

Dalton Transactions

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COMMUNICATION

Unexpected formation of μ -carbido diruthenium(IV) complex during metalation of phthalocyanine with $\text{Ru}_3(\text{CO})_{12}$ and its catalytic activity in the carbene transfer reactions

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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μ -Carbido diruthenium(IV) phthalocyanine complex was prepared for the first time from the free-base octabutoxyphthalocyanine by the direct metalation with $\text{Ru}_3(\text{CO})_{12}$. The first examples of catalytic activity of Ru(IV) binuclear phthalocyanines were demonstrated by the cyclopropanation of aromatic olefins and carbene insertion to N-H bonds of aromatic or aliphatic amines with turnover numbers of 680-1000 and 580-1000, respectively.

Ruthenium complexes with tetrapyrrolic ligands can be considered as close analogues of iron porphyrins which constitute active sites of hemoproteins playing crucial roles in the transfer of small molecules and oxidation of organic substrates in Nature. Up-to-date, ruthenium porphyrins have already found wide catalytic applications in various synthetic procedures,¹ including oxidation,² nitrene and carbene transfer reactions,³ amination⁴ and other reactions.⁵ Myoglobin modified through iron cofactor substitution with ruthenium porphyrin showed moderate activity for carbene insertion reactions.⁶ By contrast, catalytic applications of related ruthenium(II) phthalocyanine analogues are limited by few examples of the oxidation⁷ and cyclopropanation reactions.⁸ At the same time, due to robust chemical properties of phthalocyanine macrocycles, their ruthenium complexes might also give rise to novel catalytic systems.

Herein we report on the unexpected synthesis and catalytic activity of μ -carbido diruthenium(IV) phthalocyanine complex in the cyclopropanation of styrenes and in the carbene insertion to N-H bond of anilines using ethyl diazoacetate (EDA) as a carbene donor.

Ruthenium phthalocyaninates are typically prepared by template condensation of phthalonitriles in the presence of ruthenium salts or complexes.⁹ Direct insertion of ruthenium into the preformed macrocycle is, however, less studied and it is used mainly for metalation of alkyl-substituted phthalocyanines with $\text{Ru}_3(\text{CO})_{12}$ in refluxing benzonitrile, affording the complexes with two axially coordinated PhCN molecules.¹⁰ Our attempt to apply this method to octa-*n*-butoxyphthalocyanine $\text{H}_2[(\text{BuO})_8\text{Pc}]$ failed.

Nevertheless, the reaction of $\text{H}_2[(\text{BuO})_8\text{Pc}]$ with $\text{Ru}_3(\text{CO})_{12}$ (Scheme 1) smoothly proceeds in refluxing *o*-dichlorobenzene (*o*-DCIB) similarly to previously published preparation of ruthenium porphyrinates.¹¹ The separation of the reaction products by size-exclusion chromatography on Bio-Beads S-X1 revealed that *two* different complexes with essentially different retention times were obtained as a result of the metalation reaction. The structures of complexes were evidenced by UV-Vis, FTIR, MALDI TOF MS and NMR techniques (Fig. 1 and ESI). One of them with the longer retention time, obtained with a 62% yield, corresponded to the *monomeric* Ru(II) complex with axially coordinated CO molecule – $[(\text{BuO})_8\text{Pc}]\text{Ru}(\text{CO})$, **1**. The complex with shorter retention time, formed with a 22% yield, had the unusual UV-Vis spectrum with the broad low-intensity Q-band centered at 607 nm (Fig. 1a). Set of spectroscopic data allowed to assign this complex to the *dimeric* phthalocyaninato-Ru(IV) complex with μ -carbido bridge $[(\text{BuO})_8\text{PcRu}]_2(\mu\text{-C})$, **2**. The HR ESI mass spectrum showed a prominent molecular cluster of a doubly-charged molecular ion centered at $m/z = 1196.512$ (Fig. S6). Their position and isotopic pattern corresponded to those in the simulated spectrum of $\text{C}_{129}\text{H}_{160}\text{N}_{18}\text{O}_{16}\text{Ru}_2$ (calcd $m/z = 1196.516$). In its FTIR spectrum the band of the Ru=C=O stretching at 1013 cm^{-1} was observed whereas the band of CO stretching (1939 cm^{-1} in the spectrum of **1**) was absent (Fig. 1b).^{12,13} The sandwich structure of this complex was further confirmed by the characteristic splitting of the O-CH₂ resonance signal in ¹H NMR spectrum of **2**.

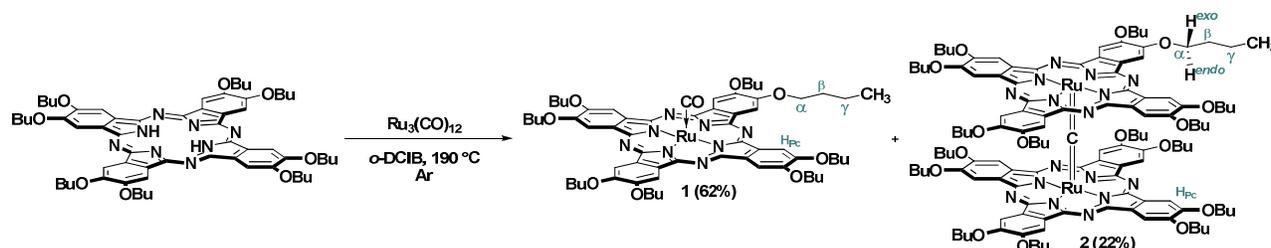
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†Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis of monomeric octabutoxyphthalocyaninoruthenium(II) carbonyl complex **1** and dimeric μ -carbido-bis[octabutoxyphthalocyaninoruthenium(IV)] complex **2** with numbering of protons used for assignment of ^1H NMR spectra.

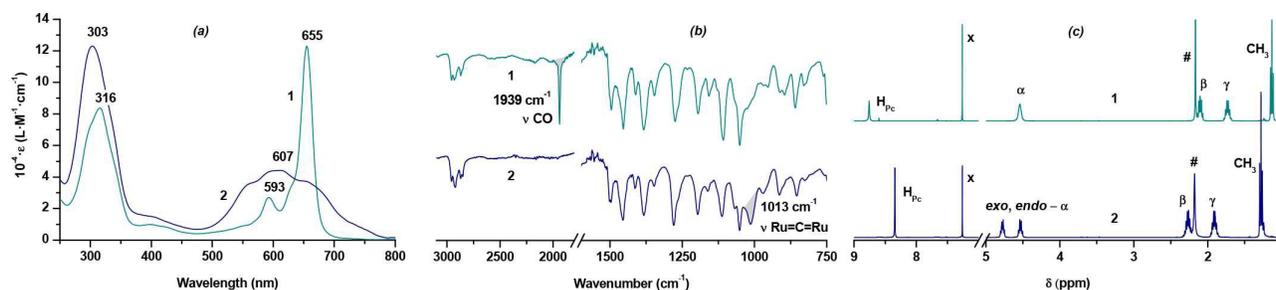


Fig. 1. (a) – UV-Vis spectra of complexes **1** and **2** in CHCl_3 ; (b) – FTIR (neat) spectra of complexes **1** and **2**; (c) – ^1H NMR spectra of complexes **1** and **2** in CDCl_3 +1 vol. % Py-d_5 , "x" and "#" mark proton resonance signals of chloroform and water.

This splitting is due to the non-equivalence of *exo*- and *endo*- protons in this group with respect to the space between the phthalocyanine ligands (Fig. 1c), which was also demonstrated by ^1H - ^{13}C HSQC NMR spectroscopy (Fig. S11).¹⁴

It is known that thermolysis of $\text{Ru}_3(\text{CO})_{12}$ can lead to carbide clusters, among them the most well-studied one is the octahedral cluster $\text{Ru}_6\text{C}(\text{CO})_{17}$, which is formed upon heating of ruthenium carbonyl in high boiling solvents.¹⁵ Therefore, we supposed that the complex **2** can be formed either by thermolysis of the carbonyl-containing complex **1**, or via reaction of $\text{H}_2[(\text{BuO})_8\text{Pc}]$ with $\text{Ru}_6\text{C}(\text{CO})_{17}$. However, neither refluxing of the later reagents in *o*-DCIB nor heating of **1** in the same solvent did not result in the formation of **2**. Therefore, we can propose that the complex **2** was formed simultaneously with **1** via the reaction of $\text{H}_2[(\text{BuO})_8\text{Pc}]$ with some intermediate products formed upon the thermolysis of $\text{Ru}_3(\text{CO})_{12}$. This tentative mechanism might be corroborated by the results of DFT calculations which suggest that among all the possible products of $\text{Ru}_3(\text{CO})_{12}$ thermolysis, $\text{Ru}_6\text{C}(\text{CO})_{17}$ has the lowest reactivity, while the other complexes $\text{Ru}_6\text{C}(\text{CO})_{23-n}$ should be less stable towards further chemical transformations.¹⁶

Although carbido complexes are well-known in ruthenium chemistry for a long time,¹⁷ the reported herein μ -carbido-dimer **2** is exceptionally rare in the chemistry of ruthenium complexes with tetrapyrrolic ligands. It is limited to the single example of the unsubstituted $(\text{PcRu})_2(\mu\text{-C})$, reported by Homborg et al. in 1997.^{13,18} This complex was synthesized by the reaction of PcRuCl with chloroform as a source of a carbon atom in the presence of KOH in *i*-PrOH and it is poorly soluble in organic solvents which limits its possible applications. In contrast, the μ -carbido complex **2** bearing substituted ligand formed in an unprecedented *one-step* procedure starting

directly from the phthalocyanine ligand is well-soluble in common solvents which facilitates the investigations of its properties.

Until recently, single-atom bridged bimetallic complexes with porphyrin and phthalocyanine ligands have been regarded as inactive forms in catalysis. However, μ -oxo diiron phthalocyanines were shown to be effective catalysts for the oxidation of aromatic compounds to quinones.¹⁹ In turn, μ -nitrido diiron phthalocyanine and porphyrin complexes were found to exhibit a rare catalytic activity²⁰ including oxidation of methane²¹ and aromatic compounds,²² oxidative dechlorination²³ and defluorination²⁴ as well as the formation of C-C bonds.²⁵ However, related μ -carbido diiron macrocyclic complexes have never been reported as catalysts for any reaction. In this context, it is much of interest to explore the possible catalytic applications of the novel μ -carbido ruthenium dimer. Thus, the catalytic activity of **2** in the cyclopropanation of styrenes and in the carbene insertion to N-H bond of anilines using ethyl diazoacetate (EDA) as a carbene donor was investigated (Scheme 2). These reactions provide an access to cyclopropanes or unnatural aminoacids and N-heterocyclic compounds, respectively, representing important building blocks used for the synthesis of numerous bioactive molecules.²⁶

The catalytic activity of **2** (0.1 mol% loading) was initially studied using 1 M styrene solution in toluene and 1.2 equiv EDA (Table 1). To limit the formation of diethyl maleate and diethyl fumarate byproducts formed from dimerization of EDA in ~90:10 ratio, the carbene precursor was slowly added to the reaction mixture. This allowed increasing the yield of ethyl 2-phenylcyclopropane-1-carboxylate from 66% to 84% at 70°C (Table 1, entries B-D).

Table 1. Cyclopropanation of olefins by EDA catalyzed by **2**.^a

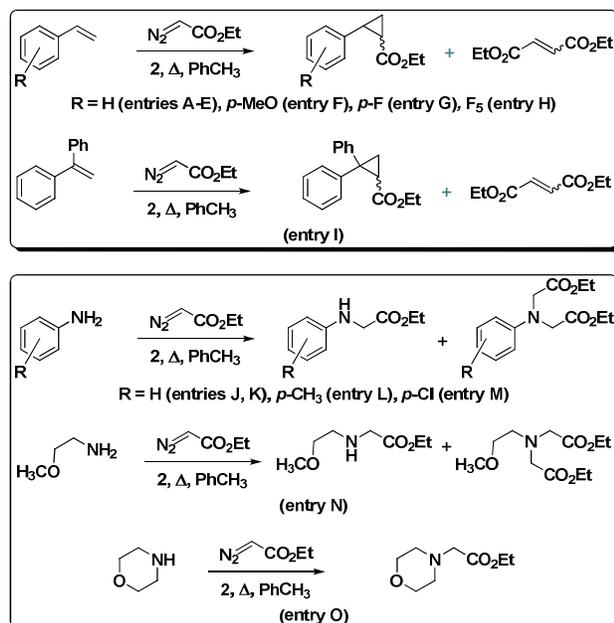
Entry	Substrate	T, °C	Addition of EDA, h	Cyclopropanation ^b		EDA dimerisation ^c		Cyclopropanes/dimers molar ratio
				Yield, %	<i>trans/cis</i>	Yield, %	<i>cis/trans</i>	
A	Styrene	25	2	3	74:26	25	88:12	0.2:1
B	Styrene	70	2	66	71:29	45	88:12	2.4:1
C	Styrene	70	4	77	68:32	40	88:12	3.2:1
D	Styrene	70	6	84	70:30	30	89:11	4.7:1
E	Styrene	90	6	92	69:31	13	89:11	11.5:1
F	<i>p</i> -methoxystyrene	90	6	100	75:25	7	90:10	25:1
G	<i>p</i> -fluorostyrene	90	6	95	70:30	9	89:11	19:1
H	Pentafluorostyrene	90	6	68	74:26	21	95:5	5.2:1
I	1,1-diphenylethene	90	6	100	-	3	92:8	50:1

^a Reactions were carried out under Ar in toluene using 1 equiv of olefin (1 M), 1.2 equiv of EDA (1.2 M) added by syringe pump over desired time and 0.1 mol% catalyst (1 mM). ^b Yield of cyclopropanation products is based on the amount of the substrate. ^c Total yield of diethyl maleate and diethyl fumarate is based on the EDA amount.

Table 2. N-H insertion of EDA to amines catalyzed by **2**.^a

Entry	Substrate	[2], mM	Reaction time, h	Yield, ^b %	RNHCH ₂ COOEt / RN(CH ₂ COOEt) ₂ ratio
J	Aniline	0.2	2.5	43	100:0
K	Aniline	1	2.5	100	83:17
L	<i>p</i> -methylaniline	1	17	100	79:21
M	<i>p</i> -chloroaniline	1	7	100	83:17
N ^c	2-methoxyethylamine	1	30	58	0:100
O	Morpholine	1	6	90	-

^a Reactions were carried out under Ar in toluene at 90°C using 1 equiv of amine (1 M), 1.2 equiv of EDA (1.2 M) added by syringe pump over 2 h. ^b Yield is based on amine amount. ^c Reaction temperature: 70°C.



The yield of the cyclopropanation product was further improved to 92% at 90°C (Table 1, entry E). In the absence of

catalyst, 4% and 12% styrene conversions were obtained at 70°C and 90°C, respectively, thus indicating the involvement of **2** in the product formation. UV-vis spectrum of the reaction mixture during the cyclopropanation of styrene in toluene exhibited the same maximum at 618 nm as the spectrum of the initial complex **2** indicating that **2** retained the dimeric structure. Aromatic olefins bearing donor and acceptor substituents were cyclopropanated with 95–100% yields. Even in the case of very electron-deficient pentafluorostyrene, a 68% yield of C₆F₅-containing cyclopropane (entry H) has been achieved. The *trans/cis* ratio of the cyclopropanation products was insensitive to the olefin nature: ~ 70:30 selectivity was observed in all cases. The yield of cyclopropane product obtained from styrene and EDA in the presence of **2** (92%) was higher than those published for mononuclear Ru(III)PcCl (59%) and Ru(II)PcF₁₆ (80%) complexes.⁸

The μ -carbido diruthenium complex also catalyzes the carbene insertion from EDA to N-H bonds of aromatic and aliphatic amines (Table 2). Importantly, even with low catalyst loading and very high aniline concentration the μ -carbido ruthenium complex **2** transfers the carbene group to the amine N-H bonds. It should be noted that many catalytic complexes coordinate the amine substrates and thus become inactivated to reaction with the carbene precursor.^{3,27} To overcome this limitation, a high concentration of catalyst and low amine concentration should be used which lead to low

turnover numbers and low efficiency. The complex **2** doesn't suffer from this and can be used in low concentration to provide turnover number up to 1000. The insertion of carbenes into N-H bond occurs cleaner than cyclopropanation. Practically no EDA dimerization products were formed. The reaction mediated by **2** was the most efficient at 90°C. In the absence of the catalyst the conversion of aniline was limited to 5%. The reaction is tolerant of both electron-donating and electron-withdrawing groups on the aromatic moiety. Substituted anilines converted to mono- and di-insertion products with ~ 80:20 ratios. However, **2** is slightly less efficient in the reaction with aliphatic amines (entries N and O) providing a 58 % yield of double insertion product with 2-methoxyethylamine and a 90 % yield with morpholine.

Previously, dinuclear Ru(I) and Ru(II) complexes with carboxylate, hydrido, silyl, phosphane, arene, cyclopentadienyl and multidentate nitrogen ligands have been used as catalysts for carbene transfer reactions.²⁸ To the best of our knowledge, carbene transfer reactions catalyzed by Ru in high oxidation state are rare. Simonneaux and coworkers have used Ru(VI) dioxo porphyrin complexes for cyclopropanation of styrenes, but active ruthenium carbene species was formed after reduction of Ru(VI) to Ru(II) complexes with EDA.²⁹ Similarly, Gross and co-workers proposed that μ -oxo diiron(IV) and mononuclear Fe(IV) corrole complexes should be initially reduced to Fe(III) state to react with EDA.³⁰ In the present case, Ru(IV)=C=Ru(IV) phthalocyaninate appears to keep a high oxidation state. For this reason, the activation of EDA occurs only at elevated temperatures. Our attempts to detect a putative active carbene complex formed by **2** were unsuccessful.

In conclusion, although several types of ruthenium complexes have emerged as suitable catalysts for carbene transfer reactions,^{3,28} μ -carbido diruthenium macrocyclic complexes have not been previously considered as catalysts. The original interest in the μ -carbido complex **2** was fuelled by the observation of the particular catalytic properties of related μ -nitrido and μ -oxo complexes.¹⁹⁻²⁵ This study represents the first example of the catalytic application of dimeric μ -carbido Ru(IV) phthalocyaninate exemplified by the carbene insertion reactions into olefinic bonds and N-H bonds of amines. Although the catalytic activity is still modest, the results obtained suggest that μ -carbido diruthenium phthalocyanine can be added to the family of catalytically active single-atom bridged bimetallic macrocyclic complexes and might find interesting applications in catalysis. Recent results from Che's group on the remarkable catalytic properties of Ru(II) porphyrin complexes bearing N-heterocyclic carbene ligands in the carbene and nitrene transfer reactions³¹ support the validity of our approach. Apart from the catalytic applications, the reported approach to μ -carbido ruthenium(IV) complexes might also attract attention from the viewpoint of elaboration of novel optoelectronic materials.³²

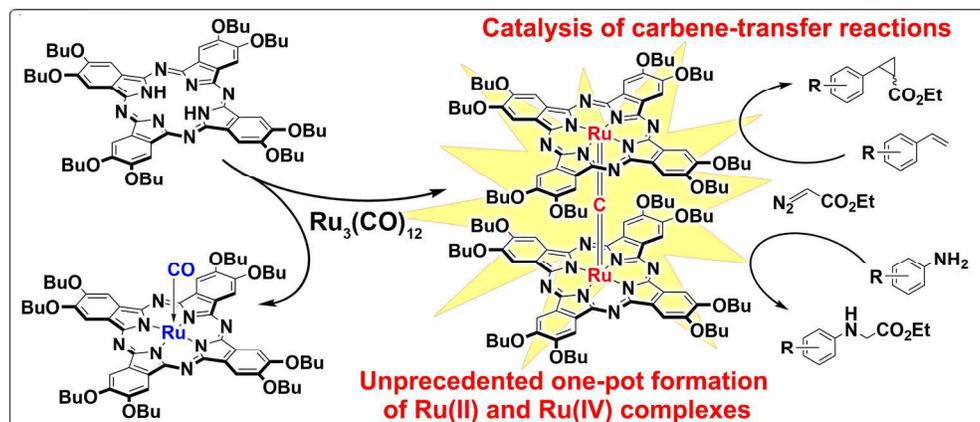
This work was supported by the Foundation of President of Russian Federation for support of young scientists and leading scientific schools (grant MK-141.2017.3), Program of RAS (I.14) and Agence Nationale de Recherches, France (grant ANR-16-

CE29-0018-01). AGM is grateful to French Embassy in Moscow for the Mechnikov Fellowship. LC is indebted to Ministère de l'Éducation Nationale, de l'Enseignement Supérieur et de la Recherche, France for the PhD fellowship.

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