

Preparation of Dimethylbis(diphenylphosphinoethane)iron(II) and Its Decomposition Pathways Involving the Formation of Carbenoid Intermediates

By TAKAO IKARIYA and AKIO YAMAMOTO*

(Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro, Tokyo 152, Japan)

Summary Reaction of $\text{Fe}(\text{acac})_3$, Me_2AlOEt , and $\text{Ph}_2\text{-PCH}_2\text{CH}_2\text{PPh}_2(\text{dpe})$ gives a new methyliron complex, $\text{FeMe}_2(\text{dpe})_2$ which on thermal decomposition and treatment with CH_2Cl_2 liberates ethylene, the formation of which suggests the intermediacy of carbenoid complexes.

In spite of the recent rapid development in organo-transition-metal chemistry, reports of preparation of alkyliron complexes without cyclopentadienyl or carbonyl ligands are still scarce.¹ We now describe the preparation and properties of a new methyliron complex, dimethylbis(diphenylphosphinoethane)iron(II) (**1**), in particular its unique decomposition behaviour which possibly involves carbenoid intermediates.

The iron complex was prepared as orange crystals by the reaction of acetylacetonatoiron(III), diphenylphosphinoethane (dpe), and Me_2AlOEt in Et_2O at -30 to 0° under N_2 . Since the complex was insoluble in some common organic solvents and decomposed in others, recrystallization and n.m.r. measurement were not feasible, but elemental analysis and chemical characterization of (**1**) supported its formulation as $\text{FeMe}_2(\text{dpe})_2$. Acidolysis with H_2SO_4 released 1.8 mol of CH_4 per Fe; iodolysis in benzene liberated CH_4 , presumably formed by hydrogen abstraction from the solvent or ligand, and C_2H_6 in a 1:2.5 ratio and yielded $\text{FeI}_2(\text{dpe})$. The reaction of (**1**) with D_2 in a toluene suspension liberated CH_3D^2 as the sole gaseous product and from the resultant solution $\text{FeD}_2(\text{dpe})_2$ was obtained which on recrystallization from benzene gave yellow crystals of composition, $\text{FeD}_2(\text{dpe})_2\text{C}_6\text{H}_6$ (**2**).

Complex (**1**) is stable in the solid state at room temperature and decomposes at 130 – 135° releasing CH_4 , C_2H_6 , and C_2H_4 in a molar ratio of 75:20:5; the amount of gas liberated was equivalent to 75% of the Me groups bonded to iron.

The formation of a significant amount of ethylene in the thermolysis product suggests that a carbenoid intermediate which gives rise to ethylene may be formed by α -hydrogen elimination from the methyliron complex. When (**1**) was decomposed in CH_2Cl_2 at room temperature, the ethylene content of the evolved gas increased further (CH_4 : C_2H_6 : C_2H_4 = 50:24:26). Treatment of (**1**) with CD_2Cl_2 (isotopic purity 99%) released a gas consisting of CH_4 , C_2H_6 , C_2H_4 , $\text{CD}_2=\text{CH}_2$, and C_2D_4 in a ratio of 50:24:8:14:4 as confirmed by i.r.³ and mass spectroscopy. Neither *cis*- or *trans*- $\text{CHD}=\text{CHD}$ nor CH_3D was detected. The amount of gas liberated in 40 h accounted for ca. 60% of the methyl groups in (**1**). From the reaction mixture an off-white powder of approximate composition $\text{Fe}(\text{dpe})\text{Cl}_2$ was recovered. These results suggest the formation of CH_2 :Fe and CD_2 :Fe type intermediates in the decomposition of (**1**) in CD_2Cl_2 . Decomposition of (**1**) in basic solvents such as pyridine and ethylamine liberated only CH_4 presumably owing to hydrogen abstraction from the solvent or ligand. The ratio of CH_4 , C_2H_6 , and $\text{CH}_2=\text{CH}_2$ in the gas evolved on dissolving (**1**) in CH_2Cl_2 varied considerably depending on experimental conditions. No ethylene was formed on treatment of (**1**) with CH_2Cl_2 in the presence of oxygen. Since addition of olefins such as styrene, hex-1-ene, and cyclohexene did not appreciably alter the gas composition in the reaction of (**1**) with CH_2Cl_2 the lifetime of the possible carbenoid species seems to be very short. Complex (**1**) acts as a Cl_2 -abstracting agent and attacks various chlorinated hydrocarbons, but no reaction with CCl_4 was observed.

Higher homologues of $\text{FeR}_2(\text{dpe})_2$ seem to be less stable than $\text{FeMe}_2(\text{dpe})_2$. With Pr^nAl and Bu^iAl $\text{FeH}_2(\text{dpe})_2$ was obtained and Et_2AlOEt gave the known complex $\text{Fe}(\text{CH}_2=\text{CH}_2)(\text{dpe})_2$.⁴

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¹ Eg., M. L. H. Green, 'Organometallic Compounds,' vol. 2, 'The Transition Elements,' Methuen, London, 1968; G. W. Parshall and J. J. Mrowca, *Adv. Organometallic Chem.*, 1968, **7**, 157; A. Yamamoto, K. Morifuji, S. Ikeda, T. Saito, Y. Uchida, and A. Misono, *J. Amer. Chem. Soc.*, 1965, **87**, 4652; 1968, **90**, 1878; T. Yamamoto, A. Yamamoto, and S. Ikeda, *Bull. Chem. Soc. Japan*, 1972, **45**, 1104, 1110; Y. Kubo, A. Yamamoto, and S. Ikeda, *J. Organometallic Chem.*, 1972, **46**, C50.

² Previously Pu and Yamamoto reported the formation of CD_4 , CHD_3 , and CH_2D_2 in addition to CH_3D and CH_4 in the reaction of $\text{CoCH}_3(\text{PPh}_3)_3$ and $\text{RhCH}_3(\text{PPh}_3)_3$ with D_2 in toluene (L. S. Pu and A. Yamamoto, *J.C.S. Chem. Comm.*, 1974, 9). Unfortunately the conclusion drawn in the paper was based on misinterpretation of the mass spectral data caused by an artifact. The mass peaks of 20 and 19 which were assigned to CD_4^+ and CD_3H^+ were later confirmed to be D_2O^+ and DHO^+ which were formed by contact of D_2 gas introduced into the mass spectrometer with a small amount of water adsorbed on the wall. The amounts of CD_4 and CD_3H therefore should be regarded as negligible and the conclusion supporting formation of the carbene-hydride intermediates should be discarded, while the experimental results in the paper indicating the formation of CH_3D and CH_4 remain valid.

³ R. L. Arnett and B. L. Crawford, Jr., *J. Chem. Phys.*, 1950, **18**, 118.

⁴ G. Hata, H. Kondo, and A. Miyake, *J. Amer. Chem. Soc.*, 1968, **90**, 2278.