

REACTION OF ACETYLENES WITH TRANSITION METALS

IX*. REACTION OF 1-CHLORO-1,2-DIPHENYL-3-ALKYL- π -ALLYLPALLADIUM COMPLEXES WITH CARBON MONOXIDE

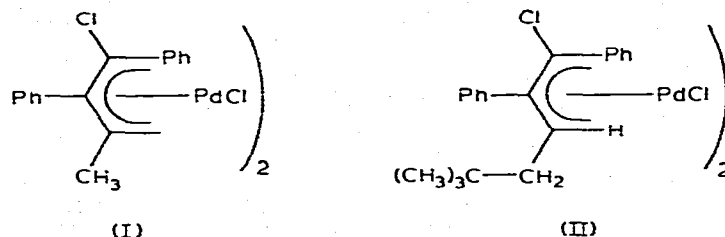
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Summary

The reaction of 1-chloro-1,2-diphenyl-3-alkyl- π -allylpalladium complexes with carbon monoxide gives methoxy esters, lactones and carbomethoxy- π -allylpalladium complexes.

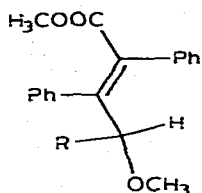
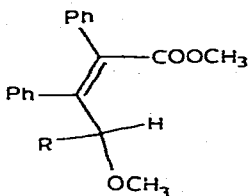
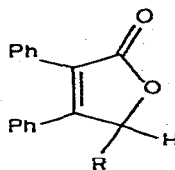
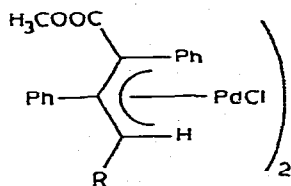
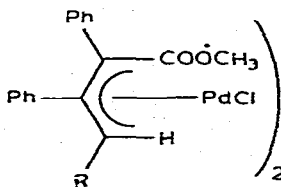
Recently we have reported [1] on the easy synthesis of 1-chloro-1,2-diphenyl-3-alkyl- π -allylpalladium complexes I and II, from diphenylacetylene, dichlorobis(benzonitrile)palladium, and ethylene or t-butylethylene. We now describe new aspects of the reactions of I and II with carbon monoxide.



The reactions were performed at room temperature, by bubbling an excess of carbon monoxide through the solution of the complexes in a mixture of methanol—methylene chloride for 8 h. After removal of the metallic palladium and the solvent in vacuo, the oily residue was chromatographed on neutral

* For Part VIII, see ref. 1.

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(III A) R = CH₃(IV A) R = CH₂C(CH₃)₃(III B) R = CH₃(IV B) R = CH₂C(CH₃)₃(V) R = CH₃(VI) R = CH₂C(CH₃)₃(VII A) R = CH₃(VIII A) R = CH₂C(CH₃)₃(VII B) R = CH₃(VIII B) R = CH₂C(CH₃)₃

alumina, yielding the methoxy esters III (19.5%) and IV (37%), the lactones V (23%) and VI (15%), and the complexes VII (39%) and VIII (37%), respectively. The structures of the products were established on the basis of the spectral data and chemical behaviour.

The chemical shift of the H(3) proton (4.11 ppm for IIIA and 4.33 for IIIB) indicate a neighbouring methoxy rather than a carbomethoxy group (3.0 ppm [2]). The *trans* orientation of the phenyl group in IIIA and IVA was assigned on the basis of the non-shielded aromatic signals (δ 7.16–7.45 ppm); in the *cis* isomers IIIB and IVB, the mutual shielding of the two phenyl rings shifted these signals to 6.90–7.20 ppm.

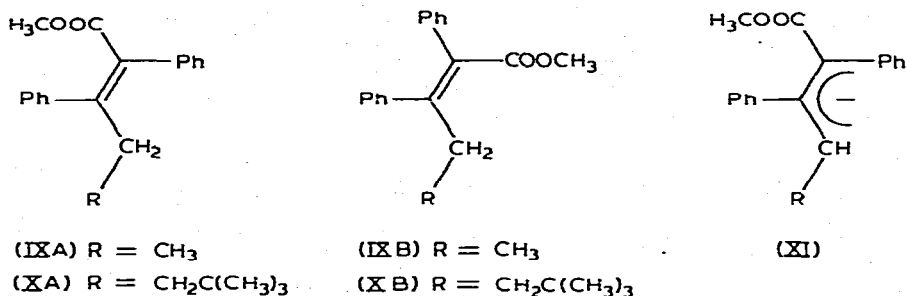
Both isomers IIIA and IIIB on reduction with H₂/Pd gave the same 1-carbomethoxy-1,2-diphenyl-3-methoxybutane (m.p. 65°C).

The structures of the known lactones V (m.p. 136°C) and VI (m.p. 60°C) were assigned on the basis of their spectra and by comparison with literature data [3].

For each of the carbomethoxy- π -allylpalladium complexes VII (m.p. 137°C, $\nu(\text{CO})$ 1725 cm⁻¹), and VIII (m.p. 145°C, $\nu(\text{CO})$ 1712 cm⁻¹), the NMR spectra indicate a mixture of two isomers (VIIA/VIIB ratio 2/1 and VIIIA/VIIIB ratio 1.5/1, evaluated by means of the NMR spectrum). The *anti* orientation of the phenyl group in VIIA and VIIIA shields the H(3) allylic proton and the signals are upfield shifted by approximately 0.75 ppm compared with VIIB and VIIIB, in which the *anti*-COOCH₃ group deshields the H(3) protons.

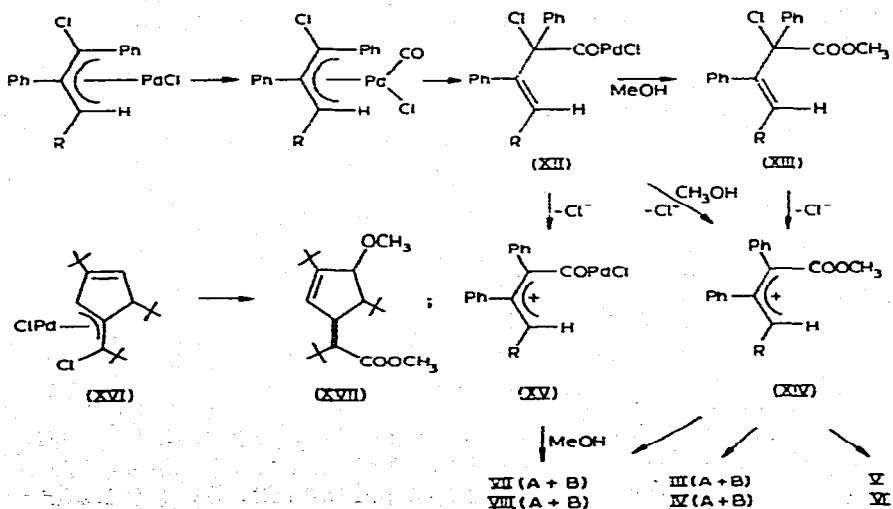
The elimination of the palladium from the complexes VII and VIII (mixture of isomers A and B) on heating with methanolic base leads to a mixture of the *trans*- and *cis*-1,2-diphenylcarbomethoxyalkenes IX and X, respectively; the

same compound IX (mixture of IXA and IXB), together with 1-carbomethoxy-1,2-diphenylbutane (m.p. 68°C) was obtained by reduction of VIIA and VIIB with NaBH_4 . The intermediacy of an allyl anion [4] such as XI accounts for the obtained products (IX and X).



The characteristic course of the carbonylation of complexes I and II is due to the presence of chlorine at C(1). We cannot at present decide whether the ionisation of the chlorine occurs in XII and XIII. The reaction of the allyl cations XIV or XV with methanol can explain the production of the isomeric carbomethoxy complexes VII and VIII; an intramolecular reaction can also account formation of the lactones V and VI as well as the methoxy esters III and IV.

The production of the esters with a methoxy group at the end of a conjugated system was also observed [2] in the case of the reaction of π -allyl complexes XVI to give XVII. It seems that this behaviour is typical of the π -allyl complexes bearing a chlorine at the end of the allyl system.



Experimental

Microanalyses were performed by Miss E. Siam and Mrs. V. Daniel. IR spectra were recorded on a double beam UR-20-Zeiss-Jena spectrophotometer. NMR spectra were determined with a Varian A-60A spectrometer (TMS as internal standard). UV spectra were recorded on a VSU-Zeiss-Jena spectrophotometer.

Reaction of complex I with carbon monoxide

Carbon monoxide was bubbled for 8 h through a solution of 2.0 g (5.2 mmol) of I in 30 ml methylene chloride and 50 ml methanol. Metallic palladium separated. The yellow solution was filtered and evaporated in vacuo, and the residue (1.7 g) was chromatographed on alumina with ether (fraction 1) and then with ether containing 10% methanol (fraction 2).

Fraction 1, 0.70 g mixture of methoxy ester III and lactone V, was chromatographed on alumina. With petroleum ether containing 5% ether, as eluent, 0.30 g (19.4%) of III (mixture of IIIA and IIIB in ratio 2.33/1) were obtained. IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1740. NMR (CDCl_3 , δ , ppm): IIIA: 1.10 (d, 3H, CH_3 , J 6 Hz), 3.25 and 3.30 (2s, 6H, OCH_3 and COOCH_3), 4.11 (q, 1 allylic H, J 6 Hz), 7.20–7.45 (m, 10 aromatic H). IIIB: 1.28 (d, 3H, CH_3 , J 6 Hz), 3.48 and 3.79 (2s, 6H, OCH_3 and COOCH_3), 4.33 (q, 1 allylic H, J 6 Hz), 6.90–7.20 (m, 10 aromatic H). Analysis found: C, 77.42; H, 6.94. $\text{C}_{19}\text{H}_{20}\text{O}_3$ calcd.: C, 77.00; H, 6.80%. On standing, white crystals of IIIA (m.p. 95°C) separated; their spectra were identical with those described above.

With a mixture of 1/1 ether/petroleum ether as eluent 0.30 g (23%) of lactone V was obtained (m.p. 136°C) (lit. [3] m.p. 136 – 140°C). IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1770. NMR (CDCl_3 , δ , ppm): 1.43 (d, 3H, CH_3 , J 6.5 Hz), 5.46 (q, 1 allylic H), 7.31 (broad s, 10 aromatic H). UV (EtOH): λ_{max} 286.1 nm ($\log \epsilon$ 4.062). Analysis found: C, 81.10; H, 5.89. $\text{C}_{17}\text{H}_{14}\text{O}_2$ calcd.: C, 81.58; H, 5.63%.

Fraction 2, 0.90 g crude carbomethoxy complexes VII was chromatographed on alumina with ether containing 10% methanol, yielding 0.83 g (39%) of VII (mixture of 65% VIIA and 35% VIIB, determined by means of NMR), m.p. 137°C . IR (KBr, cm^{-1}): $\nu(\text{C}=\text{O})$ 1725. NMR (CDCl_3 , δ , ppm): VIIA: 1.16 (d, 3H, CH_3 -3, J 6.5 Hz), 3.29 (s, 3H, COOCH_3), 4.46 (q, 1 allylic H, J 6.5 Hz), 6.80–7.80 (m, 10 aromatic H). VIIB: 1.16 (d, 3H, CH_3 -3, J 6.5 Hz), 3.68 (s, 3H, COOCH_3), 5.26 (q, 1 allylic H, J 6.5 Hz), 6.80–7.80 (m, 10 aromatic H). Analysis found: C, 53.40; H, 4.39; Cl, 9.82; Pd, 25.53. $\text{C}_{18}\text{H}_{17}\text{ClOPd}$ calcd.: C, 53.10; H, 4.20; Cl, 8.70; Pd, 26.13%.

Reaction of complex II with carbon monoxide

Carbon monoxide was bubbled for 8 h through a solution of 0.70 g (1.75 mmol) of II in 20 ml methylene chloride and 30 ml methanol. The yellow solution was filtered, then evaporated, and the residue (0.65 g) was chromatographed on alumina with ether (fraction 1) and then with ether containing 10% methanol (fraction 2) as eluants.

Fraction 1 (0.35 g) was chromatographed on alumina. Use of petroleum ether with 10% ether as eluant gave 0.23 g (37.7%) of IV (mixture of IVA and IVB in ratio 1/1). IR (CCl_4 , cm^{-1}): $\nu(\text{C}=\text{O})$ 1735. NMR (CDCl_3 , δ , ppm): IVA: 0.75 (s, 9H, t-Bu), 1.20–1.55 (m, 2H, CH_2), 3.16 and 3.26 (2s, 6H, OCH_3 and

COOCH₃), 4.05–4.30 (m, 1 allylic H), 7.16–7.40 (m, 10 aromatic H). IVB: 0.86 (s, 9H, t-Bu), 1.20–1.55 (m, 2H, CH₂), 3.38 and 3.70 (2s, 6H, OCH₃, and COOCH₃), 4.05–4.30 (m, 1 allylic H), 6.90–7.16 (m, 10 aromatic H). Analysis found: C, 78.03; H, 8.03. C₂₃H₂₈O₃ calcd.: C, 78.37; H, 8.01%.

With ether as eluant 79 mg (15%) of VI were obtained; m.p. 60°C (methanol). IR (CCl₄, cm⁻¹): ν(C=O) 1770. NMR (CDCl₃, δ, ppm): 1.03 (s, 9H, t-Bu), 0.95–1.75 (m, 2H, CH₂), 5.43 (q, 1H, H-3, *J* 3.2 and 8.2 Hz), 7.30 (s, 10 aromatic H). Analysis found: C, 81.76; H, 7.36. C₂₁H₂₂O₂ calcd.: C, 82.32; H, 7.24%.

Fraction 2 (0.35 g) was chromatographed on alumina with methanol as eluant, yielding 0.30 g (37.5%) of VIII (mixture of VIIIA and VIIIB in ratio 1.5/1) as yellow crystals (m.p. 145°C, methanol). IR (KBr, cm⁻¹): ν(C=O) 1712. NMR (CDCl₃, δ, ppm): VIIIA: 0.78 (s, 9H, t-Bu), 1.45–1.85 (broad, 2H, CH₂), 3.25 and 3.55 (2s, 3H, COOCH₃), 4.50 (broad s, 1 allylic H), 7.20–7.70 (m, 10 aromatic H). VIIIB: 0.88 (s, 9H, t-Bu), 1.45–1.85 (broad, 2H, CH₂), 3.70 and 3.80 (2s, 3H, COOCH₃), 5.25 (broad s, 1 allylic H), 6.90–7.30 (m, 10 aromatic H). Analysis found: C, 57.26; H, 5.47; Cl, 8.95; Pd, 24.00. C₂₂H₂₅ClO₂Pd calcd.: C, 57.03; H, 5.44; Cl, 7.65; Pd, 23.00%.

Reduction of the methoxy esters III

A solution of 0.10 g (0.34 mmol) of III (mixture of IIIA and IIIB) in 20 ml of methanol was hydrogenated in presence of Pd/C to give 0.080 g (80%) of 1-carbomethoxy-1,2-diphenyl-3-methoxybutane (m.p. 65°C). IR (CCl₄, cm⁻¹): ν(C=O) 1736, ν(C–O) 1161. NMR (CCl₄, δ, ppm): 0.92 (d, 3H, CH₃, *J* 6.0 Hz), 3.35 and 3.66 (2s, 6H, OCH₃ and COOCH₃), 3.75 (q, 1H tert., *J* 6.0 Hz), 3.10–3.80 (m, 2H tert., H(1) and H(2)), 6.90–7.30 (m, 10 aromatic H). Analysis found: C, 76.23; H, 7.55. C₁₉H₂₂O₃ calcd.: C, 76.48; H, 7.42%.

Reaction of complexes VII with NaBH₄

A suspension of 0.5 g (1.23 mmol) VII (mixture of VIIA and VIIB) in 5 ml water and 30 ml diethyl ether was treated with 1.5 g NaBH₄ in portions and the mixture was left at room temperature for 24 h. The ethereal layer was separated, washed with water, dried and evaporated, and the residue was chromatographed on alumina. Use of petroleum ether as eluant gave 60 mg (18%) of 1-carbomethoxy-1,2-diphenylbutane (m.p. 68°C, methanol). IR (CCl₄, cm⁻¹): ν(C=O) 1748. NMR (CCl₄, δ, ppm): 0.75 (t, 3H, CH₃, *J* 7.0 Hz), 1.40–2.10 (m, 2H, CH₂, *J* 7.0 Hz), 1.50–2.40 (m, 2H, H(1) and H(2)), 3.64 (s, 3H, COOCH₃), 6.80–7.20 (m, 10 aromatic H). Analysis found: C, 80.90; H, 7.60. C₁₈H₂₀O₂ calcd.: C, 80.56; H, 7.51%.

With diethyl ether as eluant, 0.20 g (61%) of a mixture of IXA and IXB were obtained. IR (CCl₄, cm⁻¹): ν(C–O) 1210, ν(C=O) 1742. NMR (CCl₄, δ, ppm): IXA: 0.85 (t, 3H, CH₃, *J* 7.5 Hz), 2.37 (q, 2H, CH₂, *J* 7.5 Hz), 3.31 (s, 3H, COOCH₃), 7.15–7.45 (m, 10 aromatic H). IXB: 1.03 (t, 3H, CH₃, *J* 7.5 Hz), 2.67 (q, 2H, CH₂, *J* 7.5 Hz), 3.71 (s, 3H, COOCH₃), 6.85–7.15 (m, 10 aromatic H). Analysis found: C, 80.83; H, 7.16. C₁₈H₁₈O₂ calcd.: C, 81.17; H, 6.81%. On standing further, white crystals of IXA (m.p. 77°C, methanol), separated; their spectra were identical with those described above.

Reaction of complexes VII with CH₃OH/K₂CO₃

A solution of 0.20 g (0.49 mmol) VII (mixture of VIIA and VIIB) in 10 ml

methanol was treated with 0.30 g (3 mmol) potassium carbonate, and the mixture was boiled for 1 h. The palladium metal was filtered off, the solution was evaporated and the residue was chromatographed on alumina with ether as eluant to give 0.085 g (65%) of IX (mixture of IXA and IXB, with spectra identical with those described above).

Reaction of complexes VIII with CH₃OH/K₂CO₃

Working as above, from 0.20 g (0.43 mmol) VIII (mixture of VIIIA and VIIIB), 0.10 g (72%) X (mixture of XA and XB) were obtained. IR (CCl₄, cm⁻¹): $\nu(\text{C}=\text{O})$ 1730. NMR (CCl₄, δ , ppm): XA: 0.70 (s, 9H, t-Bu), 1.20–2.80 (m, 4H, CH₂–CH₂), 3.31 (s, 3H, COOCH₃), 7.15–7.50 (m, 10 aromatic H). XB: 0.88 (s, 9H, t-Bu), 1.20–2.80 (m, 4H, CH₂–CH₂), 3.70 (s, 3H, COOCH₃), 6.85–7.15 (m, 10 aromatic H).

References

- 1 S. Stalcu, I.G. Dinulescu, F. Chiraleu and M. Avram, *J. Organometal. Chem.*, 113 (1976) C69.
- 2 E. Avram and M. Avram, *Rev. Roumaine Chim.*, 20 (1975) 775.
- 3 A. Zweig, K.R. Huffman, J.B. Gallivan, M.K. Orloff and F. Halverson, *J. Amer. Chem. Soc.*, 96 (1974) 1449.
- 4 R. Hüttel and P. Kochs, *Chem. Ber.*, 101 (1968) 1043; H. Christ and R. Hüttel, *Angew. Chem.*, 75 (1963) 921.