Journal of Organometallic Chemistry, 247 (1983) C63—C65
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

REACTIONS OF 2,4-PENTADIENOIC ACID METHYL ESTER WITH NICKEL(0) AND PLATINUM(0) COMPOUNDS

H.M. BUCH, G. SCHROTH, R. MYNOTT and P. BINGER*

Max-Planck-Institut für Kohlenforschung, Lembkestr. 5, D-4330 Mülheim/Ruhr (Federal Republic of Germany)

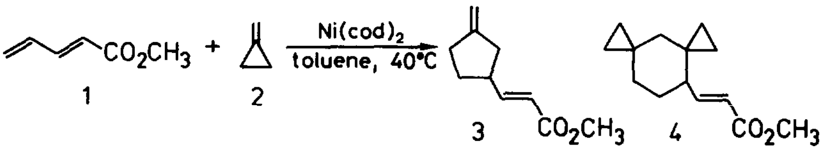
(Received February 18th, 1983)

Summary

The course of the reaction of the title compound with nickel(0) and platinum(0) complexes strongly depends on the kind and number of the additional ligands attached to the metal, and a variety of metal complexes can be formed.

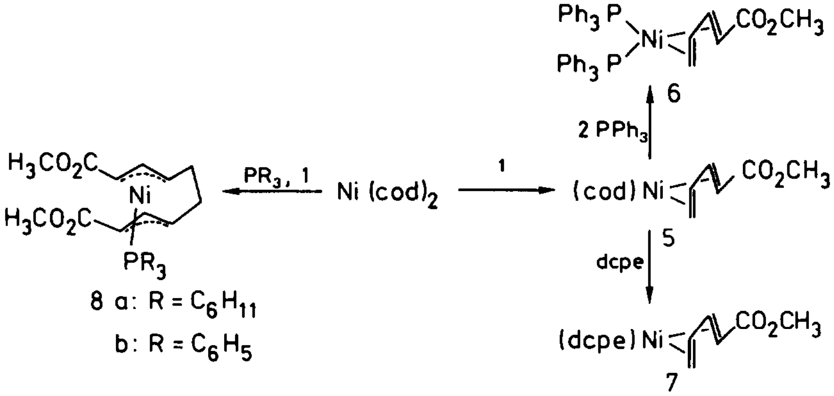
A recent publication [1] on the nickel(0)-catalysed cyclo-dimerisation of functionalized dienes prompted us to communicate some results we have obtained with 2,4-pentadienoic acid methyl ester (I).

Our initial observation [2] was that 1 can be smoothly co-oligomerised with methylenecyclopropane (2) in the presence of catalytic amounts of di-1,5-cyclooctadiene-nickel [Ni(cod)$_2$] to give the codimer 3 and the cotrimer 4 as the main products [3]. This unexpected behaviour of 1 prompted a study of its stoichiometric reactions with some nickel(0) and platinum(0) complexes directed at providing information about the reactivity and coordinating ability of this diene.

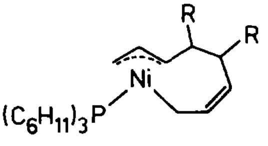


At 0°C 1 displaces only one cod ligand of Ni(cod)$_2$ to give 5 as red crystals [4]. Its ^{1}H NMR spectrum is consistent with a η^4-bonded 1. The second cod ligand can easily be replaced by two triphenylphosphine molecules yielding red-violet crystals of 6. An X-ray analysis of the similarly prepared complex 7 will be reported elsewhere [5].

0022-328X/83/$03.00



In the presence of one molar equivalent of a phosphine (PPh_3, $P(C_6H_{11})_3$) **1** reacts with $Ni(cod)_2$ even at 0°C with C—C-bond formation to give the *syn,syn*-bis-(η^3-allyl) complexes **8a, 8b** as dark red crystals. For both phosphines only one isomer was obtained in high yield (>85%) as established by ^{31}P NMR spectroscopy. This is in contrast to corresponding reactions with butadiene and piperylene [6]. When tricyclohexylphosphine was used as a ligand, η^3-allyl-η^1-allyl complexes (**9a, 9b**) were obtained, while in the presence of triphenylphosphine bis-(η^3-allyl) complexes were isolated. It should also be noticed that piperylene gives a head to head dimer while **1** couples via tail to tail.

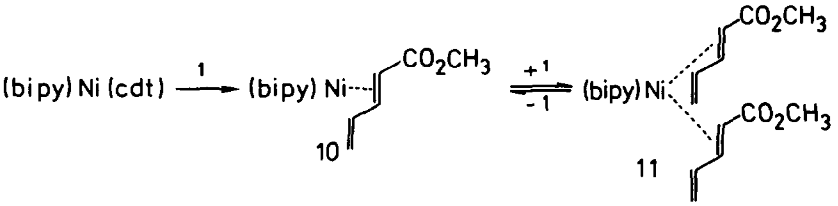


9 a: R = H
b: R = CH_3

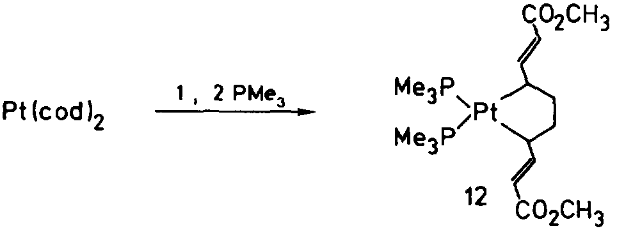
The ^{13}C NMR spectrum of **8a** reveals the presence of a mirror plane [7] while the *syn,syn*-conformation of the two allyl groups can be deduced from the ^1H NMR spectrum ($J_{meso,anti}$ 10.5 and 11.5 Hz). This observation indicated that a catalytic cyclo-dimerisation of **1**, proceeding via organonickel intermediates similar to **5**—**8**, should be possible. We tested this by treating **1** with catalytic amounts of $Ni(cod)_2/P(C_6H_{11})_3$ (1/1) at 80°C for 2 h, and this gave a mixture of five cyclodimers (as established by GLC combined with mass spectroscopy and subsequent hydrogenation) in the ratio 2.5/67.3/2.3/17.0/6.9. This mixture contained only 2.5% of a disubstituted cyclooctadiene derivative which was described in ref. 1. The main products were isomeric vinylcyclohexene derivatives (^1H NMR).

$$1 \xrightarrow[\text{toluene, 80°C, 2h}]{Ni(cod)_2/P(C_6H_{11})_3\ (1:1)} \underset{\text{(5 isomers)}}{C_8H_{10}(CO_2CH_3)_2} \qquad [77\%]$$

When 2,2′-bipyridine (bipy) was used as ligand, another type of complex was obtained. When **1** was added to a solution of all-*trans*-1,5,9-cyclododecatrienenickel [Ni(cdt)] and bipy (1/1) a quantitative yield was obtained of dark green microcrystalline complex **10**, in which **1** is η^2-bonded through the di-substituted CC double bond (IR: ν(C=C) 1650 cm^{-1}; ^{1}H NMR: δ 4,55—5.57 ppm, free vinyl group) indicating that in this complex **1** behaves like an activated olefin [8]. With additional **1** complex **10** reacts reversibly to give the dark red crystalline 18-electron complex **11**.



In contrast to Ni(cod)$_2$, Pt(cod)$_2$ reacts with excess **1** in the presence of two moles of trimethylphosphine to give white crystals of **12** in 78% yield. The platinacyclopentane structure of **12** was unambiguously derived from spectroscopic data [9]. A similar divinylplatinacyclopentane has previously been obtained by treating butadiene with Pt(cod)$_2$ [10].



It can be seen from these experiments that the reactivity of **1** can be controlled over a wide range by variation of the metal matrix and that stoichiometric as well as catalytic reactions can be achieved under mild conditions.

References

1 P. Brun, A. Tenaglia and B. Waegell, Tetrahedron Lett., 24 (1983) 385.

2 H.M. Büch, Diplomarbeit, Universität Kaiserslautern, 1979.

3 Compounds 3 and 4 were isolated by fractional distillation and preparative GLC, respectively, and were characterised by means of ^{1}H and ^{13}C NMR (3): ^{13}C NMR: (CDCl$_3$): 167.43(s), 152.38(d), 150.99(s), 119.98(d), 106.20(t), 51.46(q), 42.78(d), 39.14(t), 32.47(t), 32.04(t) ppm; (4): ^{13}C NMR (C_6D_6): 166.35(s), 150.38(d), 122.12(d), 50.92(q), 44.76(d), 42.49(t), 32.61(t), 29.53(t), 21.48(s), 18.62(s). 11.88(t), 11.37(t), 11.18(t), 8.88(t) ppm.

4 All transition metal complexes described herein were air-sensitive, diamagnetic, crystalline compounds which gave satisfactory elemental analyses. They were characterized by IR, ^{1}H NMR (where appropriate) and/or ^{31}P NMR spectroscopy. Molecular weights were determined (where possible) cryoscopically.

5 H.M. Büch, P. Binger, R. Goddard and C. Krüger, submitted.

6 R. Benn, B. Büssemeier, S. Holle, P.W. Jolly, R. Mynott, I. Tkatchenko and G. Wilke, Z. Naturforsch., in press.

7 (8a) ^{13}C NMR (C_6D_6): 171.95, 103.07(d), 71.43(d), 55.80(d), 50.64(q), 36.88, 36.18, 30.29, 28.11, 26.94.

8 cf. F. Ozawa, T. Ito, Y. Nakamura and A. Yamamoto, J. Organomet. Chem., 168 (1979) 375.

9 (11) ^{31}P NMR (32 MHz, C_6D_6): −27.8 (J_{PPt} = 2110.6); ^{1}H NMR (400 MHz, C_6D_6): 7.87 (m, 2H), 6.01 (m, 2H), 3.51 (m, 6H), 3.22 (m, 2H), 2.50 (m, 2H), 2.40 (m, 2H), 0.87 (m, 18H); ^{13}C NMR (100 MHz, $C_6D_5CD_3$): AA′X or ABX spectra with ^{195}Pt satellites (AA′MX or ABMX); 169.0, 157.5 (J^*_{PC} = 2.5 Hz, J_{PtC} = 61.0), 106.8 (J^*_{PC} = 3.3, J_{PtC} = 45.8), 50.1, 49.1 ($|J_{PC}|$ = 70.8, $|J_{P'C}|$ = 6.5, J_{PtC} = 479.6), 35.3 ($|J_{PC}|$ = 6.3, $|J_{P'C}|$ = 3.0), 16.6 ($|J_{PC}|$ = 26.4, $|J_{P'C}|$ = 4.1, J_{PtC} = 24.2, $J_{PP'}$ = 16.1);
*) $J_{PC} = |J_{PC} + J_{P'C}|/2$
m.p. 92°C.

10 G.K. Barker, M. Green, J.A.K. Howard, J.L. Spencer, and F.G.A. Stone, J. Chem. Soc. Dalton, (1978) 1839.