Interaction between Organoaluminum Compounds and Ditertiary Phosphines Studied by Proton Magnetic Resonance

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(Received October 14, 1971)

The adduct formation of triethylaluminum or diethylaluminum chloride with ditertiary phosphines ($Ph_2P(CH_2)_nPPh_2$ $n=1,2,3,4$, and 6) in benzene solution was investigated by PMR. The adducts have a composition of $(AlEt_3)_2$ (diphosphine) except in the case of $Ph_2PCH_2PPh_2$, which makes two kinds of adducts (1 : 1 and 2 : 1). Electronegativity of the complexed aluminum is also calculated from Dailey-Shoolery equation.

During the course of an investigation of the effect of ligands on butadiene-ethylene codimerization reaction catalyzed by $CoCl_2(Ph_2P(CH_2)_nPPh_2)$-$AlEt_3$,[1] it became desirable to study the interaction of ditertiary phosphine ligand with triethylaluminum. In such catalyst system, the organoaluminum compound may be considered not only to reduce the metal to low oxidation state, but also to activate the low oxidation state complex to make the coordination site(s) vacant.[2] Such activation may be caused by the interaction of ditertiary phosphine(Lewis base) with organoaluminum compound(Lewis acid).

On the other hand, interaction of Lewis bases such as ethers and tertiary amines with organoaluminum compounds has been extensively studied.[3] But much less is studied about the interaction with phosphines,[4] especially ditertiary phosphines.

The object of this paper is to describe the interaction of triethylaluminum or diethylaluminum chloride with ditertiary phosphines $Ph_2P(CH_2)_nPPh_2$ ($n=1,2,3,4$, and 6) by PMR and to discuss the effect of the methylene chain length of phosphines.

Experimental

All operations were performed under dry nitrogen atmosphere.

Reagent. $AlEt_3$ and $AlEt_2Cl$(Ethyl Corp., USA) were distilled under vacuum and ditertiary phosphines $Ph_2P(CH_2)_nPPh_2$ ($n=1,2,3,4,6$)[5] were synthesized according to the method of Hewertson and Watson,[6] and purified toluene and benzene were stored under dry nitrogen.

Procedure. An appropriate amount of 14.5 wt% benzene solution of triethylaluminum was mixed with an appropriate amount of ditertiary phosphine and a small amount of toluene as an internal standard, and this homogeneous solution was poured into 5.0 mm diameter pyrex tube by syringe and the tube was sealed off. Proton magnetic resonance spectra were run at room temperature on Hitachi Perkin-Elmer R-20A at 60 MHz.

Results and Discussion

PMR Spectra of Ditertirary Phosphines and Organoaluminum Compounds. Spectra of 1,1-bis(diphenylphosphino)methane and 1,2-bis(diphenylphosphino)-ethane in benzene solution were observed as a triplet due to the coupling between ^{31}P and ^{1}H, and the coupling constants were as follows; DPM: $|\,^2J_{PH}\,|=1.8$ cps, DPE: $|\,^2J_{PH}+{}^3J_{PH}\,|=ca.$ 8.4 cps. The methylene proton resonaces of other longer methylene chain ditertiary phosphines occurred as a broad band and were not analysed further.

The signals of methyl and methylene protons of triethylaluminum, which has been analysed as A_2B_3 system,[7] were simply analysed as triplet and quartet respectively in this paper.

Ditertiary Phosphines-Organoaluminum Compounds Systems. Spectrum of ditertiary phosphine-$AlEt_3$ system consists of singnals due to methylene protons of ditertiary phosphine, a triplet of methyl protons and a quartet of methylene protons of $AlEt_3$. The chemical shift and the coupling constant (^1H-^{31}P) of ditertiary phosphines and the chemical shift of two kinds of protons of $AlEt_3$ vary with molar ratio of ditertiary phosphine/$AlEt_3$. This is considered to be a result of adduct formation by the interaction of diphosphine as a Lewis base with triethylaluminum as a Lewis acid in solution. Consequently, a composition of this adduct will be estimated from the variation of these parameters (namely chemical shift and coupling constant) with molar ratio.

The variation in the chemical shift of methylene protons of DPE, and of methyl and methylene protons of aluminum compounds with DPE/Al molar ratio in DPE-$AlEt_3$ or $AlEt_2Cl$ systems is shown in Fig. 1. The chemical shift of DPE is constant until the molar ratio becomes 0.5, but that of methyl- and methylene protons of aluminum are linearly increased. On the further addition of DPE a monotonous and nearly linear decrease in chemical shift of DPE is observed,

1) T. Kagawa, Y. Inoue, and H. Hashimoto, This Bulletin, **43**, 1250 (1970).

2) M. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **71**, 233 (1968).

3) M. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds" Vol. 1, Third Edition, Methuen, London, (1967), p. 304.

4) a) B. M. Cohen, A. R. Cullingworth, and J. D. Smith, *J. Chem. Soc., A*, **1969**, 2193. b) A. R. Cullingworth, A. Pidcock, and J. D. Smith, *Chem. Commun.*, **1966**, 89. c) D. F. Clemens, H. H. Sisler, and W. S. Brey, Jr., *Inorg. Chem.*, **5**, 527 (1966). d) K. Issleib and F. Krech, *Z. Anorg. Allgem. Chem.*, **328**, 21 (1964).

5) Abbreviation:
$n=1$: DPM 1,1-bis(diphenylphosphino)methane
$n=2$: DPE 1,2-bis(diphenylphosphino)ethane, in a similar manner, $n=3$: DPP, $n=4$: DPB, $n=6$: DPH.

6) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1940.

7) a) O. Yamamoto, This Bulletin, **36**, 1463 (1963) b) O. Yamamoto, *ibid.*, **37**, 1125 (1964).

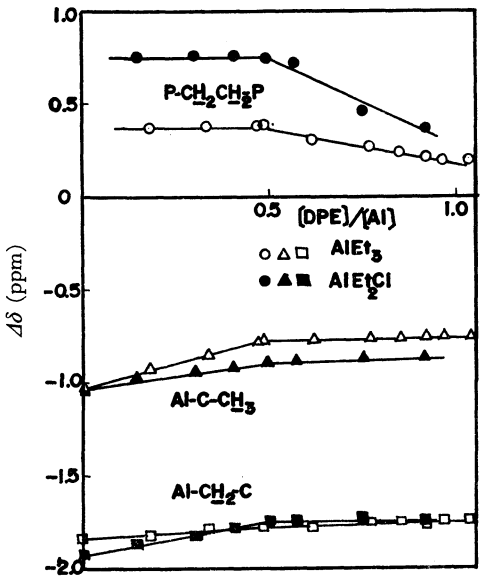

Fig. 1. The variation of chemical shift with molar ratio of DPE/$AlEt_3$ or $AlEt_2Cl$ system.

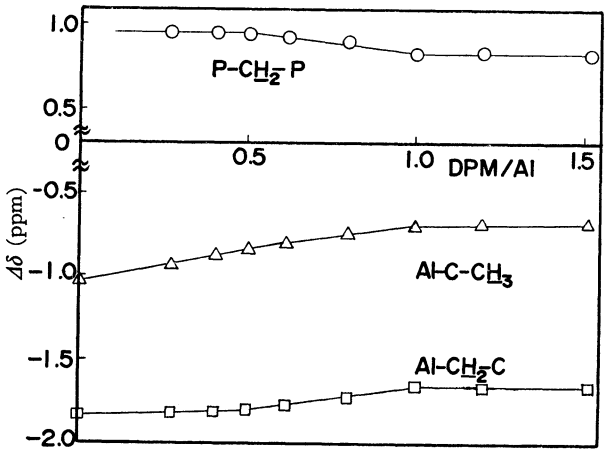

Fig. 2. The variation of chemical shift with DPM/Al of DPM-$AlEt_3$ system.
○ P-C$\underline{H}_2$-P, △ Al-C-C$\underline{H}_3$, □ Al-C$\underline{H}_2$-C

but the ethyl signals of aluminum part are almost constant. This may show that DPE and $AlEt_3$ form 1 : 2 adduct in solution. Similar behavior has been observed in a system of $AlEt_3$-PMe_3 by Cullingworth and co-workers[4b] and a change of chemical shift occurs at the molar ratio of 1 : 1. The variation of these parameters in the system of DPM-$AlEt_3$ is slightly different from that of DPE system and shown in Fig. 2. In this case the parameters vary at molar ratio of 0.5 and 1.0, and two kinds of adduct, *i.e.*, 1 : 2 and 1 : 1, may be present.

Other ditertiary phosphines (DPP, DPB, and DPH) were examined with combination of triethylaluminum and the results are the same as DPE system. Using triphenylphosphine as a monophosphine, chemical shifts of $AlEt_3$ vary at 1 : 1 molar ratio like PMe_3.

The coupling constants J_{PH} of DPE and DPM changed also with the molar ratio and this variation

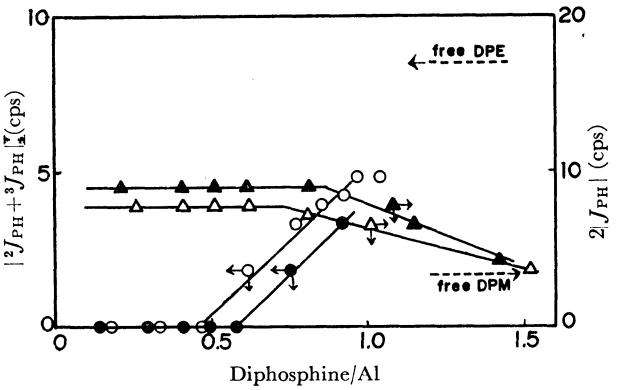

Fig. 3. Change in coupling constant ($^1H-^{31}P$) of DPM and DPE.
DPM: △ $AlEt_3$ ▲ $AlEt_2Cl$
DPE: ○ $AlEt_3$ ● $AlEt_2Cl$

is given in Fig. 3. As seen in Fig. 3, the change in DPE system occurs at the ratio of 0.5 in a similar manner to the chemical shift described above, and this is a piece of evidence in support of the formation of 1 : 2 adduct. But the changing point in the DPM system is at molar ratio of ca 0.8 and this may also show that there are two kinds of adduct in solution. The reasons why $|\,^2J_{PH}\,|$ of complexed DPM is larger than that of free one and why $|\,^2J_{PH}+{}^3J_{PH}\,|$ of complexed DPE is smaller than that of free ligand are not clear. It may be necessary to know the sign of coupling constants between ^1H and ^{31}P.

It is now concluded by the variations of chemical shift and the coupling constant with molar ratio that ditertiary phosphines ($Ph_2P(CH_2)_nPPh_2$, n=2,3,4,6) form 1 : 2 adduct with triethylaluminum in solution, while DPM forms 1 : 1 and 1 : 2 adducts. These results are similar to those of ditertiary amine-trimethylaluminum systems[10], in which $Me_2NCH_2NMe_2$ forms 1 : 1 complex, and $Me_2N(CH_2)_2NMe_2$ and $Me_2N(CH_2)_3NMe_2$ form 1 : 2 complex. The relationship between composition of the adduct and the methylene chain length*(n)* is same in both cases except n=1.

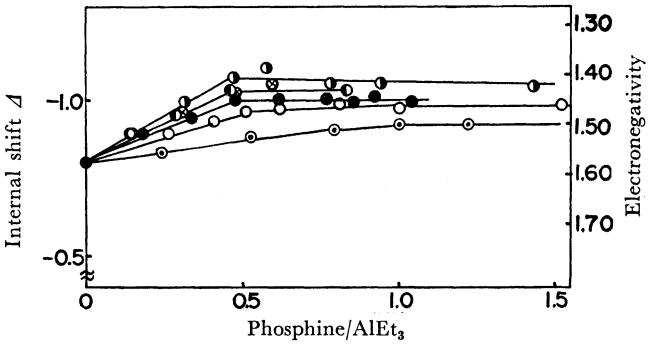

Fig. 4. Changes in electronegativity of aluminum by coordination of diphosphines.
$\chi=0.62\Delta+2.07$ $\Delta=\tau_{CH_3}-\tau_{CH_2}$
diphosphine-$AlEt_3$ system
○: DPM ●: DPE ◑: DPP
◐: DPB ⊗: DPH ⊙: PPh_3

8) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).
9) A. J. Carty and R. K. Harris, *Chem. Commun.*, **1967**, 234.
10) a) N. R. Fetter, B. Bartocha, F. E. Brinckman, Jr., and D. W. Moore, *Can. J. Chem.*, **41**, 1359 (1963) b) N. R. Fetter and D. W. Moore, *ibid.*, **42**, 885 (1964).

An empirical linear relationship between the electronegativity χ of a metal atom (CH_3CH_2M) and its internal shift Δ: a difference in the chemical shift of methylene and methyl protons, was known as Dailey-Shoolery equation and this equation has been useful in studying the change of electronegativity with coordination of donor molecules.[11]

$$\chi = 0.62\Delta + 2.07$$

11) T. Takeshita and W. E. Frankle, *Tetrahedron Lett.*, **1968**, 5913.

The Lewis acidity of aluminum coordinated with diphosphine was evaluated by application of Dailey-Shoolery equation to ditertiary phosphine-$AlEt_3$ system. The variation in the internal shift with the molar ratio of diphosphine/$AlEt_3$ was calculated from above data and shown in Fig. 4. As expected, the complex formation with phosphine results in decreasing the electronegativity of aluminum. The effect of the length of methylene chain in the ditertirary phosphines is not so remarkable but the following order of donor ability to aluminum was obtained: DPP>DPB≈DPH≳DPE>DPM.