Journal of Organometallic Chemistry, 413 (1991) 411–417
Elsevier Sequoia S.A., Lausanne
JOM 21539

Catalytic hydrogenation of the phosphorus–carbon double bond in phosphaalkene complexes *

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(Received October 22nd, 1990)

Abstract

The catalytic transformations of phosphaalkene P–$W(CO)_5$ complexes under H_2 pressure in the presence of rhodium catalysts have been studied. In the presence of the cationic complex $Rh(diphos)^+$ isomerization of phosphaalkene into secondary vinylphosphine complexes is greatly favoured. On the other hand, in the presence of the covalent Rh(diphos)Cl complex hydrogenation of the P=C double bond is greatly predominant. Experiments with deuterium in place of hydrogen indicated that there is clean *cis* addition of H_2 or D_2 to the double bond. No scrambling between tungsten and rhodium is observed in the postulated transient η^1-P, η^2-PC 4-electron phosphaalkene complexes.

Introduction

Phosphaalkenes are characterized by two closely spaced HOMO's, corresponding to the π-bond and the lone pair at phosphorus [1]. Since the π-bond is practically apolar [2], it is theoretically possible to mimic the chemistry of the π-bond of alkenes with the π-bond of phosphaalkenes whenever the lone pair at phosphorus does not interfere. To ensure this it is necessary to block this lone pair, and so use of relatively inert complexing groups is the best way to proceed. A very significant example of this approach was recently reported from our laboratory [3]. Whereas oxidation of phosphaalkenes leads to the cleavage of the P=C double bond via an initial attack at the phosphorus lone pair [4], clean epoxidation of phosphaalkene P–$W(CO)_5$ complexes can be achieved with peracids [3]. ntit

Catalytic reactions using soluble transition metal catalysts are of great importance in the chemistry of alkenes. They include, *inter alia*, polymerisation, hydrogenation, and hydroformylation. We wished to check whether or not it was possible to carry over this kind of chemistry to the P=C double bond. Since low valent soft transition metal centres such as those used in most of the soluble catalysts readily coordinate to phosphorus, it was obviously necessary to block the phosphaalkene

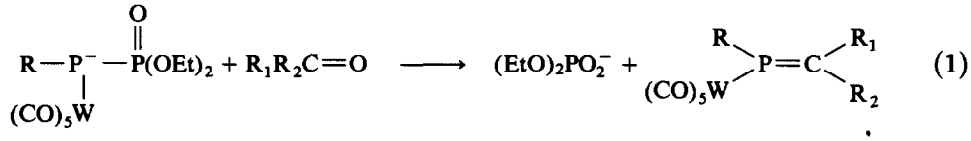
* Dedicated to Professor Peter L. Pauson, one of the pioneers of modern transition metal chemistry.

0022-328X/91/$03.50

lone pair in order to obtain clear-cut results. We thus decided to investigate the catalytic transformations of phosphaalkene P–$W(CO)_5$ complexes and chose catalytic hydrogenation as the model reaction.

Results and discussion

The phosphaalkene substrates were prepared via the so called "phospha-Wittig" reactions [5] (Eq. 1).

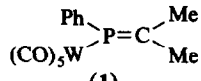
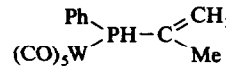
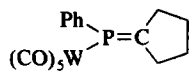
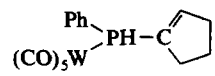
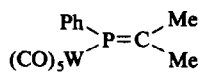
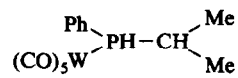
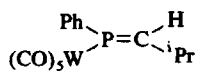
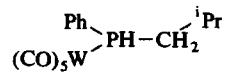
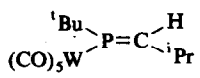
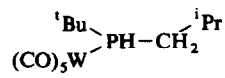
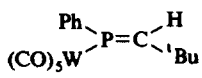
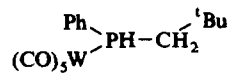


(1)

The preliminary experiments were performed with the classical cationic rhodium catalyst $Rh(diphos)^+PF_6^-$ [6] and complexes **1** or **4** under 8 bars of H_2 (see Table 1, entries 1 and 2). After a few hours, we mainly observed the isomerization of the

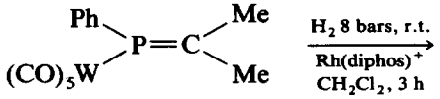
Table 1

Catalytic hydrogenation or isomerization of phosphaalkene complexes [a]

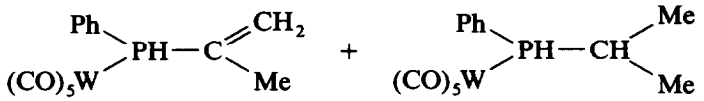
Entry	Substrate [b]	Catalyst	Solvent	T [c] (h)	Main product	R [d] (%)
1	 (1)	$Rh(diphos)^+$	CH_2Cl_2	3	 (2)	84
2	 (4)	$Rh(diphos)^+$	CH_2Cl_2	1	 (5)	84
3	 (1)	Rh(diphos)Cl	$Me_2C{=}O$	25	 (3)	71
4	 (*Z*-6)	$Rh(diphos)^+$	CH_2Cl_2	1	 (7)	77
5	 (*Z*-8)	$Rh(diphos)^+$	CH_2Cl_2	24	 (9)	35
6	 (11)	$Rh(diphos)^+$	CH_2Cl_2	3	 (12)	83

[a] Reaction conditions: $p(H_2) = 8$ bars, 25 °C, catalyst/substrate = 1/10. [b] $^iPr = CH(Me)_2$, $^tBu = C(Me)_3$, diphos = $Ph_2PCH_2CH_2PPh_2$. [c] Reaction time. [d] Yield after purification by chromatography.

phosphaalkene into the corresponding secondary vinylphosphine complex, and the expected hydrogenation of the P=C double bond occured only to a very limited extent. An example is depicted in Eq. 2. Even after a further 20 h the composition of the reaction mixture was unchanged, and complex **2** was not hydrogenated to give complex **3**.



(1)
$\delta^{31}P = +169.7$ ppm



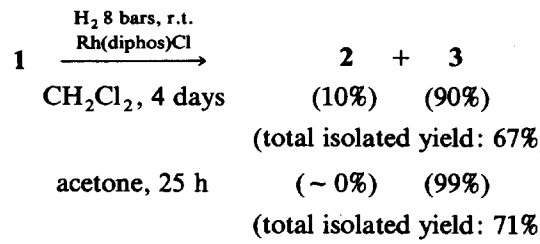
(2)

(2, 95%)
$\delta^{31}P = +0.8$ ppm

(3, 5%)
$\delta^{31}P = -7.9$ ppm

(total isolated yield: 84%)

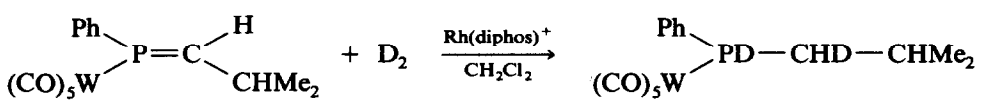
Similar results were obtained with phosphaalkene **4** (Table 1, entry 2). The resistance of the hindered P=C and C=C double bonds of **1** and **2** toward hydrogenation under mild conditions was not in itself surprising. But we were more surprised when we observed that the covalent complex Rh(diphos)Cl was able to catalyse the slow hydrogenation of **1** to give **3** in fair yield (Eq. 3) (entry 3).



(3)

Comparison of the details in Eqs. 2 and 3 suggests that both the Lewis acidity of the catalyst and of the solvent favour isomerization over hydrogenation. The competition between hydrogenation and isomerization was also shown to be highly dependent on the substitution scheme of the P=C double bond. Even with the cationic rhodium catalyst, the C-monosubstituted P=C double bonds do not isomerize (entries 4 and 5, Table I).

The formation of **7** and **9** from **6** and **8** could be interpreted as the result of the hydrogenation of the isomeric vinylphosphine complexes. This was shown not to be the case by using deuterium in place of hydrogen (Eq. 4).

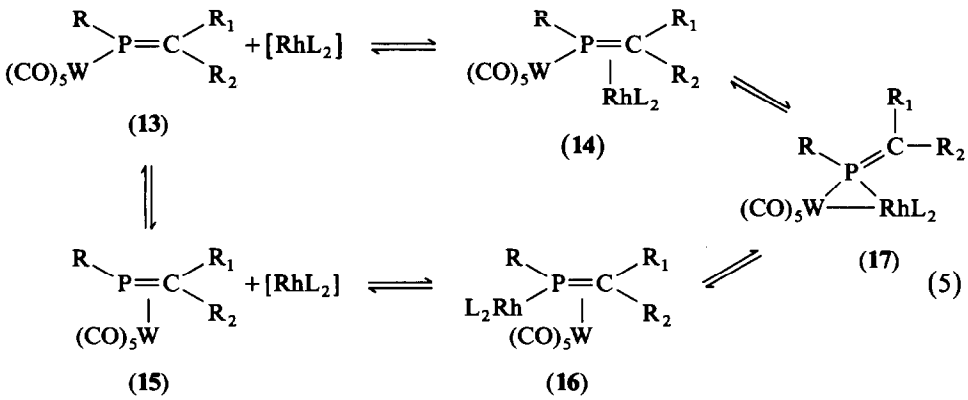


(6)

(10)
$\delta^{31}P = -35.6$ ppm (t)

(4)

The deuterated complex **10** was obtained as a mixture of two diastereomers which can be distinguished by examining the C*H*D resonance. The ^{31}P NMR spectrum shows a characteristic triplet at -35.6 ppm ($^1J(P-D) = 51.3$ Hz). By using the two C*H*D resonances (doublet at 1.58 and triplet at 1.75 ppm) we were able to monitor the variation of the diastereomeric ratio of **10** upon variation of the *Z*/*E* ratio of **6**. Experiments with *Z*/*E* ratios of 90/10, 70/30 and 30/70 gave corresponding diastereomeric ratios for **10**. This observation very probably reflects a clean *cis*-addition of D_2 to the P=C double bond in aprotic solvents [7]. Finally, comparison of entries 4, 5 and 6 (Table 1) shows that the hydrogenation reaction is drastically slowed down by the presence of a bulky substituent at phosphorus but that the bulk of the substituent on the sp^2 carbon has only a limited influence. The available data are too limited to allow discussion in depth of the mechanism of the catalytic hydrogenation of P=C double bonds, but some features can be pointed out, namely that these successful hydrogenation experiments mean that phosphaalkene P–W(CO)$_5$ complexes such as **13** can give labile σ,π-complexes such as **14**, and furthermore that there is no scrambling between rhodium and tungsten via a potential equilibrium between **13** and **15** or via **17** (Eq. 5). (Such transformations have precedent in the literature [8].)



(5)

It is evident that phosphaalkene P–W(CO)$_5$ complexes are appropriate substrates for the study of the transformations of P=C double bonds catalysed by rhodium catalysts.

Experimental

The rhodium catalysts were prepared by literature methods [6]. The hydrogenations were performed in a constant volume apparatus. Silica gel (70-230 mesh) was used for chromatographic separations. NMR spectra were recorded on a Bruker AC 200 SY spectrometer operating at 200.13 MHz for ^1H and 50.32 MHz for ^{13}C and a Bruker WP 80 SY spectrometer operating at 32.44 MHz for ^{31}P. Chemical shifts are expressed in parts per million downfield from internal TMS (^1H and ^{13}C) and 85% H_3PO_4 (^{31}P). Mass spectra were obtained at 70 eV with a Shimadzu GC-MS QP 1000 instrument by the direct-inlet method. Infrared spectra were recorded with a Perkin–Elmer model 297 spectrometer. Elemental analyses were performed by the "Service d'analyse du CNRS", Gif-sur-Yvette, France. The synthesis of phosphaalkene complexes **1**, **4**, **6**, **8** and **11** was previously described [5].

General procedure for the hydrogenation experiments

The phosphaalkene complex (2 mmol) was added to a solution of 0.2 mmol of the rhodium complex $Rh(COD)_2PF_6$ (or 0.1 mmol of $[RhCl(COD)]_2$) and 0.2 mmol of diphos in CH_2Cl_2 or acetone (10 ml). The mixture was introduced into the hydrogenation flask under inert atmosphere. The flask was evacuated and then filled with hydrogen up to a total pressure of 8 bars. The mixture was stirred at room temperature and the extent of hydrogenation was determined by ^{31}P NMR spectroscopy. The final product was purified by column chromatography with hexane as eluent.

Hydrogenation of complex 1: reactions 2 and 3

A mixture of **2** and **3** was obtained. The ratio **2**:**3** was established by ^{31}P NMR spectroscopy. Complex **2** was described previously [5b]. Complex **3** was obtained in 71% yield after 25 h of reaction in acetone with Rh(diphos)Cl as catalyst: colorless oil; ^{31}P NMR ($CDCl_3$): δ −0.95 ($^1J(^{31}P-^{183}W) = 225$ Hz). ^1H NMR ($CDCl_3$): δ 1.07 (dd, $^3J(H-H) = 6.8$, $^3J(H-P) = 17.3$ Hz, 3H, CH_3); 1.13 (dd, $^3J(H-H) = 6.9$, $^3J(H-P) = 18.0$ Hz, 3H, CH_3); 2.2 (m, 1H, C*H*Me_2); 5.53 (dd, $^3J(H-H) = 4.7$ Hz, $^1J(H-P) = 332.4$ Hz, PH). ^{13}C NMR ($CDCl_3$): δ 19.84 (s, CH_3); 20.54 (s, CH_3); 29.40 (d, $^1J(C-P) = 25.7$ Hz, P*C*H); 196.52 (d, $^2J(C-P) = 6.7$ Hz, *cis*-CO); 199.25 (d, $^2J(C-P) = 21.4$ Hz, *trans*-CO) ppm. IR (decalin): ν(CO) 2070m, 1940vs cm^{-1}. Mass spectrum (^{184}W) *m/z* 476 (*M*, 42%), 392 (*M* − 3CO, 100%).

Hydrogenation of complex 6 (Z + E): entry 4, Table 1

Complex **7** was obtained in 77% yield after 1 h of reaction in CH_2Cl_2 with Rh(diphos)$^+PF_6^-$ as catalyst: colorless oil; ^{31}P NMR (hexane): δ −31.9 ($^1J(^{31}P-^{183}W) = 229$ Hz). ^1H NMR ($CDCl_3$): δ 0.89 (d, $^3J(H-H) = 7.0$ Hz, 3H, CH_3); 0.92 (d, $^3J(H-H) = 7.8$ Hz, 3H, CH_3); 1.6 (m, 1H, C*H*Me_2); 1.8–2.2 (m, 2H, PCH_2); 5.74 (ddd, $^1J(H-P) = 336.2$ Hz, $^3J(H-H) = 8.9$ Hz, $^3J(H-H) = 5.1$ Hz, PH). ^{13}C NMR ($CDCl_3$): δ 22.58 (d, $^3J(C-P) = 6.8$ Hz, CH_3); 23.71 (d, $^3J(C-P) = 7.9$ Hz, CH_3); 26.67 (d, $^2J(C-P) = 4.2$ Hz, C*H*Me_2); 39.27 (d, $^1J(C-P) = 24.0$ Hz, PCH_2); 196.30 (d, $^2J(C-P) = 7.0$ Hz, *cis*-CO); 199.22 (d, $^2J(C-P) = 21.0$ Hz, *trans*-CO) ppm. Mass spectrum (^{184}W) *m/z* 490 (*M*, 28%), 406 (*M* − 3CO, 79%), 348 (100%). Anal. Found; C, 36.98; H, 3.35. $C_{15}H_{15}O_5PW$ calcd.: C, 36.76; H, 3.08%.

Deuteration of complex 6 (Z + E): reaction 4

The same procedure was used as for hydrogenation but with D_2 in place of H_2. After 6 h at room temperature in the presence of 10% Rh(diphos)$^+PF_6^-$ as catalyst, complex **10** was obtained in 82% yield. Starting from a mixture of the (*Z*) and (*E*) isomers of complex **6** with a *Z*/*E* ratio of about 70/30, two isomers of **10** were obtained in a similar ratio. The superposition of the ^1H NMR signals prevented the accurate measurement of the isomer ratio. Complex **10**: colorless oil; ^{31}P NMR (C_6D_6): δ −37.53 (t, $^1J(P-D) = 51.3$ Hz). ^1H NMR (C_6D_6): δ 0.59 (d, $^3J(H-H) = 6.7$ Hz, 3H, CH_3); 0.62 (d, $^3J(H-H) = 6.7$ Hz, 3H, CH_3); 1.5 (m, 1H, C*H*Me_2); 1.60 (d) and 1.75 (t) (1H, PC*H*D-two isomers). ^{13}C NMR (C_6D_6): δ 22.46 (d, $^3J(C-P) = 7.0$ Hz, CH_3); 23.40 (d, $^3J(C-P) = 7.8$ Hz, CH_3); 26.60 (d, $^2J(C-P) = 3.5$ Hz, *C*HMe_2); 38.39 (m, $^1J(C-D) \sim {}^1J(C-P) = 23$ Hz); 196.73 (d, $^2J(C-P) = 6.5$ Hz, *cis*-CO); 199.53 (d, $^2J(C-P) = 20.1$ Hz, *trans*-CO) ppm. Mass spectrum (^{184}W) *m/z* 492 (*M*, 42%), 408 (*M* − 3CO, 98%), 348 (100%).

Hydrogenation of complex 8 (Z): entry 5, Table 1

After 24 h at room temperature, complex **9** was obtained in 35% yield. Complex **9**: colorless oil; ^{31}P NMR (C_6D_6): δ −7.43 ($^1J(^{31}P-^{183}W)$ = 224.6 Hz). ^1H NMR (C_6D_6): δ 0.72 (d, $^3J(H-H)$ = 6.4 Hz, 3H, CH_3); 0.80 (d, $^3J(H-P)$ = 14.9 Hz, CMe_3); 0.87 (dd, $^3J(H-H)$ = 6.4 Hz, $^4J(H-H)$ = 1.5 Hz, 3H, CH_3); 1.2–1.9 (m, 3H); 4.14 (ddd, $^1J(H-P)$ = 319.9 Hz, $^3J(H-H)$ = 10.5 Hz, $^3J(H-H)$ = 3.0 Hz, PH) ppm. IR (decalin): ν(CO) 2070m, 1940vs cm^{-1}. Mass spectrum (^{184}W) *m/z* 470 (*M*, 34%), 410 (91%), 326 (100%).

Hydrogenation of complex 11 (Z): entry 6, Table 1

After 3 h at room temperature in CH_2Cl_2, complex **12** was obtained in 83% yield. Complex **12**: low melting solid; ^{31}P NMR ($CDCl_3$): δ −44.1 ($^1J(^{183}W-^{31}P)$ = 224.6 Hz). ^1H NMR (C_6D_6): δ 0.6 (d, $^4J(H-P)$ = 1.1 Hz, 9H, CMe_3); 1.9 (m, 2H, CH_2); 5.6 (ddd, $^1J(H-P)$ = 340.2 Hz, $^3J(H-H)$ = 7.5 Hz, $^3J(H-H)$ = 4.1 Hz, PH) ppm. ^{13}C NMR ($CDCl_3$): δ 30.16 (d, $^3J(C-P)$ = 6.1 Hz, CH_3); 33.02 (d, $^2J(C-P)$ = 7.6 Hz, CMe_3); 45.53 (d, $^1J(C-P)$ = 21.3 Hz, PCH_2); 196.65 (d, $^2J(C-P)$ = 7.5 Hz, *cis*-CO), 199.58 (d, $^2J(C-P)$ = 21 Hz, *trans*-CO) ppm. IR (decalin): ν(CO) 2065m, 1940vs cm^{-1}. Mass spectrum (^{184}W) *m/z* 504 (*M*, 28%), 420 (*M* − 3CO, 100%). Anal. Found: C, 37.90; H, 3.26. $C_{16}H_{17}O_5PW$ calcd.: C, 38.12; H, 3.40%.

Isomerization of complex 4: entry 2, Table 1

When complex **4** was submitted to the standard hydrogenation conditions in the presence of Rh(diphos)$^+PF_6^-$ as catalyst, no hydrogenation product was detected. The isomerized complex **5** was isolated in 84% yield after 1 h of reaction.

Complex **5**: colorless oil; ^{31}P NMR (C_6D_6): δ −34.37 ($^1J(^{183}W-^{31}P)$ = 225 Hz). ^1H NMR ($CDCl_3$): δ 2.0 (m, 2H); 2.3–2.6 (m, 4H); 6.36 (d, $^1J(H-P)$ = 342.7 Hz, PH); 6.4 (d, br, J = 11.1 Hz, =C*H*). ^{13}C NMR ($CDCl_3$): δ 24.51 (d, $^3J(C-P)$ = 6.4 Hz, CH_2); 34.47 (d, $J(C-P)$ = 13.9 Hz, CH_2); 35.84 (d, $J(C-P)$ = 7.4 Hz); 146.05 (d, $J(C-P)$ = 16.1 Hz, =C); 196.36 (d, $^2J(C-P)$ = 6.7 Hz, *cis*-CO) ppm. IR (decalin): ν(CO) 2070m, 1945vs cm^{-1}. Mass spectrum (^{184}W) *m/z* 500 (*M*, 19%), 416 (*M* − 3CO, 30%), 356 (100%). Anal. Found: C, 38.73; H, 2.88. $C_{16}H_{13}O_5PW$ calcd.: C, 38.43; H, 2.62%.

Acknowledgements

We thank Elf Aquitaine - Groupement de Recherches de Lacq for financial support and Dr. Jean-Alex Laffitte for fruitful discussions.

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