Journal of Organometallic Chemistry, 267 (1984) 171–177
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

STABILITY OF PHOSPHINES UNDER HYDROFORMYLATION CONDITIONS

TOSHIYASU SAKAKURA, TOSHI-AKI KOBAYASHI, TERUYUKI HAYASHI, YASUJIRO KAWABATA, MASATO TANAKA*, and IKUEI OGATA

National Chemical Laboratory for Industry, Yatabe, Ibaraki 305 (Japan)

(Received December 21st, 1984)

Summary

Phosphorus–carbon bonds of *p*-substituted triphenylphosphines were found to be cleaved under hydroformylation conditions in the presence of a rhodium, ruthenium, or cobalt carbonyl. Only *p*-isomers of the decomposition products (substituted benzaldehyde, benzyl alcohol, and/or biphenyl) were formed. The ability of metal carbonyls to cleave the P–C bonds was Rh > Co > Ru. Tributylphosphine was stable under the conditions. The stability of metal carbonyl–phosphine catalyst systems was also examined and compared with the extent of P–C bond cleavage.

Introduction

Tertiary phosphines have been used in many transition metal complex-catalyzed reactions as efficient ligands, and their effects on catalysis have been extensively reviewed [1,2]. In these catalytic reactions, the stability of P–C bonds seems to have been overlooked. As a matter of fact, an increasing number of papers have reported P–C bond cleavage promoted by transition metal complexes [3–12], and in some cases, triarylphosphines are used even as sources for aryl groups in synthetic applications [13–20]. In hydroformylation reactions of olefins, an important class of industrially-applied reactions, phosphines are often used as additional ligands in order to raise the selectivity for n-aldehydes (vs. iso-aldehydes) [21]. However, the stability of phosphines under hydroformylation and other related reactions has not been studied systematically, and only some isolated results of P–C bond cleavage have been reported [22–28]. The study of this phenomenon is undoubtedly important in relation to the poisoning and the decay of catalysis. In this paper, we will report the results of decomposition of phosphines under hydroformylation conditions using cobalt, rhodium, and ruthenium as the catalyst.

0022-328X/84/$03.00

Results and discussion

Tertiary phosphines gave various decomposition products when treated with metal carbonyls under synthesis gas (eq. 1).

$$Ar_3P \xrightarrow[CO/H_2]{M_m(CO)_n} ArH + ArCHO + ArCH_2OH + Ar\text{–}Ar + Ar\text{–}CO\text{–}Ar + Ar_3P{=}O + Ar_2HP \quad (1)$$

(M = Co, Rh, Ru)

The results are summarized in Table 1. Runs 1–9 are the results of control experiments (GLC analyses of mixtures of a metal carbonyl and a phosphine before treatment with synthesis gas: injection temperature was 260°C), while runs 10–18 are those obtained for the reaction mixtures (200°C, CO/H_2 = 1/1, 300 atm at the reaction temperature, 6 h).

Effects of metals and p-substituents on the P–Ar bond cleavage

The amount of phosphines recovered after the reaction decreased in the order Rh > Ru > Co. On the other hand, the decreasing order Rh > Co > Ru was ob-

TABLE 1

P–C BOND CLEAVAGE OF TRIARYLPHOSPHINE, $(p\text{-}XC_6H_4)_3P$, UNDER SYNTHESIS GAS IN THE PRESENCE OF METAL CARBONYLS, $M_m(CO)_n$ [a]

Run	X	M	Yield (mmol)						
			PAr_3	ArH	ArCHO	$ArCH_2OH$	Ar–Ar	ArCOAr	$Ar_3P{=}O$
1	H	Rh	0.51	0	0	0	0.04	0.01	0.04
2	H	Ru	0.89	0	0	0	tr	tr	0
3	H	Co	0.86	0	0	0	tr	0	0.04
4	CH_3	Rh	0.38	0	0	0	0.05	tr	0.36
5	CH_3	Ru	0.94	0	0	0	tr	0	0.01
6	CH_3	Co	0.86	0	0	0	0	0	0.04
7 [b]	Cl	Rh	0.43		tr	0	0.01	0	0.22
8 [b]	Cl	Ru	0.95	0	tr	0	0	0	0
9 [b]	Cl	Co	0.84	0	tr	0	tr	0	0.01
10 [c]	H	Rh	0.76	0.16	0.21	0	tr	tr	0
11	H	Ru	0.64	0	0	0	0.01	0.01	0.01
12 [d]	H	Co	0.65	0.06	0.04	0.11	0.01	tr	0.02
13	CH_3	Rh	0.79	0.07	0.23	0.01	tr	tr	0.02
14	CH_3	Ru	0.62	0	0	0	tr	0	0.01
15	CH_3	Co	0.45	0	0.01	0.02	0	0	0.04
16 [b]	Cl	Rh	0.80	0.12	0.14	0.05	tr	0	0 01
17 [b]	Cl	Ru	0.60	0	tr	0	tr	0	0.01
18 [b]	Cl	Co	0.47	0.03	tr	0.05	tr	tr	0

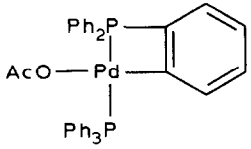
[a] Runs 1–9 are control experiments (see the text). Runs 10–18 are synthesis gas reactions which were effected under the following conditions: catalyst $[Rh_4(CO)_{12}$, $Ru_3(CO)_{12}$, or $Co_2(CO)_8]$ 0.2 mg-atom, PAr_3 1.0 mmol, cumene 10 ml, 200°C, synthesis gas (1/1) 300 atm (at 200°C), 6 h. [b] Phenylbis(*p*-chlorophenyl)phosphine was also formed (0.005–0.008 mmol in the control experiments and 0.018–0.029 mmol after the synthesis gas reactions). [c] Diphenylphosphine (0.0012 mmol) was also formed. [d] Diphenylphosphine (0.0027 mmol) was also formed.

served for the total amount of the products derived from P–Ar bond cleavage. Although these two orders seem to be incompatible with each other, the apparent incompatibility may be understood if we consider that only those phosphines that are free from metals in the mixture or can become free upon being injected into a gas chromatograph are analyzed, and that phosphines which are strongly coordinated even after injection are not. The use of rhodium resulted in the lowest phosphine recovery in the control experiments, which was even lower than that observed after the reactions. In addition, after the synthesis gas reactions, there was the highest phosphine recovery in the case of the rhodium catalyst. These results seem to indicate that rhodium forms phosphine complexes very easily, and that these phosphinerhodium complexes, albeit rather thermally-stable at the temperature of GLC analysis, readily decomposes under the conditions of the synthesis gas reaction. On the contrary, ruthenium and cobalt require more severe conditions to promote formation of phosphine complexes and the metal to phosphorus bonds may be more stable under the reaction conditions than those in the rhodium complexes. These may be the factors from which the incompatibility arose. We conclude that the ability of metals to cleave the aryl–P bonds of the phosphines during the reaction decreases in the order Rh > Co > Ru.

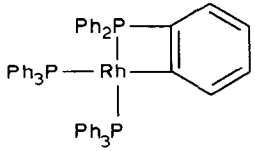
In the thermal decomposition of triarylphosphinenickel complexes, an electron-donating group at the *para* position facilitated aryl–P bond cleavage [7], while an opposite trend was reported for the Pd^{II} catalyzed arylation of olefins by arylphosphines [14]. From both reactions, arylated products which exclusively had *p*-substituted aryl groups were formed. Also in our experiments, substituted benzaldehydes, benzyl alcohols, and biaryls were only *p*-isomers *. However, the nature of the substituents showed little influence on the reactivity for aryl–P bond cleavage **.

Mechanism of P–C bond cleavage

In hydrocarboxylation of 1-octene by use of the $PdCl_2/PPh_3/LiOAc$ catalyst system, Fenton recovered palladium complexes among which the *ortho*-metallated compound I was found [23]. Gregorio et al. [27] have reported benzaldehyde and



(I)



(II)

n-propyldiphenylphosphine formation from $HRh(CO)(PPh_3)_3$ when used as the catalyst for hydroformylation of propene. Benzaldehyde was also obtained when

* Recently, Garrou et al. also observed *p*-methylbenzyl alcohol formation in hydroformylation reaction mixtures by use of the $Co_2(CO)_8/(p\text{-}CH_3C_6H_4)_3P$ catalyst system [29].

** Although oxidative addition of the aryl–Cl bond in $(p\text{-}ClC_6H_4)_3P$ would have been likely under the conditions of the synthesis gas reaction, we could not detect any products other than phenylbis(*p*-chlorophenyl)phosphine derivable from this oxidative addition process. Note that the amount of recovered $(p\text{-}ClC_6H_4)_3P$ was similar to those of the other phosphines.

either $HRh(CO)(PPh_3)_3$ or Keim's complex (II) was heated under carbon monoxide. From these results, they speculated participation of *ortho*-metallated species responsible for aryl–P bond cleavage. On the other hand, Kaneda et al. reported that only the *p*-isomer of tolualdehyde was formed from catalytic carbonylation of tri-*p*-tolylphosphine by $Rh_6(CO)_{16}$ [24]. This result is not consistent with the *ortho*-metallation mechanism. In addition to this, apart from carbonylation conditions, all papers, to our knowledge, which dealt with the decomposition of *p*-substituted triarylphosphines, reported only *p*-isomer formation [7,9,13,14,20]. These earlier papers combined with our results may serve to rule out the *ortho*-metallation mechanism. We prefer the aryl–P bond cleavage being initiated through oxidative addition process of the bond also under hydroformylation conditions, though the more precise nature of the process is not clear yet. In our view, it is quite possible that *ortho*-metallation occurs under hydroformylation conditions as was observed in hydrocarboxylation [23]. However, it may not be responsible for the aryl–P bond scission.

Effect of reaction conditions

As is well known, the selectivity (n/iso) of hydroformylation is very much affected by the reaction conditions. In this connection, we briefly studied the effect of conditions on the aryl–P bond cleavage in rhodium- and cobalt-catalyzed reactions.

Figure 1 shows that, at higher pressures of synthesis gas, benzaldehyde formation in rhodium-catalyzed reactions was promoted, while benzene formation by cobalt catalysts was suppressed. The amount of benzene formed in rhodium-catalyzed reactions and that of benzaldehyde (including benzyl alcohol) by cobalt catalysts remained nearly constant.

Regarding the effect of temperature, as Fig. 2 shows, rhodium- and cobalt-catalyzed cleavage was promoted by raising the temperature.

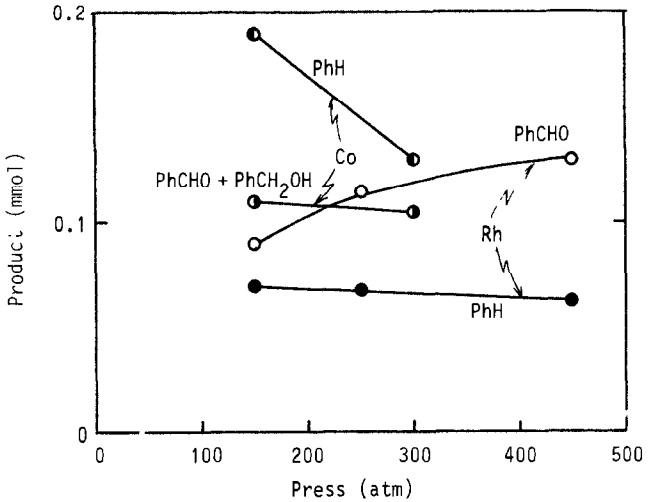


Fig. 1. Effect of synthesis gas pressure on the decomposition of triphenylphosphine (Rh, 0.1 mg-atom; PPh_3, 1.0 mmol; toluene, 10 ml; 200°, 4 h; Co, 0.2 mg-atom; PPh_3, 1.0 mmol; toluene, 5 ml; 200°, 6 h).

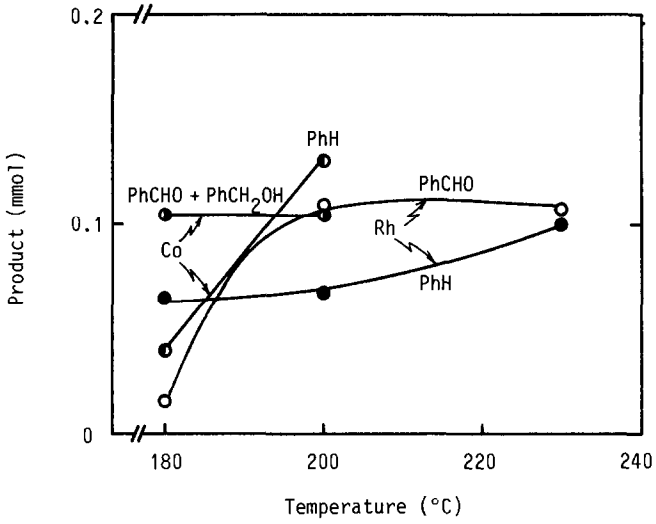


Fig. 2. Effect of the reaction temperature on the decomposition of triphenylphosphine (Rh, 0.1 mg-atom; PPh_3, 1.0 mmol; toluene, 10 ml; 250 atm, 4 h; Co, 0.2 mg-atom; PPh_3, 1.0 mmol; toluene, 5 ml; 300 atm, 6 h).

Stability of the P–C bond of tributylphosphine

For comparison with triphenylphosphine, the P–C bond cleavage of tributylphosphine was also briefly examined under similar conditions. No products, which should have been formed from P–butyl bond cleavage, such as C_4 hydrocarbons, C_5 aldehydes, or alcohols were detected in the reaction mixture. Thus the P–C bond in trialkylphosphines is much more stable than that in triarylphosphines under hydroformylation conditions. Similar results have been described by Kikukawa et al. for palladium(II)-catalyzed reactions [17].

Stability of the catalyst systems

As has been described, the phosphines are degraded under hydroformylation conditions. Jamerson et al. described the formation of the phosphide complex $Rh_4(\mu\text{-}PPh_2)_4(CO)_5(PPh_3)$ from $HRh(CO)(PPh_3)_3$ under hydroformylation conditions, though no product derivable from the phenyl group originally bound to phosphorus was identified [26]. In order to check the relevance of the P–C bond cleavage to the decay of catalysis, the catalytic activity of metal carbonyl phosphine systems for hydroformylation of 1-pentene was examined before and after treatment with synthesis gas in the absence of olefin. The relative rates (by monitoring gas absorption) obtained for the metal/ligand combinations are listed in Table 2, where the rate before the synthesis gas treatment is set at 1 for each combination. From Table 2, the stability of the catalyst systems is as follows: $Co\text{–}PBu_3 > Ru\text{–}PBu_3 > Rh\text{–}PBu_3 \geqslant Co\text{–}PPh_3 > Ru\text{–}PPh_3 > Rh\text{–}PPh_3$. This trend is compatible with the stability of ligand, $PBu_3 > PPh_3$. However, it is not consistent with the ability of metal carbonyls to promote P–C bond scission, Rh > Co > Ru, indicating that other processes may also take part in the decay of catalysis.

This study shows the long-known cobalt/trialkylphosphine catalyst systems in

TABLE 2

COMPARISON OF HYDROFORMYLATION ACTIVITY FOR 1-PENTENE BEFORE AND AFTER THE HIGH TEMPERATURE SYNTHESIS GAS TREATMENT OF THE CATALYST SYSTEMS[a]

Ligand	Metal carbonyls		
	$Rh_4(CO)_{12}$	$Ru_3(CO)_{12}$	$Co_2(CO)_8$
PPh_3	0	0.17	0.33
PBu_3	0.35	0.56	1.00

[a] Synthesis gas treatment was effected under 150 atm (at room temperature) of 1/1 synthesis gas at 200°C for 4 h without the olefin. Hydroformylation was run under 100 atm of 1/1 synthesis gas at 70, 145, 195°C for rhodium, ruthenium, cobalt, respectively. Two ml of 1-pentene, 1 mmol of phosphine, and 10 ml of toluene were used for each run. The amount of metal carbonyl catalysts was 0.1, 0.3, or 0.2 mg-atom Rh, Ru, or Co, respectively.

the Shell oxo process are not only selective for straight-chained products, but very stable under the operating conditions.

Experimental

Materials

Solvents were dried and purified by standard techniques. Triruthenium dodecacarbonyl was purchased from Strem Chemicals and used as received. Dicobalt octacarbonyl, triphenylphosphine, and tributylphosphine were also commercial products and were purified by recrystallization or distillation. Tetrarhodium dodecacarbonyl was prepared by the method of Martinengo et al. [30].

Reaction of phosphines under synthesis gas

In a typical experiment, a phosphine (1 mmol), a catalyst (0.2 mg-atom), and 10 ml of cumene were charged into a 40-ml stainless steel autoclave. Synthesis gas (1/1) of 220 atm at room temperature was introduced, and the autoclave was heated at 200°C for 6 h.

Analysis

All products were identified by comparing the retention times on gas chromatograms with authentic samples purchased or prepared by different routes. Octadecane was used as an internal standard. The column packings employed were as follows. Silicone OV-17 on Uniport HP (4 m) for benzene derivatives. Diethylene glycol succinate on Neopak AS (3 m) for benzaldehyde and benzyl alcohol derivatives. Apiezon grease L on Chromosorb WAW-DMCS (2 m) for biphenyl, benzophenone, and triphenylphosphine derivatives. Silicone OV-101 on Chromosorb W HP (1 m) for triphenylphosphine oxide derivatives.

Aknowledgement

We thank Dr. Garrou for communication of his results prior to publication.

References

1 C.A. Tolman, Chem. Rev., 77 (1977) 313.
2 T. Hayashi, J. Synth. Org. Chem., 41 (1983) 239.
3 D.R. Coulson, Chem. Commun., (1968) 1530.
4 M.L.H. Green and M.J. Smith, Chem. Commun., (1971) 158.
5 R. Mason, I. Søtofte, S.D. Robinson, and M.F. Uttley, J. Orgaonomet. Chem., 46 (1972) C61.
6 C.W. Bradford and R.S. Nyholm, J. Chem. Soc. Dalton Trans., (1973) 529.
7 A. Nakamura and S. Otsuka, Tetrahedron Lett., (1974) 463.
8 J.R. Blickensderfer and H.D. Kaesz, J. Am. Chem. Soc., 97 (1975) 2681.
9 P.S. Braterman, R.J. Cross, and G.B. Young, J. Chem. Soc. Dalton Trans., (1976) 1306.
10 D.R. Fahey and J.E. Mahan, J. Am. Chem. Soc., 98 (1976) 4499.
11 S.A. Maclaughlin, A.J. Carty, and N.J. Taylor, Can. J. Chem., 60 (1982) 88.
12 C.W. Jung, J.D. Fellmann, and P.E. Garrou, Organometallics, 2 (1982) 1042.
13 M. Lewin, Z. Alzenshtat, and J. Blum, J. Organomet. Chem., 184 (1980) 255.
14 T. Yamane, K. Kikukawa, M. Takagi, and T. Matsuda, Tetrahedron, 29 (1973) 955.
15 T. Kawamura, K. Kikukawa, M. Takagi, and T. Matsuda, Bull. Chem. Soc. Japan, 50 (1977) 2021.
16 K. Kikukawa, M. Takagi, and T. Matsuda, Bull. Chem. Soc. Japan, 52 (1979) 1493.
17 K. Kikukawa, T. Yamane, Y. Ohbe, M. Takagi, and T. Matsuda, Bull. Chem. Soc. Japan, 52 (1979) 1187.
18 K. Kikukawa and T. Matsuda, J. Organomet. Chem., 235 (1983) 243.
19 A.D. Ryabov and A.K. Yatsimirsky, J. Mol. Catal., 4 (1978) 449.
20 R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi Bull. Chem. Soc. Japan, 46 (1973) 2910.
21 J. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer-Verlag, Berlin, 1980.
22 P. Chini, S. Martinengo, and G. Garlaschelli, J. Chem. Soc. Chem. Commun., (1972) 702.
23 D.M. Fenton, J. Org. Chem., 38 (1973) 3192.
24 K. Kaneda, K. Sano, and S. Teranishi, Chem. Lett., (1979) 821.
25 E. Billig, J.D. Jamerson, and R.L. Pruett, J. Organomet. Chem., 192 (1980) C49.
26 J.D. Jamerson, R.L. Pruett, E. Billig, and F.A. Fiato, J. Organomet. Chem., 193 (1980) C43.
27 G. Gregorio, G. Montrasi, M. Tampieri, P. Cavalieri d'Oro, G. Pagani, and A. Andreetta, Chim. Ind. (Milan), 62 (1980) 389.
28 A.J. Abatjoglou and D.R. Bryant, XIth Intern. Conf. Organomet. Chem., Preprint p. 207, Oct. 14, 1983, Georgia, U.S.A.
29 P.E. Garrou, private communication.
30 S. Martinengo, P. Chini, and G. Giordano, J. Organomet. Chem., 27 (1971) 389.