCl), from which the cyclopentene derivative **5** could be isolated (eq. 3).

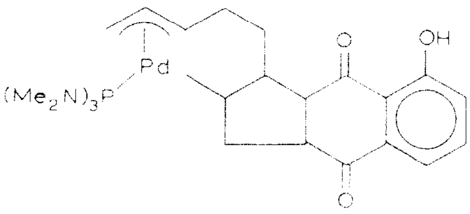


(3)

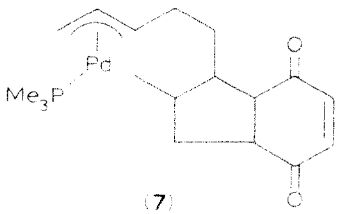
(**4**) (**5**)

No complexes could be isolated from reactions with other alkynes: alkyl-substituted alkynes failed to react below the decomposition point of **2**, and a multi-component mixture, which was not investigated further, was obtained from the reaction with phenylacetylene.

Related complexes (**6**, **7**) were obtained by treating **2** (R = NMe$_2$) with 5-hydroxynaphthoquinone and **2** (R = Me) with *p*-benzoquinone. Clearly reductive coupling of the Pd-bonded organic moiety in **7** will lead to **1**, suggesting the intermediacy of **2** in its formation. Attempts to turn this into a catalytic process in the presence of butadiene have so far been unsuccessful.



(**6**)



(**7**)

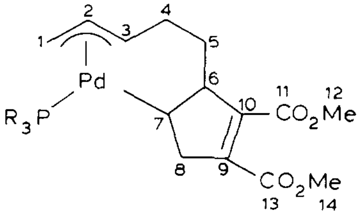
The mechanism of these reactions remains open, but one can suppose that the 1,3-dipolar addition is preceded by complexation of the alkyne or alkene to a fifth coordination position at the palladium atom in **2**.

Experimental

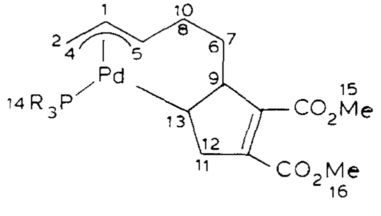
*$[\mathrm{Pd(PMe_3)}(\eta^1\text{-}\overline{\mathrm{CHCH_2C(CO_2Me)=C(CO_2Me)C}}\mathrm{H(CH_2)_2}\text{-}\eta^3\text{-}\mathrm{C_3H_4})]$ (**4**, R = Me)*

Acetylenedicarboxylic acid dimethyl ester (0.5 ml, 4.07 mmol) was added to a solution of **2** (R = Me) (0.76 g, 2.57 mmol) [4] in THF (30 ml) at −78°C. The yellow solution became orange and was stirred at −30°C for 3 h then cooled to −78°C, and the resultant white precipitate was filtered off, washed with cold pentane, and dried at 0°C under high vacuum. Yield 0.74 g (81% theory).

Found: C, 47.05; H, 6.19; P, 7.13; Pd, 24.35. $C_{17}H_{27}O_4PPd$ (432.8) calcd.: C, 47.18; H, 6.29; P, 7.16; Pd, 24.59%. IR (KBr): ν_{allyl} 1511, ν(C=C) 1630, ν(C=O) 1702, 1729 cm^{-1}. ^{31}P NMR (32.4 MHz, THF-d_8, −30°C): δ −18.3 ppm. ^{13}C NMR (75.5 MHz, toluene-d_8, −30°C) (**a**): δ(C-1), 55.81, δ(C-2) 118.13 (J(P, C) 2.0), δ(C-3) 77.06 (J(P, C) 30.5), δ(C-4) 29.84, δ(C-5) 37.51, δ(C-6) 51.28, δ(C-7) 32.06 (J(P, C) 10.2), δ(C-8) 41.01, δ(C-9) 139.46, δ(C-10) 151.16, δ(C-11/13) 168.02, 167.02, δ(C-12/14) 51.44, 51.28, δ(C-15) 17.01 ppm (J(P, C) 23.4 Hz). ^{1}H NMR (400 MHz, toluene-d_8, −30°C) (**b**) δ(H-1) 4.74 (m, $J_{1,2}$ 7.5, $J_{1,4}$ 13.1, $J_{1,5}$ 11.7), δ(H-2) 3.23 (d), δ(H-4) 2.40 (d), δ(H-5) 2.68 (m), δ(H-6) 1.55 (m), δ(H-7) 1.37 (m), δ(H-8) 2.91 (m), δ(H-9) 2.41 (m, $J_{9,11}$ 2.2), δ(H-10) 2.41 (m), δ(H-11) 3.10 (m, $J_{11,12}$ −6.8, $J_{11,13}$ 12.1, $J_{11,\mathrm{P}}$ ~0.8), δ(H-12) 2.91 (m, $J_{12,13}$ 7.7), δ(H-13) 2.41 (m), δ(H-14) 0.78 (d, $J_{14,\mathrm{P}}$ 8.0 Hz), δ(H-15/16) 3.44, 3.55 ppm.



(a)



(b)

*$[\mathrm{Pd(P(NMe_2)_3)}(\eta^1\text{-}\overline{\mathrm{CHCH_2C(CO_2Me)=C(CO_2Me)C}}\mathrm{H(CH_2)_2}\text{-}\eta^3\text{-}\mathrm{C_3H_4})]$ (**4**, R = NMe$_2$)*

Complex **4** (R = NMe$_2$) was prepared similarly as a yellow solid from **2** (R = NMe$_2$) [4] in 55% yield.

Found: C, 46.32; H, 6.97; N, 7.98; P, 5.79; Pd, 20.35. $C_{20}H_{36}N_3O_4PPd$ (519.9) calcd.: C, 46.21; H, 6.98; N, 8.08; P, 5.96; Pd, 20.47%. ^{31}P NMR (32.4 MHz, THF-d_8), −30°C): δ 132.7 ppm. ^{13}C NMR (75.5 MHz, toluene-d_8, −10°C) (**a**): δ((C-1) 56.45, δ(C-2) 118.56 (J(P, C) 4.1), δ(C-3) 79.33 (J(P, C) 38.7), δ(C-4) 23.40, δ(C-5) 40.73, δ(C-6) 49.84, δ(C-7) 30.57 (J(P, C) 11.2), δ(C-8) 44.41, δ(C-9) 140.69, δ(C-10) 148.27, δ(C-11/13) 167.74, 166.61, δ(C-12/14) 51.31, 51.15, δ(C-15) 38.09 ppm (J(P, C) 10.2 Hz). ^{1}H NMR (80 MHz, toluene-d_8, −30°C) (**b**): δ(H-1) 4.60 (m, $J_{1,2}$ 7.6, $J_{1,4}$ 13.4, $J_{1,5}$ 12.0), δ(H-2) 3.72 (d), δ(H-4) 2.32 (d), δ(H-5) 2.88 (m, $J_{5,\mathrm{P}}$ 10.8), δ(H-12) 3.15 (m), δ(H-13) 3.02 (m, $J_{13,\mathrm{P}}$ 13.8 Hz), δ(H-14) 2.30, δ(H-15/16) 3.55, 3.46 ppm.

*$[\mathrm{Pd(PPh_3)}(\eta^1\text{-}\overline{\mathrm{CHCH_2C(CO_2Me)=C(CO_2Me)C}}\mathrm{H(CH_2)_2}\text{-}\eta^3\text{-}\mathrm{C_3H_4})]$ (**4**, R = Ph)*

Complex **4** (R = Ph) was prepared similarly as a yellow solid from **2** (R = Ph) [4] in 55% yield.

Found: C, 61.89; H, 5.41; P, 4.88; Pd, 17.36. $C_{32}H_{33}O_4PPd$ (618.9) calcd.: C, 62.09; H, 5.37; P, 5.00; Pd, 17.19%. ^{31}P NMR (32.4 MHz, toluene-d_8, −30°C): δ 32.3 ppm. ^1H NMR (80 MHz, toluene-d_8, −30°C) (**b**): δ(H-1) 4.84 (m), δ(H-2) 3.62 (m), δ(H-4) 2.42 (m), δ(H-15/16) 3.44, 3.35 ppm.

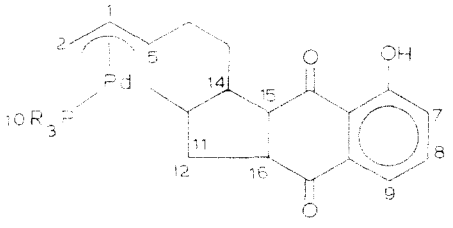
*$[Pd(P(NMe_2)_3)(\eta^1,\eta^3\text{-}C_{10}H_6O_3C_8H_{12})]$ (**6**)*

Complex **2** (R = NMe_2) (0.658 g, 1.74 mmol) and 5-hydroxynaphthoquinone (0.304 g, 1.74 mmol) were dissolved in THF (30 ml) at −40°C. The red solution was stirred for 4 h at −20°C, concentrated and treated with cold pentane (10 ml). The orange precipitate was filtered off, washed with pentane, and dried at −30°C under high vacuum. Yield 0.4 g (42% theory).

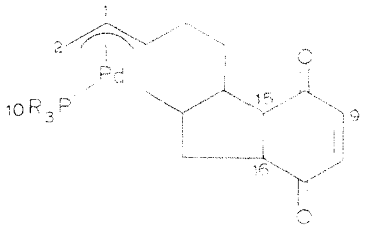
Found: C, 52.2; H, 6.4; N, 8.1; P, 5.7; Pd, 19.3. $C_{24}H_{36}N_3O_3PPd$ (551.6) calcd.: C, 52.2; H, 6.5; N, 7.6; P, 5.6; Pd, 19.3%. IR (KBr): ν(C=O) 1640, 1680, ν_{allyl} 1515 cm^{-1}. ^{31}P NMR (32.4 MHz, THF-d_8, −30°C): δ 129.9 ppm. ^1H NMR (200 MHz, THF-d_8, −30°C) (**c**): δ(H-1) 4.86 (m, $J_{1,2}$ 7.6, $J_{1,4}$ − 13.6, $J_{1,5}$ − 11.4), δ(H-2) 3.64 (d), δ(H-7) 7.18, δ(H-8) 7.67, δ(H-9) 7.49, δ(H-10) 2.41 ($J_{10,P}$ 9.7), δ(H-15) 3.14 (m, $J_{14,15}$ − 2.8, $J_{15,16}$ − 7.8), δ(H-16) 3.46 ppm (m, $J_{11,16}$ − 3.6, $J_{12,16}$ − 10.2 Hz).

$[Pd(PMe_3)(\eta^1,\eta^3\text{-}C_6H_4O_2C_8H_{12})]$ (7)

Complex **2** (R = Me) (0.67 g, 2.3 mmol) and *p*-benzoquinone (0.25 g, 2.3 mmol) were dissolved in ether (30 ml) at −40°C, and the solution was stirred for 5 h. The yellow precipitate was filtered off, washed with cold pentane, and dried under high vacuum. Yield 0.42 g (43% theory).



(**c**)



(**d**)

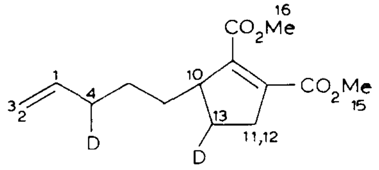
Found: C, 51.4; H, 6.3; P, 7.9; Pd, 26.5. $C_{17}H_{25}O_2PPd$ (398.5) calcd.: C, 51.2; H, 6.3; P, 7.8; Pd, 26.7%. IR (KBr): ν(C=C) 1610, ν(C=O) 1604, 1670 cm^{-1}. ^{31}P NMR (32.4 MHz, toluene-d_8, −30°C): δ −19.5 ppm. ^1H NMR (200 MHz, toluene-d_8, −30°C) (**d**): δ(H-1) 4.75, δ(H-2) 3.21, δ(H-9) 6.25, δ(H-10) 0.81, δ(H-15) 2.65, δ(H-16) 2.98 ppm.

*Reaction of **4** (R = Me) with DCl*

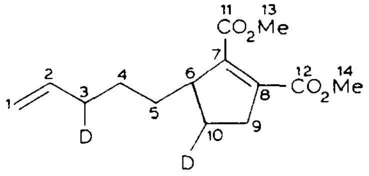
A solution of **4** (R = Me) (0.33 g) in ether (10 ml) was treated with 0.2 ml of a 37% solution of DCl in D_2O then stirred for 4 h at room temperature. The orange precipitate was filtered off and the pale-yellow filtrate was distilled to remove excess DCl and solvent, and the presence of **5** confirmed by NMR spectroscopy. Analogous results were obtained from the reaction of **4** (R = Me) with HCl.

^1H NMR (400 MHz, toluene-d_8) (**e**): δ(H-1) 5.67 (m, $J_{1,2}$ 10.2, $J_{1,3}$ 17.1, $J_{1,4}$ 6.6), δ(H-2) 4.92 (m, $J_{2,3}$ 2.1, $J_{2,4}$ − 1.3), δ(H-3) 4.95 (m, $J_{3,4}$ − 1.6), δ(H-4) 1.86 (m), δ(H-10) 2.89 (m, $J_{10,12}$ 2.1), δ(H-11) 2.54 (m, $J_{11,12}$ 17.0), δ(H-12) 2.35 (m, $J_{12,13}$ 9.2 Hz), δ(H-13) 1.74 (m), δ(H-15) 3.50 (s), δ(H-16) 3.60 (s) ppm. ^{13}C NMR

(75.5 MHz, toluene-d_8) (**f**): δ(C-1) 114.8, δ(C-2) 139.3, δ(C-3) 34.2 ($J_{C,D}$ 18.8), δ(C-4) 27.2, δ(C-5) 33.5, δ(C-6) 48.6, δ(C-7) 146.4, δ(C-8) 137.7, δ(C-9) 33.1, δ(C-10) 29.1 ($J_{C,D}$ 19.9), δ(C-11/12) 166.7, 165.4, δ(C-13/14) 51.63, 51.60 ppm.



(**e**)



(**f**)

References

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