Usage Report for Fiscal Year 2020

Project Title:

Computational Studies on the Electronic Structures and the Reaction Mechanisms of Rare-Earth- and Transition-Metal Complexes

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1. Background and purpose of the project, relationship of the project with other projects

The rare-earth- and transition-metal complexes catalyzed chemical transformations are important procedures in both industrial and academia fields, thus, the development of more efficient and reactive rare-earth- and transition-metal catalysts is one of the important topics in modern chemistry. To date, a diverse of rare-earth- and transition-metal catalysts have been successfully developed, and numerous valuable chemical products have been produced by using these organometallic complexes. The reactivity and selectivity of organometallic catalysts could be mainly ascribed to its unique physical and chemical properties, which could be modulated by the cooperation effect between metal center and auxiliary ligand. Although much effort has been made to intensively develop the new catalyst by modification of the ligand sphere, the rational design of new catalyst, especially the computational guided catalyst design, is the state-of-the-art approach.

To develop new catalysts more efficiently, the fully understanding of the catalytic mechanism is of fundamental importance, in which the key factors controlling the catalytic reactivity and selectivity could be found. However, it is difficult for traditional experimental to investigate the detailed reaction mechanism, because the intermediates and transition states during reaction are highly reactive and rarely detected, which hinders the rational catalyst design. Instead, the computational chemistry, as a powerful tool for studying chemical process at the molecular and atomic level, could help to elucidate the detailed reaction mechanisms, the electronic structures of catalysts, the key factors controlling the reactivity and selectivity, and *etc.* These mechanistic insights would help improve the performance of existing catalysts and further provide instructive information for rational catalyst design. Therefore, based on the experiment results, a series of computational jobs were carried out for better understanding of the related mechanisms which could contribute to the development of new catalysts and reactions.

2. Specific usage status of the system and calculation method

During the FY2020, a large number of specified computational resources were used for the theoretical calculations. In general, the geometry structures were optimized by DFT method using Gaussian 09 and Gaussian 16 software. The electronic structures of key active species and transition states were characterized by utilizing the ADF software. Natural Bond Orbital (NBO) analyses were also performed using some programs such as Gaussian 09, Gaussian 16 and so on.

The B3LYP, B3PW91, TPSS and M06 functionals were utilized for DFT calculations. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke−Johnson damping (GD3BJ) as well. For calculation of the relatively large catalytic system, such as multinuclear clusters, large polymerization systems, and the bioactive systems, the QM/MM method (ONIOM) was also adopted for accelerating the calculations and analyses.

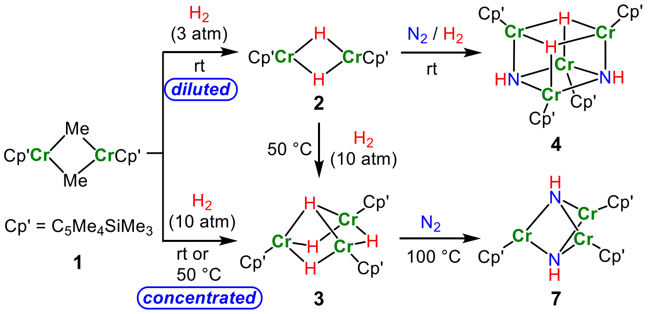
3. Results

(a) DFT study on dinitrogen activation by multinuclear transition metal polyhydride complexes.

The cleavage and hydrogenation of dinitrogen are of great importance because they are the fundamental steps of nitrogen fixation, including conversion of N_2 to NH_3 or value-added products. While heterogeneous catalytic systems are capable of achieving such transformations, although often under harsh conditions such as that for the Haber−Bosch process, homogeneous transition metals involved molecular systems are also attractive because of relatively mild reaction conditions and eases of selectivity regulation and mechanism exploration. In the latter case, bi/multinuclear metal complexes have received considerable attention, thanks to potential intermetallic cooperation being relevant to the industrial Haber−Bosch process. In this context, dinitrogen reduction in some cases requires extra reductants and proton sources. An alternative strategy is to use bi/multinuclear metal polyhydrides for dinitrogen hydrogenation, where additional reductants and proton sources are unnecessary. Therefore, the activation and hydrogenation of dinitrogen (N_2) by well-defined molecular transition-metal hydride complexes is an important research subject, which may help researchers better understand the N_2 transformation mechanism at the molecular level and thereby lead to the development of efficient catalysts for ammonia synthesis under mild conditions.

We reported the synthesis and N_2 activation of the $C_5Me_4SiMe_3$-ligated di- and trinuclear chromium polyhydride complexes [Cp′Cr(μ-H)$_2$CrCp′] (**2**) and [(Cp′Cr)$_3$(μ$_3$-H)(μ-H)$_3$] (**3**) (Cp′ = $C_5Me_4SiMe_3$). In sharp contrast with the previously reported C_5Me_5- and C_5Me_4Et coordinated tetranuclear chromium polyhydrides, which are inert to N_2, the di- and trinuclear chromium polyhydride complexes bearing the $C_5Me_4SiMe_3$ ligands enable N_2 cleavage and hydrogenation under mild conditions without the need for any extra reagents. Computational studies have also been carried out to gain information on the reaction mechanism.

Computational studies revealed that the reaction was initiated by N_2 coordination to a Cr atom, followed by hydride ligand rearrangement and H_2 release through reductive elimination of two hydride ligands. The subsequent N−N bond cleavage and migration of the remaining two hydride ligands to the two nitride ligands afforded the diimide product. Although the overall steps of the reaction of **3** with N_2 were comparable to those of the analogous trinuclear titanium polyhydride complex reported previously, its energy profiles and final product were in contrast with those of the titanium complex, reflecting the metal influence.

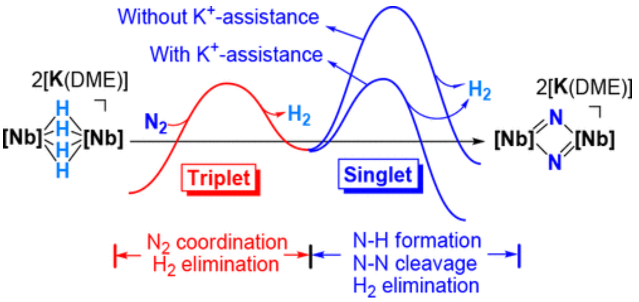


Scheme 1. Dinitrogen activation and hydrogenation by $C_5Me_4SiMe_3$–ligated di- and trinuclear chromium hydride complexes.

(published in *Journal of the American Chemical Society* **2020**, *142*, 9007–9016)

Besides multinuclear chromium hydride complexes, we also reported comprehensive density functional theory (DFT) studies of the N_2 activation by biniobium tetrahydride complex [(*anti*-O_3)Nb]$_2$(*μ*-H)$_4$[K(DME)]$_2$ (*anti*-O_3 = tripodal triaryloxide ligand), addressing the initial two-electron reduction of N_2 and the potential role of the potassium cation.

The mechanism of diniobium tetrahydride mediated N_2 activation has been comprehensively investigated through DFT calculations, during which a “two-state reactivity” scenario is disclosed. This reaction is initiated with N_2 coordination and H2 elimination via a triplet pathway, followed by a singlet route going through N−H formation, N−N cleavage, and the second H_2 release to give an experimentally observed nitride product. Interestingly, the potassium cation was found to play an important role in decreasing the activation barrier of N−H formation and the second H_2 elimination in particular. It was the geometrical predeformation caused by K···N coordination interactions that the alkali cation accelerated the second H_2 elimination event. This work not only discloses a distinct two-state reactivity but also reveals the noteworthy role of the alkali metal cations in N_2 activation chemistry, which are expected to offer useful information for the development of effective molecular systems toward dinitrogen activation and hydrogenation. The exploration of such a multistate reactivity and coordination interaction of alkali metal in a cooperative activation of dinitrogen mediated by multinuclear complexes with redox-active metal center is ongoing.



Scheme 2. Theoretical mechanistic insights into dinitrogen activation by a diniobium tetrahydride: two-state reactivity and the role of potassium cation promoter

(published in *Inorganic Chemistry* 2020, *59*, 4626–4633)

(b) DFT study on polymerization of conjugated polar alkenes by rare-earth/phosphorus Lewis pairs.

It is known that rare-earth metal complexes were reported to not only mediate the synthesis of small molecules but also catalyze the polymerizations of non-polar or polar olefins. To regulate the acidity of Lewis acids in LPP, Xu et al. developed intramolecular and intermolecular rare-earth/phosphorus (RE/P) Lewis pairs (Chart 1) for polymerizing conjugated polar monomers such as methyl methacrylate (MMA).

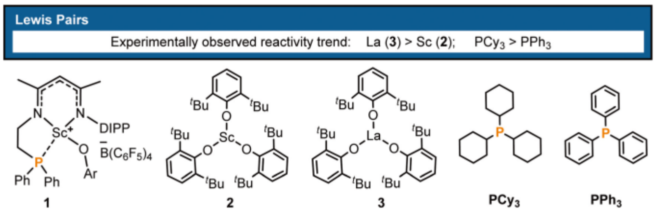
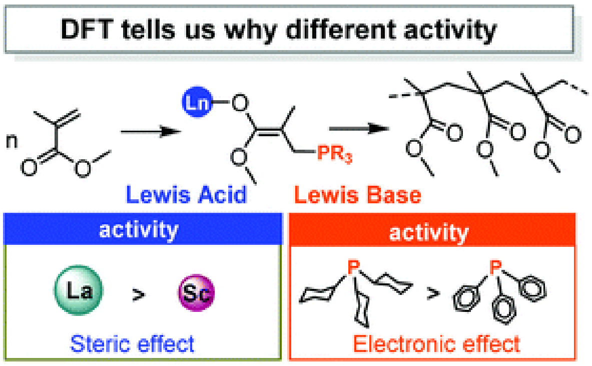


Chart 1. Rare-earth metal Lewis pairs reported for LPP.

To obtain better understanding of the priority of the bimetallic mechanism, the polymerization mechanism of methyl methacrylate (MMA) catalyzed by rare-earth/phosphorus (RE/P) Lewis pairs has been systematically studied through density functional theory (DFT) calculations. Having achieved an agreement between theory and experiment, it is found that the polymerization of MMA mediated by intermolecular RE/P Lewis pairs mainly follows the bimetallic mechanism, while the monometallic pathway could not be excluded in the case of a La analogue. In comparison with phenyl phosphorus as a Lewis base, the higher activity of cyclohexyl phosphorus toward MMA polymerization could be ascribed to the electron-donation ability, rendering more electron flow in the addition reaction. Besides, a computational modelling of analogous intramolecular RE/P systems indicates that the size of the central metal and the length of the chain connecting Lewis pairs play an important role in the catalytic activity. (published in *Inorganic Chemistry Frontiers* 2020, *7*, 4600–4610)

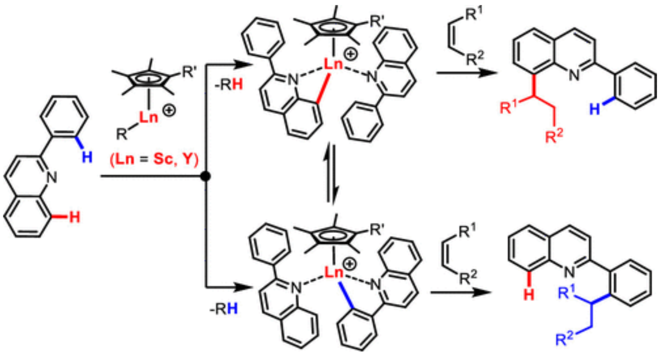


Scheme 3. The polymerization mechanism of methyl methacrylate (MMA) catalyzed by

rare-earth/phosphorus (RE/P) Lewis pairs has been systematically studied through density functional theory (DFT) calculations.

(c) Regiodivergent C–H Alkylation of Quinolines with Alkenes by Half-Sandwich Rare-Earth Catalysts

The regiodivergent catalysis of C–H alkylation with alkenes is of great interest and importance but has remained hardly explored to date. We report herein the first regiodivergent C–H alkylation of quinolines with alkenes by half-sandwich rare-earth catalysts. The regiodivergence was achieved by fine-tuning the metal/ligand combination or steric and electronic properties of the catalysts. The use of the C_5Me_5-ligated scandium catalyst **Sc-3** for the reaction of quinolines with styrenes and that of the C_5Me_4H-ligated yttrium catalyst **Y-2** for the reaction with aliphatic olefins exclusively afforded the corresponding C8–H alkylation products, thus constituting the first example of direct C8–H alkylation of neutral quinolines. In contrast, the **Sc-3**-catalyzed reaction of 2-arylquinolines with aliphatic olefins and the **Y-2**-catalyzed reaction with styrenes selectively gave the 2-aryl *o*-C–H alkylation products. On the basis of the catalyst/substrate-controlled regiodivergence, the sequential regiospecific dialkylation of quinolines with two different alkenes has also been achieved. DFT studies revealed that the C–H activation of 2-phenylquinoline at both the C8 position and an *ortho* position of the 2-phenyl substituent was possible, and these two types of initially formed C–H activation products were interconvertible through the coordination and C–H activation of another molecule of quinoline. The regioselectivity for the C–H alkylation reactions was governed not only by the ease of the initial formation of the C–H activation products but also by the energy barriers for their interconversions, as well as by the energy barriers or steric and electronic influences in the subsequent alkene insertion processes. This work has not only constituted an efficient protocol for the selective synthesis of diversified quinoline derivatives but also offered unprecedented insights into the C–H activation and transformation of quinolines and may help in the design of more efficient, selective, or complementary catalysts.



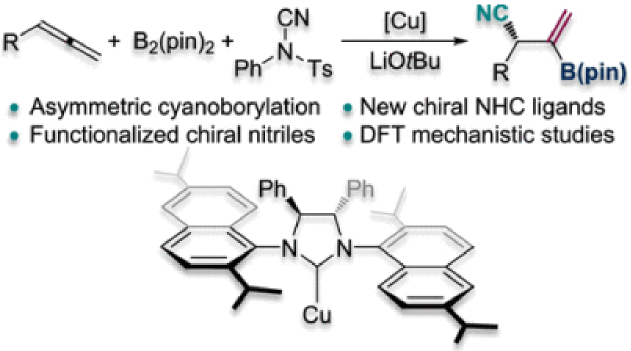
Scheme 4. Regiodivergent C–H alkylation of quinolines with alkenes by half-sandwich rare-earth catalysts

(published in *Journal of the American Chemical Society*, 2020, 142, 18128-18137)

(d) Enantioselective Cyanoborylation of Allenes by *N*-Heterocyclic Carbene-Copper Catalysts

The simultaneous incorporation of both a cyano group and a boryl unit into the C=C double bonds of allenes in a regio- and stereoselective fashion is of much interest and importance but remains a significant challenge. We report herein a copper-catalyzed chemo-, regio-, and enantioselective cyanoborylation of allenes, which afforded a family of valuable enantiopure β-boryl allyl nitriles. The high enantioselectivity was achieved by installing of appropriate substituents at the C2 and C6 positions of the naphthyl groups in our newly synthesized *N*-heterocyclic carbene (NHC) ligands. The reaction mechanism has been clarified by some stoichiometric reactions and computational studies. This work provides an inspiring example of the development of selective catalytic reactions for the synthesis of functional molecules through fine-tuning the ligands in catalysis.

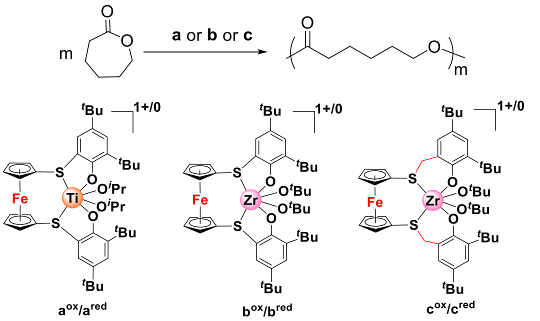
(published in *ACS Catalysis*, 2020, 10, 11685–11692)



Scheme 5. Enantioselective cyanoborylation of allenes by *N*-heterocyclic carbene-copper catalysts

(e) DFT study on the Redox-switchable Ring-Opening Polymerization of ε-Caprolactone catalyzed by Group 4 Metal Complexes.

Redox-switchable polymerization has drawn increasing attention, in particular for the ring-opening polymerization (ROP) of biomass-derived monomers. However, an understanding of how the switch determines the observed changes is still limited. In this study, DFT calculations were employed to understand the redox-switchable ROP mechanism of ε-caprolactone catalyzed by group 4 metal complexes bearing [OSSO]-type bis(phenolato) ferrocene ligands (Scheme 1).



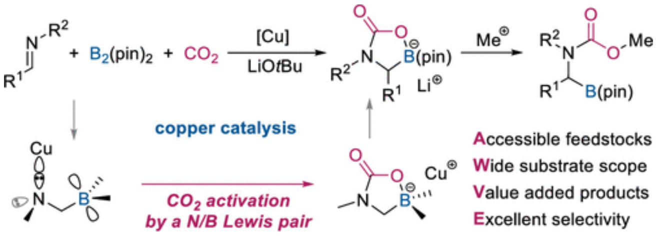
Scheme 6. Group 4 metal catalysts bearing [OSSO]-type bis(phenolato) ferrocene-based ligands for ε-caprolactone (CL) polymerization.

Having achieved an agreement between calculation and experiment, it was found that the higher activity of the oxidized forms $\mathbf{a}^{ox}$ and $\mathbf{c}^{ox}$ compared to that of their corresponding reduced forms stems from the higher Lewis acidity of the catalytic metal center in the oxidized species. In contrast, the lower activity of the oxidized species $\mathbf{b}^{ox}$ compared to that of bred is due to an increased stability of the intermediate following the monomer coordination that results in a high energy barrier. The current results also indicate that the stronger Lewis acidity of the catalytic metal center generally increases the activity of the catalyst. However, it could also increase the energy barrier of a reaction when the Lewis acidity of metal center is strong enough to overstabilize the coordination complex.

In the series of [OSSO]-type bis(phenolato) ferrocene-based group 4 metal complexes, our computational modelling indicates that a Hf analogue may possess better redox-switchable property for the ROP of CL compared to its corresponding Zr complex. Furthermore, the redox-switchable activity of the Zr complexes with different bridging-heteroatoms in their ancillary ligands follows the order of O < S < Se. These findings are expected to provide useful information on developing new redox-switchable polymerization catalysts for the synthesis of biodegradable polymers from biomass-derived monomers. (published in *Inorganic Chemistry Frontier* 2020, 7, 961–971.)

(f) CO_2 Activation by Lewis Pairs Generated Under Copper Catalysis Enables Difunctionalization of Imines

Integration of distinct substrate activation modes in a catalytic circle is critical for the development of new, powerful synthetic methodologies toward complex and value-added chemicals from simple and readily available feedstocks. Here, we describe a highly selective difunctionalization of imines through incorporation of activation of CO_2 by intramolecular N/B Lewis pairs into a copper catalytic cycle. Experimental and computational studies on the mechanistic aspect revealed an α-borylalkylamido intermediate, a metal amide-based Lewis pair formed by borylation of a C–N double bond, and enabled an unprecedented CO_2 fixation pattern that is in sharp contrast to the traditional CO_2 insertion into transition-metal-element bonds. The unique lithium cyclic boracarbamate products could be easily transformed into multifunctional N-carboxylated α-amino boronates. The highly diastereoselective reactions of chiral *N-tert*-butanesulfinyl aldimines were also achieved. We hope that our findings may inspire further development of selective multicomponent reactions by incorporation of Lewis pair chemistry into transition-metal catalysis.



Scheme 7. CO_2 activation by Lewis pairs generated under copper catalysis enables difunctionalization of imines

(published in *Journal of the American Chemical Society*, 2020, 142, 1966−1974)

4. Conclusion

With the help of HOKUSAI system, (1) the reaction mechanism of N_2 cleavage and hydrogenation by a chromium hydride complex has been studied by DFT calculations. This work represents the first example of N_2 cleavage and hydrogenation by well-defined chromium hydride complexes. (2) A “two-state reactivity” scenario has been computationally disclosed for dinitrogen activation by a diniobium tetrahydride, and the effect of various alkali metal cations has also been investigated systematically. Both studies are expected to offer useful information for the development of effective molecular systems toward dinitrogen activation and hydrogenation. (3) DFT calculations have been conducted for the RE/P Lewis pairs toward the polymerization of MMA, the origin of different activity between Sc and La analogues and the effects of different Lewis bases have been elucidated, which could provide a piece of information for the development of LPP systems. (4) DFT studies offered unprecedented insights into the C–H activation and transformations of quinolines by half-sandwich rare-earth catalysts. (5) Computational studies found that the stability of the borocupration transition states governs the regioselectivity of cyanoborylation of allenes by *N*-heterocyclic carbene-copper catalysts and set up an enlightening model for the development of selective catalytic processes through fine-tuning ligand design. (6) Mechanistic aspect redox-switchable ring-opening polymerization of ε-Caprolactone catalyzed by Group 4 Metal Complexes, offering the mechanistic information of Redox-switchable ring-opening polymerization of ε-Caprolactone. (7) Mechanistic insights of highly selective difunctionalization of imines through incorporation of activation of CO_2 by intramolecular N/B Lewis pairs into a copper catalytic cycle has been studied by DFT calculations.

These studies were successful in unveiling the key role of rare-earth- and transition-metal complexes in chemical reactions.

5. Schedule and prospect for the future

In the future, the reaction mechanism of inert molecule activation (such as H_2, N_2, NH_3) catalyzed by multinuclear cluster will be studied continuously. Besides, we will focus on the copolymerization of ethylene and polar monomer mediated by rare-earth- and transition-metal complexes. Furthermore, date analysis of the polymerization will be carried out, the multiple linear regression and machine learning methods will be also performed.

We wish to continue to use HOKUSAI system for the current long-term project. Although some primary results have been obtained, more systematic studies on the mechanism of newly discovered reactions mediated by rare-earth- and transition-metal complexes are obviously necessary.

Fiscal Year 2020 List of Publications Resulting from the Use of the supercomputer

[Paper accepted by a journal]

(1) Takanori Shima, Jimin Yang, Gen Luo, **Yi Luo***, and **Zhaomin Hou*** "Dinitrogen Activation and Hydrogenation by $C_5Me_4SiMe_3$-Ligated Di- and Trinuclear Chromium Hydride Complexes" *Journal of the American Chemical Society* **2020**, *142*, 9007–9016. (SCI, Impact Factor: 14.612)

(2) Jimin Yang, Gen Luo*, Yang Yu, Jingping Qu, **Zhaomin Hou**, and **Yi Luo*** "Theoretical Mechanistic Insights into Dinitrogen Activation by a Diniobium Tetrahydride: Two-State Reactivity and the Role of Potassium Cation Promoter" *Inorganic Chemistry* **2020**, *59*, 4626–4633. (SCI, Impact Factor: 4.825)

(3) Yanan Zhao, Gen Luo, Xin Xu, **Zhaomin Hou** and **Yi Luo*** "A computational study of the reactivity of rare-earth/phosphorus Lewis pairs toward polymerization of conjugated polar alkenes" *Inorganic Chemistry Frontiers* **2020**, *7*, 4600–4610. (SCI, Impact Factor: 5.958)

(4) Shao-Jie Lou, Liang Zhang, Yong Luo, Masayoshi Nishiura, Gen Luo*, **Yi Luo**, and **Zhaomin Hou***. Regiodivergent C–H alkylation of quinolines with alkenes by half-sandwich rare-earth catalysts. *Journal of the American Chemical Society,* **2020**, *142*, 18128-18137. (SCI, Impact Factor: 14.612)

(5) Zhenghua Li, Liang Zhang*, Masayoshi Nishiura, Gen Luo*, **Yi Luo**, and **Zhaomin Hou***. Enantioselective cyanoborylation of allenes by N-heterocyclic carbene-copper catalysts. *ACS Catalysis*, **2020**, 10, 11685–11692. (SCI, Impact Factor: 12.35, selected as ACS Editors' Choice)

(6) Xiaowei Xu, Gen Luo,* **Zhaomin Hou**, Paula L. Diaconescu,* and **Yi Luo*** "Theoretical Insight into the Redox-switchable Activity of Group 4 Metal Complexes for the Ring-Opening Polymerization of ε-Caprolactone" *Inorganic Chemistry Frontier* **2020**, 7, 961–971. (SCI, Impact Factor: 5.958)

(7) Zhenghua Li, Liang Zhang, Masayoshi Nishiura, Gen Luo*, **Yi Luo**, **Zhaomin, Hou*** "CO_2 Activation by Lewis Pairs Generated Under Copper Catalysis Enables Difunctionalization of Imines" *Journal of the American Chemical Society* **2020**, 142, 1966–1974. (SCI, Impact Factor: 14.612)