Journal of Molecular Structure 1084 (2015) 302–307

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Study of the nature of counterion of α-diimine radical-anion complexes found in Brookhart-type catalytic systems

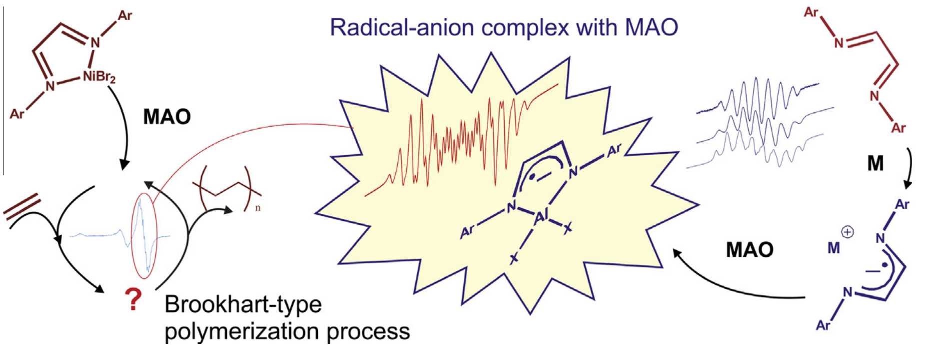
Stanislav K. Petrovskii [*], Vitaly V. Saraev, Natalya S. Gurinovich, E.B. Kuznetsova, D.A. Matveev, P.B. Kraikivskii

Irkutsk State University, Karl Marx str., 1, 664003 Irkutsk, Russian Federation

HIGHLIGHTS

- The radical-anions of two diimines generated by reduction with alkali metals are studied.
- Spin exchange coupling effect is found for sodium complexes.
- Theoretical model for description of the observed spectra is developed.
- It is shown that in catalytic systems radical-anion of ligand is bound with aluminum center.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 September 2014
Received in revised form 5 December 2014
Accepted 15 December 2014
Available online 23 December 2014

Keywords:
Brookhart-type catalysts
α-Diimine ligands
Diimine radical-anions
ESR spectroscopy
Spin exchange coupling

ABSTRACT

The purpose of this work is to reveal the nature of counterion that stabilizes radical-anions found in Brookhart-type catalytic systems. Radical-anions of two typical α-diimine ligands for Brookhart-type catalytic systems bis(2,6-diisopropylphenyl)diazabutadiene and bis-(2,6-diisopropylphenyl)-bis(imino)acenaphthene generated by reduction of a ligand with alkali metals has been investigated. It has been found that the reduction results in different products. In case of sodium complexes, it is shown that the formation of structured associates takes place in which the effect of spin exchange coupling appears. It is noticeable that this is a first example of spin exchange coupling described for diimine compounds. It has been shown that the interaction of diimine radical-anion complexes of both ligands with alkali metals with methylaluminoxane yields in formation of aluminum radical-anion complexes. Their ESR spectra are the same to ones registered in the catalytic systems.

Introduction

At the present time redox-active ligands attract attention of scientists due to their unique properties and, consequently, opportunities of using in different fields of chemistry such as catalysis of many reactions [1], photochemical processes [2] and others. Transition metal complexes bearing diimine ligands mimic natural enzymes that are the most active and selective known catalysts. [3] Among all different redox-active ligands diimine ones may be noted. These compounds allow easily attaining required steric, electron and other properties by varying a structure of both diimine fragment and substituents at nitrogen atoms.

The most significant catalytic processes with using diimine ligands are polymerization and copolymerization of ethylene and propylene [1]. They were developed in the laboratory of M. Brookhart in the second half of 90ths. These catalysts are nickel and palladium diimine complexes activated with organoaluminum

---

[*] Corresponding author. Fax: +7 (3952)242238.
E-mail address: stas1234567892007@yandex.ru (S.K. Petrovskii).

http://dx.doi.org/10.1016/j.molstruc.2014.12.051

compounds. In addition to other features of these systems, an unusual character of nickel ones should be noted. Thus, since Karl Ziegler's works such phenomenon as “nickel effect” – a significant increase of the share of low-molecular products of catalytic polymerization of ethylene when adding nickel compounds to the system – is known [4]. However, Brookhart-type systems are very efficient catalysts of polymerization processes. Moreover, the process of polymerization passes under extremely mild conditions [5]. Despite many researches of the mechanism of functioning of these catalysts [6], questions about nature of active centers of these catalytic systems, and about the processes that occur when initial nickel complexes are activated with organoaluminium compound and a substrate is added, are still opened.

During our recent researches of the system NiBr$_2$(DPP-DAB) + 20 MAO (DPP-DAB = bis(2,6-diisopropylphenyl)diazabutadiene, MAO = methylaluminoxane) by ESR spectroscopy we have revealed that under conditions of activation and functioning of the catalyst the spectra of two types of paramagnetic species in the system are observed [7]. The spectra are attributed to complexes of monovalent nickel with diimine ligands, and radical-anion species [8].

A lot of researches are devoted to the study of diimine, triimine and tetramine radical-anions. Schumann and coworkers [9] have described bis-(2,6-diisopropylphenyl)-bis(imino)acenaphthene (DPP-BIAN) radical-anion complexes with aluminum alkyls. The complexes have been studied by XRD and ESR spectroscopy. Complexes of first row transition metals (Mn, Fe, Co, Ni, Cu, Zn) [10–13], iridium and rhodium [14,15], ruthenium [16] and osmium [17] with diimine and iminopyridine radical-anion ligands are described. Experimental spectroscopic and structural investigations [10–15] and quantum calculations [18] of electron transfer show that an unpaired electron in these complexes is localized mostly on diimine ligands.

Possibility of metal to ligand single electron transfer from Ni (I) to tetraaza macrocyclic ligand and equilibrium between Ni^{2+}L$^-$ and Ni$^+$L are described in [19]. However, DFT calculations of Budzelaar [18] have shown that in case of Ni(I) diimine complexes a tendency to MTL electron transfer is very weak.

However, there are very few works devoted to investigation of radical-anion species in real catalytic systems. Gambarotta and co-workers [10] described the formation of radical-anion species in Fe based Ziegler-type catalytic systems. Interaction between iron bis(imino)pyridine complex with organoaluminum compounds resulted in formation of aluminum complex bearing radical-anion diimine ligand. The species was not active in catalysis, so it has been concluded that they form during the deactivation of the catalyst. Authors have succeeded in isolation and analysis of complexes with trialkylaluminum, however the complexes with MAO have not been isolated individually (which may be explained by the structure of MAO which contains multiple aluminum centers in different surrounding).

The purpose of this work is to reveal the nature of counterion that stabilizes radical-anions in Brookhart-type catalytic systems. The present work contains the results of research of radical-anions of DPP-DAP and DPP-BIAN, which are examples of the most widely used ligands for Brookhart-type catalysts, by ESR spectroscopy. The radical-anions have been generated by reduction of neutral ligands by alkaline metals in toluene. Complexes with MAO were obtained by treating of toluene solutions of M$^+$L$^{\cdot-}$ (M – alkaline metal, L$^{\cdot-}$ – radical-anion of diimine ligand) with MAO solution in toluene.

Experimental

Since radical-anions are very sensitive to oxygen and moisture, all manipulations have been carried out in vacuo or under an atmosphere of argon by using standard Schlenk techniques.

Toluene has been dried with sodium and benzophenone and kept under an atmosphere of argon.

DPP-DAB has been prepared according to [20]. DPP-BIAN has been prepared according to [9]. Purity of products has been controlled by NMR spectroscopy.

Alkali metals have been shredded in boiling toluene.

All other commercial reagents and gases (Sigma–Aldrich) were used without further purification. Room temperature ESR spectra have been recorded with a CMS 8400 ESR spectrometer (frequency 9.6 GHz) in 3 mm glass tubes. The free radical diphenylpicrylhydrazyl (DPPH) and Mn^{2+} in MgO were used for the calibration of the spectrometer. ESR spectra simulations was carried out with WIN-ESR SimFonia, version 1.2. In the case of exchange coupling, the simulation was conducted by using the original algorithm described in this work.

Results and discussion

Complexes of diimine radical-anions with alkali metals

When adding toluene solution of DPP-DAB to shredded metals (Na or K) or metal chips (lithium) in toluene saturated with argon, the color of the solution changes from light yellow to dark red. ESR spectrum of radical-anions of the ligand has been registered (Fig. 1).

As seen in Fig. 1, the shape of the spectrum and number of lines depends on the nature of alkali metal. The number of lines and spectrum shape of ESR signals a and b can be easily explained by coupling of an unpaired electron with two magnetically equivalent ^{14}N (A_N = 5.64 G) and two magnetically equivalent ^{1}H (A_H = 4.74 G). In addition, the spectrum of lithium complex (b) has hyperfine structure from one ^{7}Li (A_{Li} = 1 G) but it is not observed in spectrum because a natural broadening of line is higher that 1G (Fig. 2 and Table 1) under our conditions. It suggests that lithium forms more intimate ion pair then potassium. The results are in good agreement with literature data concerning interaction of alkali metals with diimine ligands. Thus, reduction of bis-(1,4-di-tert-butyl-1,4-diazabutadiene) (Bu$^t_2$DAB) with metal lithium yields paramagnetic product (Bu$^t_2$DAB)$^{\cdot-}$Li$^+$(Bu$^t_2$DAB) [21], which spectrum is very similar to the spectrum of [DPP-DAP]$^{\cdot-}$Li$^+$ registered by us. Metal potassium (or potassium hydride) depending on the reaction conditions and reagents ratio can give mono- and dianionic complexes, which seem to be solvated ion pairs [6].

However, the spectrum of ligand radical-anion with sodium (Fig. 1c) cannot be explained this way. It should be noted that stable isotopes of all three alkaline metals have the same value of nuclear spin 3/2 [22]. In addition, values of hyperfine coupling constants with alkaline metals in such electron transfer complexes are

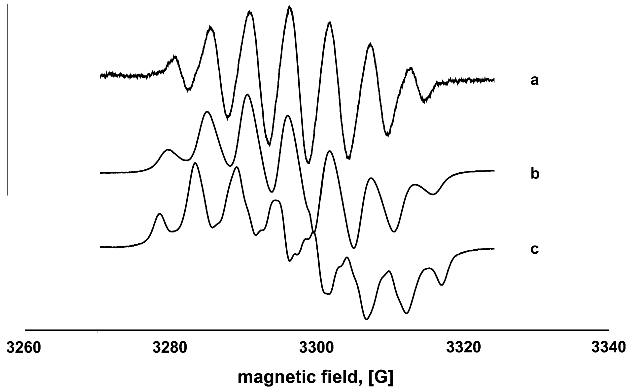


Fig. 1. Room temperature ESR spectra of radical-anions of DPP-DAB: [DPP-DAP]$^{\cdot-}$K$^+$ (a), [DPP-DAP]$^{\cdot-}$Li$^+$ (b) and [DPP-DAP]$^{\cdot-}$Na$^+$ (c).