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REVERSE METHYL MIGRATION FROM A METHYLIRON COMPLEX TO TRIMETHYLALUMINUM FORMING AN IONIC COMPLEX $[Fe(dmpe)_2(acac)]^+ [AlMe_4]^-$

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Summary

A stable cationic iron(II) complex $[Fe(dmpe)_2(acac)]^+ [AlMe_4]^-$ (**1**) (dmpe = 1,2-bis(dimethylphosphino)ethane, acac = 2,4-pentanedionato ligand) has been prepared by the reaction of $Fe^{III}(acac)_3$ with $AlMe_3$ in the presence of dmpe. The tetramethylaluminate anion is considered to be formed by the methyl back transfer reaction from Fe to $AlMe_3$. Ion exchange of **1** with $NaBPh_4$ affords $[Fe(dmpe)_2(acac)]^+$ BPh_4^- in a high yield. These complexes have been characterized on the basis of ^1H and $^{31}P\{^1H\}$ NMR and IR spectroscopy, elemental analysis and by chemical reactions.

Introduction

Alkylaluminum compounds generally serve as alkylating agents for transition metal halides and acetylacetonates. In some cases the alkyl groups bonded to a transition metal may be back transferred to the aluminum component [1]. Formation of a complex having an aluminate anion has been assumed in Ziegler type catalyst mixtures prepared from transition metal compounds and alkylaluminum compounds [2]. Reported examples where an ionic complex with an aluminate anion has been

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isolated are rare. Previously we reported the first isolation of stable cationic dialkylcobalt complexes having an aluminate anion from the alkylation reaction of $Co(acac)_3$ with excess AlR_3 in the presence of 2,2′-bipyridine [3]. Further studies suggest that this is a general reaction. Here we report the preparation of a cationic iron(II) complex $[Fe(dmpe)_2(acac)]^+ [AlMe_4]^-$ by the reaction of $Fe(acac)_3$ with $AlMe_3$ in the presence of dmpe ligand.

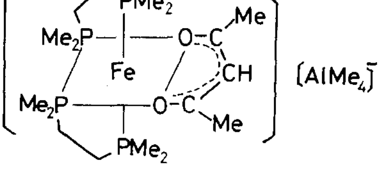
Results and discussion

Reaction of $Fe(acac)_3$ with an excess of $AlMe_3$ in the presence of two equivalents of dmpe in diethyl ether at room temperature gave a red cationic iron(II) complex $[Fe(dmpe)_2(acac)]^+ [AlMe_4]^-$ (**1**) in a good yield.

$$Fe(acac)_3 + dmpe + AlMe_3 \rightarrow \underset{(\mathbf{1})}{[Fe(dmpe)_2(acac)]^+ [AlMe_4]^-}$$

Complex **1** was characterized mainly by IR and NMR spectroscopy, as well as by chemical reactions. It has a high thermal stability (m.p. 156–158°C (dec)) and it slowly decomposes in air. High electric conductivity of **1** in THF strongly supports its ionic structure. Acidolysis of **1** with dry HCl in diethyl ether liberated four equivalents of methane per mole of Fe, supporting the formulation of **1** with the $AlMe_4^-$ moiety.

The IR spectrum of **1** shows bands at 2790–3000 cm^{-1} (s), characteristic of ν(C–H) in $AlMe_4^-$, and ν(C=O) bands at 1580 and 1510 cm^{-1} (s) arising from the bidentate *O*-bonded acac ligand [4], together with the bands assignable to dmpe ligand. ^1H and $^{31}P\{^1H\}$ NMR spectral data of **1** are summarized in the experimental part. Methyl protons of the $AlMe_4^-$ moiety appear at $\delta -1.28$ ppm as a characteristic sextet due to coupling with the Al ($I = 5/2$) nucleus, similar to the NMR spectra of known transition metal aluminate complexes [3]. Sharp singlets for the methyl and methine protons of the acac ligand (δ 1.72 (6H) and 5.18 ppm (1H)) suggest that the acac ligand is coordinated to iron in a bidentate fashion through the oxygen atoms in agreement with the IR data. The signals assigned to the methyl groups of the dmpe ligand are two triplets and two multiplets: the former seem to arise from the virtual coupling with phosphorus nuclei *trans* to each other and the latter due to couplings with the *cis* phosphorus nuclei. $^{31}P\{^1H\}$ NMR of **1** shows a somewhat complicated A_2B_2 pattern due to second order couplings of the phosphorus nuclei (Fig. 1). There is good agreement between the theoretical spectrum [5], where $J/\nu_0\Delta\delta$ is assumed to be 0.23, and the observed spectra as shown in Fig. 1. These spectral data strongly support the following *cis* structure of **1**.



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Ion exchange of **1** with $NaBPh_4$ in acetone afforded an air stable, orange complex in high yield (87%) which is formulated as $[Fe(dmpe)_2(acac)]^+BPh_4^-$ (**2**). IR as well as ^1H and $^{31}P\{^1H\}$ NMR spectra of **2** are similar to those of **1** except for the

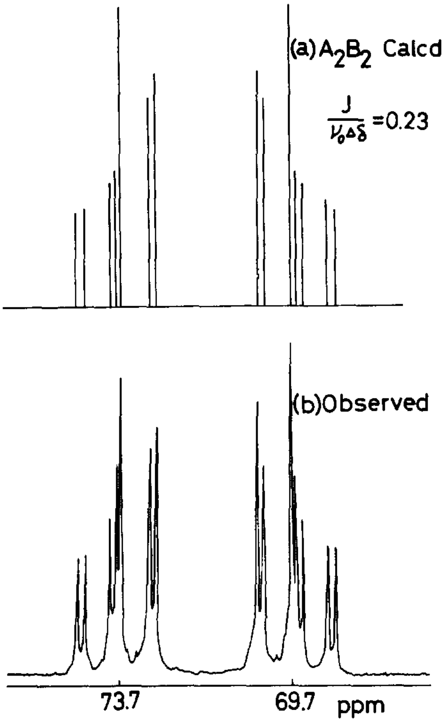

Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[Fe(dmpe)_2(acac)]^+$ $[AlMe_4]^-$ in CD_2Cl_2 at room temperature. (a) Calculated spectrum of A_2B_2 spin system where $J/\nu_0\Delta\delta = 0.23$. (b) Observed spectrum at 40 MHz. Chemical shift; referred to external PPh_3.

difference caused by replacement of $AlMe_4^-$ with BPh_4^-. The results indicate that the coordination environment around the iron atom is unchanged by the ion exchange reaction:

$$\mathbf{1} + NaBPh_4 \rightarrow \underset{(\mathbf{2})}{[Fe(dmpe)_2(acac)]^+ BPh_4^-}$$

Although addition of excess $AlMe_3$ in the synthesis of **1** did not give any isolable methyliron complex, methylation of the cationic complexes **2** to a dimethyliron(II) complex could be accomplished with a more powerful alkylating reagent, MeLi. Thus, treatment of **2** with MeLi in THF afforded $FeMe_2(dmpe)_2$ (**3**) as a mixture of *cis* and *trans* isomers:

$$\mathbf{2} + MeLi \rightarrow \underset{(\mathbf{3})}{FeMe_2(dmpe)_2}$$

Preparation of similar dialkyliron(II) complexes having two bidentate bipyridine ligands has been reported [6].

In the reaction of $Fe(acac)_3$ with $AlMe_3$ in the presence of dmpe, stepwise color changes from red to deep blue and then to red were observed and were accompanied by the evolution of methane and ethane. It is likely that during these color changes methylation of $Fe(acac)_3$ to give methyliron(III) 2,4-pentanedionate took place followed by the thermal decomposition of the methyliron(III) complex to iron(II) liberating methane and ethane [6a]. Formation of **1** can be accounted for by further methylation of iron(II) 2,4-pentanedionate and back transfer of the methyl group from iron to $AlMe_3$, although it could not be confirmed where the reverse methyl transfer took place. Treatment of **3** with an excess of $AlMe_3$ gave no isolable complex. Since formation of the $AlMe_4$ entity by other pathways such as disproportionation of $AlMe_3$ seems improbable, formation of **1** can be most reasonably accounted for by the reverse methyl transfer from a methyl(2,4-pentanedionato) iron(II) species to $AlMe_3$ as discussed in the formation of $[Co(bpy)_2R_2]^+ [AlR_4]^-$ [3b]. Similar back transfer from dicyclopentadienyltrimethyltantalum to $AlMe_3$ was recently noted by Schrock [7].

Experimental

All manipulations were carried out under N_2 or Ar. IR spectra were recorded on a Hitachi-295 spectrometer. ^1H and $^{31}P\{^1H\}$ NMR were measured on JEOL FX-100, FX-90Q and JNM-100 spectrometers. Chemical shifts are referred to TMS and external PPh_3 for ^1H and ^{31}P NMR spectra, respectively. Equivalent electric conductivity was measured using a TOA conductivity meter model CM-5B. Microanalysis was performed using a Yanagimoto CHN Autocorder Type MT-2.

Preparation of $[Fe(dmpe)_2(acac)]^+ [AlMe_4]^-$ (1)

$AlMe_3$ (1.3 ml, 14 mmol) was added to an Et_2O suspension (20 ml) containing $Fe(acac)_3$ (1.0 g, 2.8 mmol) and dmpe (1.0 ml, 5.8 mmol) at −40°C. On raising the temperature to room temperature, the heterogeneous red mixture became a dark blue homogeneous solution, and finally **1** was obtained as a bright red precipitate. Considerable amounts of methane and ethane were evolved as detected by GLC during the reaction. The red precipitate was separated by filtration, washed with hexane and dried in vacuo. Complex **1** can be recrystallized from THF/Et_2O with some decomposition: yield 61%, m.p. 156–158°C(dec), Λ 33 S cm^2 mol^{-1} (in THF at room temperature). ^1H NMR (CD_2Cl_2, r.t.): δ −1.28 ppm (sextet, J 6 Hz, 12H) for $Al\mathit{Me}_4$, 1.12 (m, 12H), 1.32 (t, J 4 Hz, 6H), 1.52 (t, J 4 Hz, 6H) for *Me* of dmpe, 1.6–2.2 (br, 8H) for methylene of dmpe, 1.72 (s, 6H) for acac-Me, 5.18 (s, 1H) for acac-H. The $^{31}P\{^1H\}$ NMR (40 MHz, CD_2Cl_2) of **1** is shown in Fig. 1: δ 69.7, 73.7 ppm (A_2B_2, J(P–P) 37.1 Hz).

Acidolysis of **1** (110 mg, 0.202 mmol) in THF (2 ml) with HCl in Et_2O (4.9 ml) released methane (0.861 mmol, 4.26 mol/Fe).

Ion exchange of 1 with $NaBPh_4$

A homogeneous THF solution (5 ml) of **1** (260 mg, 0.478 mmol) was treated with $NaBPh_4$ (163 mg, 0.478 mmol) to give a red solution. Addition of a few drops of water caused evolution of methane and then further addition of a large amount of water afforded an orange precipitate, **2**, which was recrystallized from an acetone/hexane mixture. Yield 87%. (Found: C, 63.5; H, 7.8. $C_{41}H_{59}O_2BP_4Fe$ calcd.: C, 63.6; H, 7.7%). M.p. 165°C (dec). Λ 30 S cm^2 mol^{-1}. IR: ν(C=O) 1580(vs), 1510(vs) cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.83 (m, 6H), 0.98 (m. 6H), 1.20 (t, J(P–H) 3.8 Hz, 6H), 1.36 (t, J(P–H) 3.2 Hz, 6H) for Me of dmpe; 1.3–1.9 (m, 8H) for CH_2 of dmpe; 1.69 (s, 6H) for Me of acac; 5.1 (s, 1H) for CH of acac; 6.8–7.4 (m, 20H) for BPh_4. $^{31}P\{^1H\}$ NMR (40 MHz, $CDCl_3$): δ 69.8, 73.7 ppm (A_2B_2, J(P–P) 37.3 Hz).

*Reaction of **2** with MeLi*

Complex **2** (117 mg, 0.15 mmol) in a mixture of THF (5 ml) and Et_2O (7 ml) was treated with a THF solution of MeLi (2 ml, 1.07 *M*) at −20°C. After stirring the solution for 20 min at room temperature, the solution was condensed in vacuo to an oily mixture which was extracted with hexane. Evaporation of hexane in vacuo gave a yellow oily material of **3**. The IR spectrum of **3** shows the absence of peaks due to the acac ligand and BPh_4. The ^1H NMR spectrum of **3** suggests the existence of *cis* and *trans* isomers in a 5/4 ratio. ^1H NMR(C_6D_6): δ −1.72 ppm (quintet, *J*(P–H) 6.4 Hz) and −0.40(m), 6H(total) for Fe–Me of *trans* and *cis* isomers, respectively: 1.0–2.0(m, 32H) for dmpe. Ligand exchange of **3** with 1,2-bis(diphenylphosphino)ethane in ether did not take place at room temperature [8].

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