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Preliminary communication

HYDROGENOLYSIS OF TERTIARY PHOSPHINES COORDINATED ON TRANSITION METALS BY HYDROGEN TRANSFER FROM AMINES

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Summary

Considerable amounts of benzene were formed by heating triphenylphosphine complexes of transition metals in several types of organic compounds, especially in amines; in the case of a tributylphosphine complex, n butane was detected. In the reactions with indoline, tetrahydroquinoline or dioxane, the hydrogen consumed for the hydrogenolysis was proved to arise from the amines or the ether.

A number of tertiary phosphine complexes have been reported to exhibit interactions between the metals and carbon—hydrogen bonds of the phosphine ligands [1]. However, little is known about the cleavage of phosphorus—carbon bonds of substituted phosphines coordinated to transition metals [2]. Bennett and Milner have observed the formation of a small amount of benzene on heating $IrCl(PPh_3)_3$ in cyclohexane and presumed that this was formed by hydrogen abstraction from the solvent [1b]. Coulson has found that a diphenylphosphine complex is formed in the reaction between $Pd(PPh_3)_4$ and $PdCl_2$ in dimethylsulfoxide [2a];

During the course of an investigation of transfer-hydrogenation [3], we have found that considerable amounts of benzene were formed on heating triphenylphosphine complexes of transition metals in several organic compounds in the absence of other hydrogen acceptors such as olefins. For example, when a pyrrolidine solution (0.05 mole in $RhCl(PPh_3)_3$) was sealed in a Pyrex glass tube under vacuum (10^{-2} mmHg) and heated at 140° for 1 h, the formation of 0.40 mole benzene was confirmed by GLC analysis. The number of benzene molecules which were released from a molecule of $RhCl(PPh_3)_3$ decreased in the following order: 8.0 (pyrrolidine), 6.9 (piperidine), 6.2 (piperazine), 4.7 (*N*-methylpiperazine), 3.0 (n-propylamine), 2.3 (di-n-propylamine), 2.1 (*N*,*N'*-di-

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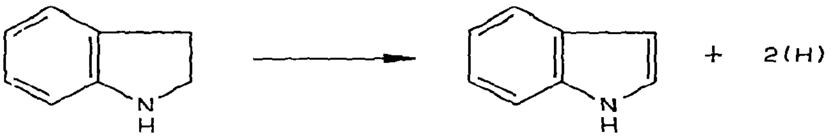
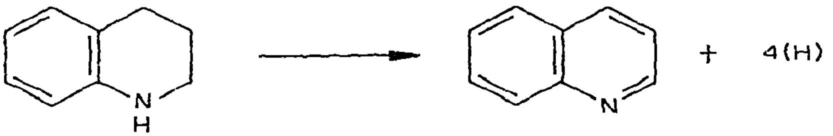
methylpiperazine), 2.0 (indoline), 1.5 (tetrahydroquinoline), 0.3 (isopropyl alcohol) and 0.2 (dioxane), where the compounds shown in parentheses were used both as solvents and as hydrogen donors. When the complex was heated in n-propyl alcohol, tri-n-propylamine, pyrrole, chlorobenzene and xylene, no benzene was detected. The transfer-hydrogenolysis of triphenylphosphine occurred at lower temperatures. For instance, a mole of RhCl(PPh$_3$)$_3$ gave 6.9 moles of benzene on heating in pyrrolidine at 100° for 20 h. This result shows that several amines have much higher hydrogen donating ability than isopropyl alcohol and dioxane which exhibited strong hydrogen-donating power in the transfer-hydrogenation of olefins [3].

Transfer-hydrogenolysis occurred in the case of other tertiary phosphine complexes. One mole of RhH(PPh$_3$)$_4$, on heating in piperidine at 140° for 1 h, gave benzene (5.0 moles), RhH$_2$(PPh$_3$)$_4$ (4.5), RuCl$_2$(PPh$_3$)$_3$ (2.9), PdCl$_2$(PPh$_3$)$_2$ (2.4), PtCl$_2$(PPh$_3$)$_2$ (2.2), RhCl(CO)(PPh$_3$)$_2$ (1.4), Pt(PPh$_3$)$_4$ (1.1); and PdCl$_2$·(P-n-Bu$_3$)$_2$ yielded n-butane (1.5 moles). These results indicate that not only aryl phosphines but also alkylphosphines undergo transfer-hydrogenolysis. However, complexes of the type MX$_2$(PPh$_3$)$_2$ (M = Co^{II} or Ni^{II}, X = Cl, Br or I), did not give benzene, even on heating in pyrrolidine at 180°.

When a xylene solution of RhCl(PPh$_3$)$_3$ (0.04 mole) and indoline (0.40 mole) was heated at 170° for 1 h, the formation of 0.14 mole benzene and 0.15 mole indole in addition to 0.26 mole of the original indoline was shown by GLC analysis. A similar reaction in which tetrahydroquinoline was used instead of indoline gave 0.12 mole benzene, 0.05 mole quinoline and 0.38 mole tetrahydroquinoline. These results may be summarized as follows: (1) the yield of benzene was almost equal to that of indole in the former reaction, (2) the yield of benzene was roughly twice that of quinoline in the latter reaction, because conversion of tetrahydroquinoline to quinoline releases two moles of hydrogen, (3) the total amounts of the recovered original amines and dehydrogenated amines were nearly equal to the amounts of amines before reaction. These facts show that benzene was formed by hydrogen transfer from the amines to the ligand of the complex. The amount of piperidine consumed was almost equal to that of benzene formed, but no lower boiling dehydrogenation products, such as pyridine, were detected. The amount of the surviving pyrrolidine could not be measured precisely and low boiling dehydrogenation products, such as pyrrolines [4] and pyrrole, were not detected. It has been reported that 1-piperideine and 1-pyrroline are unstable and





undergo rapid trimerization [5] and addition reactions with amines [6]. Therefore, it is inferred that such unstable dehydrogenation intermediates yielded products of high boiling points which were not detected by GLC analysis. In the reaction in dioxane, the amount of the dehydrogenation product, dioxene [3], was equal to that of benzene.

Diphenylphosphine was detected in the reaction mixtures which had been treated with a KOH/KCN aqueous solution by comparison with an authentic sample [7]. The formation of phenylphosphine was obscured, partly because the peak of phenylphosphine [8] was covered in GLC analysis by broad and strong peaks of the amines and impurities.

References

1 (a) G.W. Parshall, Accounts Chem. Res., 3 (1970) 139 and ref. therein; (b) M.A. Bennett and D.L. Milner, Chem. Commun., (1967) 581; (c) M.A. Bennett, P.W Clark, R.B. Robertson and P.O. Whimp, ibid., (1972) 1011; (d) S. Komiya, A. Yamamoto and S. Ikeda, J. Organometal. Chem., 42 (1972) C63, (e) G.W. Parshall, J. Amer. Chem. Soc., 90 (1968) 1669; (f) W.H. Knoth, ibid., 90 (1968) 7172; (g) T. Ito, S. Kitazume, A. Yamamoto and S. Ikeda, ibid., 92 (1970) 3011; (h) M.A. Bennett, R.N. Johnson and I.B. Tomkins, ibid., 96 (1974) 61; (i) M. Giustiniani, G. Dolcetti, M. Nicolini and U. Belluco, J. Chem. Soc. A, (1969) 3143; (j) D.F.E. Wing, B. Hudson, D.E. Webster and P.B. Wells, J. Chem. Soc. Dalton, (1972) 1287, (k) M.A. Bennett and P.A. Longstaff, J. Amer. Chem. Soc., 91 (1969) 6266; (l) F.G. Moers and J.P. Langhout, Rec. Trav. Chim. Pays Bas, (1972) 591.

2 (a) D.R. Coulson, Chem. Commun., (1968) 1530; (b) R. Asano, I. Moritani, Y. Fujiwara and S. Teranishi, Bull. Chem. Soc. Japan, 46 (1973) 2910; (c) K. Kikukawa, T. Yamane, M. Takagi and T. Matsuda, Chem. Commun., (1972) 695.

3 (a) T. Nishiguchi and K. Fukuzumi, J. Amer. Chem. Soc., 96 (1974) 1893; (b) T. Nishiguchi, K. Tachi and K. Fukuzumi, ibid., 94 (1972) 8916; (c) H. Imai, T. Nishiguchi and K. Fukuzumi, J. Org. Chem., 39 (1974) 1622; (d) T. Nishiguchi, A. Kurooka and K. Fukuzumi, J. Org. Chem., in press.

4 L.H. Andrews and S.M. McElvain, J. Amer. Chem. Soc., 51 (1929) 887.

5 (a) D.W. Fuhlhange and C.A. VanderWerf, J. Amer. Chem. Soc., 80 (1958) 6249; (b) C. Schöpf, H. Arm and H. Krimm, Chem. Ber., 84 (1951) 690.

6 N. Yoshimura, I. Moritani, T. Shimamura and S. Murahashi, J. Amer. Chem. Soc., 95 (1973) 3098.

7 D Wittenberg and H. Gilman, J. Org. Chem., 23 (1958) 1063.

8 H. Köhler and A. Michaelis. Chem. Ber., 10 (1877) 807