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HETEROCYCLIC CARBENE COMPLEXES OF NICKEL, PALLADIUM, AND COPPER(I) AS EFFECTIVE CATALYSTS FOR THE REDUCTION OF KETONES *

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Carbene complexes of nickel, palladium, and copper(I) effectively catalyze the reduction of aromatic ketones under the influence of 2-propanol in the presence of potassium hydroxide. Bis(1,3-dimethylbenzimidazol-2-ylidene)copper(I) iodide and the polymeric complex of crown-biscarbene with copper(I) iodide show the highest catalytic efficiency.

Keywords: heterocyclic carbene complexes of copper(I), nickel, and palladium, catalysis, reduction of ketones.

It is known that carbene complexes of transition metals catalyze condensation reactions (Suzuki-Miyaura, Sonogashira, Stille, Kumada, Mizoroki-Heck reactions), olefin metathesis, reduction of multiple bonds, olefin polymerization, etc. [1–3]. Stable carbenes are also reactive in transesterification, the Claisen condensation, and the benzoin and formoin condensations [4]. Especially valuable in this respect are heterocyclic carbenes and their complexes which have the most stable carbene structures. Among these catalytic conversions, reduction by a hydrogen transfer from alcohols to the multiple bonds, which includes reduction of carbonyl compounds, imines and olefins [1], is interesting but rather poorly studied. It is known that these reactions are catalyzed by rhodium(I-III), iridium(I-III) and ruthenium(I-III) carbene complexes [5–24]. Complexes of the type of compounds **1-9** (Fig.1) which with similar effectiveness noticeably accelerate reduction of ketones by 2-propanol in alkaline media (hydrogen transfer) should be distinguished among them.

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*Dedicated to the memory of Academician E. Lukevics.

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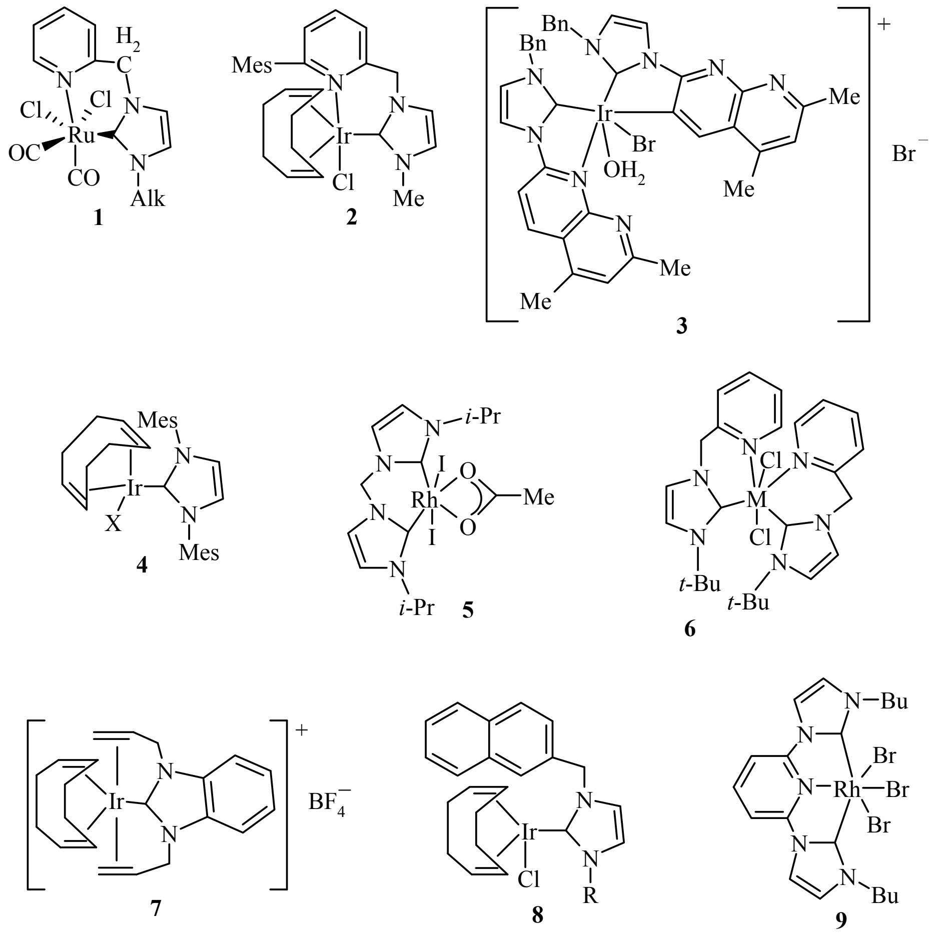
To assess the catalytic activity turnover numbers (TON) and turnover frequencies (TOF) are often used in literature. In case of the benzophenone reduction by ruthenium complex catalyst **1** TON is equal to 4700, while TOF is equal to 780 h^{-1} [16]. Similar process with iridium complex **8** is characterized by TON equal to 1800, and TOF equal to 1800 h^{-1} [18]. When using rhodium complex **9** for catalyzing the benzophenone reduction, the highest TON is obtained (10580), however TOF in this case is substantially lower (441 h^{-1}) [7]. Reaction time in case of using this catalyst is still quite long (up to 24 h), and reduction product yields do not exceed 85–86%. Significant disadvantage of all mentioned catalysts **1–9** is a high price of rhodium, ruthenium and iridium derivatives.


1 **2** **3** **4** **5** **6** **7** **8** **9**

6 M = Rh, Ir; **8** R = Alk, Bn

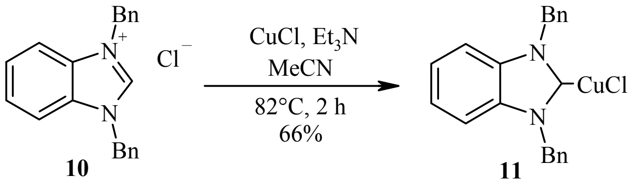
Figure 1. Carbene complexes used as hydrogen transfer catalysts.

The objective of this work is to study the catalytic efficiency of carbenes and carbene complexes of such transition metals as nickel(II), palladium(II), and copper(I) in the reduction of ketones with 2-propanol in the presence of potassium hydroxide.

Mono- and biscarbene complexes of copper(I), carbene chelate and biscarbene complexes of nickel and palladium, and polymeric complexes of copper(I) were used as carbene complex catalysts.

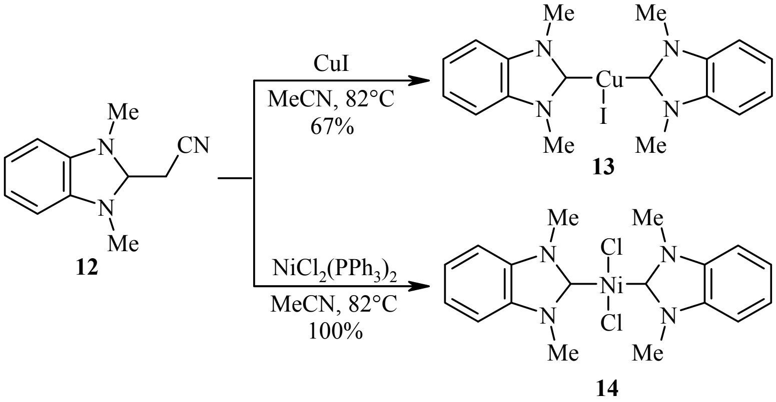
According to our proposed method, monocarbene complex **11** (Scheme 1) was synthesized by reaction of the salt **10** with copper(I) chloride in acetonitrile in the presence of triethylamine.

Scheme 1



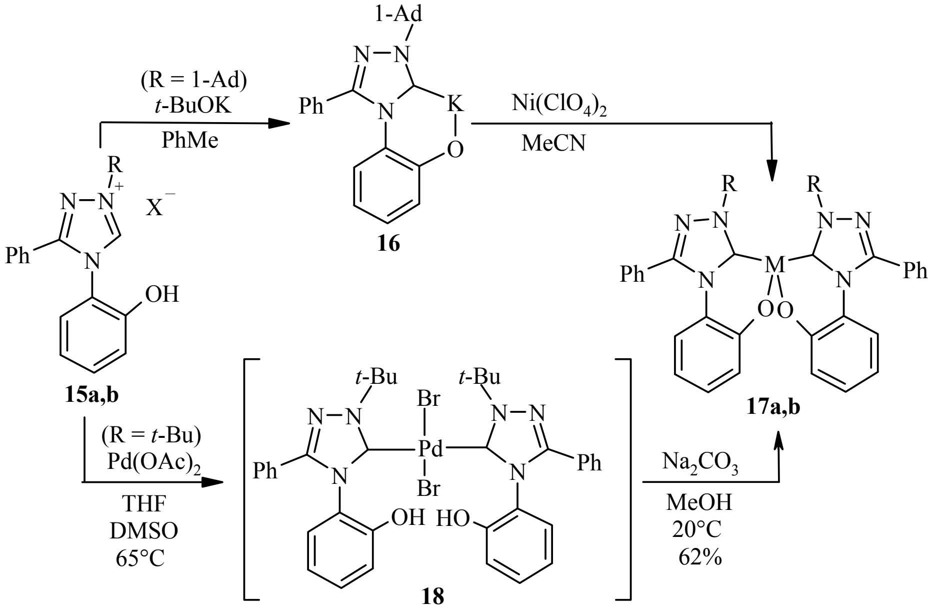
Biscarbene complexes **13, 14** (Scheme 2) were obtained by refluxing the solutions of 2*H*-cyanomethylbenzimidazoline (**12**) with transition metal salts (copper(I) iodide or bis(triphenylphosphine)nickel(II) chloride) in acetonitrile. X-ray structural analysis results for complexes **11** and **13** are presented in [25].

Scheme 2



The potassium complex **16** was obtained by interaction of the hydroxyphenyl-substituted salt **15a** with potassium *tert*-butoxide in toluene. According to the method described in paper [26], the chelate carbene complex **17a** (Scheme 3) was formed in the reaction of the compound obtained with nickel perchlorate (dimethyl formamide complex, 1:4-1:5). The X-ray data for structure **17a** are given in papers [26, 27].

Scheme 3

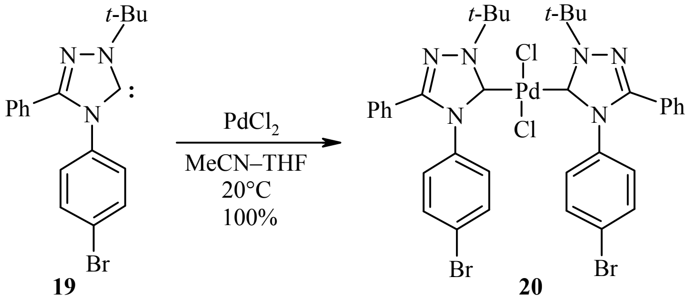


15, **17** **a** R = 1-Ad, M = Ni; **b** R = *t*-Bu, M = Pd

By heating salt **15b** with palladium acetate the palladium bistriazolylidene complex of **18** was formed, which was further dehydrobrominated *in situ* for chelation, following the method described in [28] (Schemes 2, 3), to give the chelate complex **17b**.

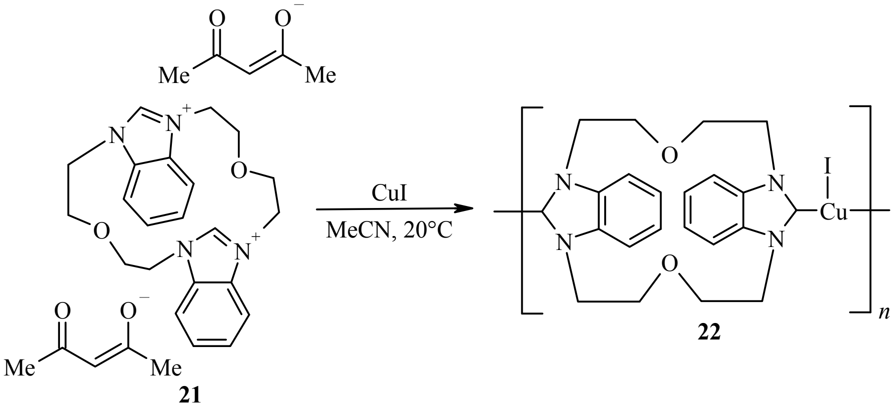
The biscarbene complex **20** (Scheme 4) was synthesized by the reaction of the corresponding stable 1,2,4-triazol-5-ylidene **19** [29] with palladium chloride in acetonitrile.

Scheme 4



The polymeric complex **22** (Scheme 5) was obtained by the reaction of the crown-salt – 1,1',3,3'-bis(3-oxa-1,5-pentylene)bisbenzimidazolium acetylacetonate (**21**) with copper(I) iodide.

Scheme 5

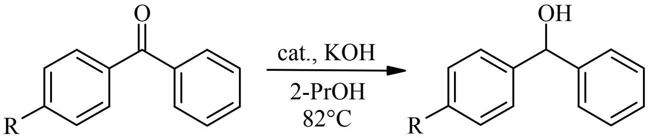


The specific signal of the benzyl CH_2 protons (5.76 ppm) was observed in the ^1H NMR spectrum of complex **11** in $CDCl_3$. In the ^{13}C NMR spectrum the signal of methylene carbon atom appears at 51.2 ppm, while the signal of C-2 carbenoid carbon atom appears at 188.6 ppm. In the ^1H NMR spectrum of the complex **13** in DMSO-d_6, a characteristic signal of methyl groups protons is observed (4.06 ppm), and in the ^{13}C NMR spectrum, signals of methyl group carbon atoms (34.3 ppm) and C-2 carbenoid carbon atom (190.7 ppm) are observed. In the ^1H NMR spectrum of the nickel complex **14** in a mixture of DMSO-d_6 and Py-d_5, a characteristic signal of the methyl group protons is observed at 4.47, which is slightly shifted downfield relatively to the same signal for the complex **13**, and in the ^{13}C NMR spectrum, the methyl group carbon signals (35.7 ppm) and carbenoid carbon signal (180.6 ppm) are observed. For the chelate complex **17b** in the ^1H NMR spectrum in $CDCl_3$, a singlet signal of the *tert*-butyl methyl protons is observed (1.60 ppm), whereas specific signals in the ^{13}C NMR spectrum are those of the $(CH_3)_3C$ group carbon atoms (30.8 and 62.6 ppm), C-3 triazole carbon atom (153.0 ppm), C–O bond carbon atom (161.7 ppm) and C-2 carbenoid carbon atom (171.1 ppm). In the ^{13}C NMR spectrum of the corresponding palladium complex **20** in DMSO-d_6, the carbenoid carbon atom signal is downfield shifted (171.0 ppm) relatively to the same signal of the nickel complex **14**, but nearly coincide with the signal from chelate palladium complex **17b**.

In the ^{1}H NMR spectrum of the macrocycle carbene complex **22** in DMSO-d_6, the bridging fragment CH_2O methylene groups signals (3.82 ppm) and CH_2N groups signals (4.30–4.70 ppm) are observed. Due to the low solubility of this complex the ^{13}C NMR spectrum measurement was performed in a solid state, and characteristic signals of the aliphatic fragments CH_2O and CH_2N carbon atoms were observed (48.3 and 69.4 ppm, respectively) as well as the C-2 carbenoid carbon atoms signals (154.8, 164.9 ppm). Molecular mass of the polymer **22** was determined by LC (see Experimental) as at average equal to 77 monomer units (M_w 43700; M_n 42400 ($M_w/M_n = 1.03$)).

Catalytic efficiency of the obtained complexes in a ketone reduction reaction was studied to compare their catalytic properties. Reduction of 4-biphenyl phenyl ketone (**23**) and benzophenone **24** (Scheme 6) carbonyl groups was carried out in boiling 2-propanol in the presence of potassium hydroxide (50–100 mol%), using catalysts listed in the Table 1. Main experimental results for reduction of the ketones **23**, **24** are presented in the Table 1.

Scheme 6



23, 24 **25, 26**

23, **25** R = Ph; **24**, **26** R = H

TABLE 1. Catalytic Efficiency of Synthesized Azolium Salts*

Expt. No.	Catalyst	Substrate	Amount of catalyst, mol%	Yield, %	Time, h	TON	TOF, h^{-1}
1*[2]	—	**23**	—	3	16	—	—
2	—	**23**	—	65	13	—	—
3*[2]	**10**	**23**	10	29	13	2.8	0.2
4*[2]	**10**	**23**	100	56	13	0.56	0.04
5	**10**	**23**	10	97	13	9.7	0.8
6	**11**	**23**	0.1	96	3	960	320
7	**17a**	**23**	0.1	96	3	960	320
8	**17b**	**23**	0.1	100	3	1000	333
9	**14**	**23**	0.1	56	3.5	560	160
10	**20**	**23**	0.1	75	0.25	750	3000
11	CuCl	**23**	0.1	75	4	750	188
12	CuI	**23**	0.1	65	6	650	108
13	**11**	**23**	0.01	53	6	5300	883
14	**13**	**23**	0.01	98	2	9800	4900
15	**17a**	**23**	0.01	45	3	4500	1500
16	**17b**	**23**	0.01	70	2	7000	3500
17	**22**	**23**	0.01	100	2	10000	5000
18	**13**	**23**	0.001	50	2.5	50000	20000
19	**22**	**23**	0.001	85	3	85000	28330
20	**13**	**24**	0.001	55	3	55000	18330
21	**22**	**24**	0.001	80	2.5	80000	32000
22	CuCl	**23**	1	76	8	76	9.5
23	CuCl	**23**	10	78	8	7.8	1

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* 10 ml of 0.1 M KOH solution in 2-propanol per 1 mmol of substrate were used.

*[2] Equivalent amount of potassium 2-propoxide was used instead of potassium hydroxide.

As it can be seen from the data in Table 1, using of potassium 2-propoxide was rather inefficient (Exp. No. 1), and noticeable better results were obtained with the use of potassium hydroxide (Exp. No. 2). Azolium alkoxide, generated from the salt **10**, has insignificant catalytic effect on the ketone **23** reduction (Exp. No. 3–5). Yields of the carbinol **25** were increased in experiments with 2-propoxide and potassium hydroxide using 10 mol% of the catalyst. Maximum yield of the carbinol **25** using potassium 2-propoxide was obtained only in case of the salt **10** amount of 100 mol% and was equal to 56 % (Exp. No. 4). Thus, potassium 2-propoxide was in all cases less effective than potassium hydroxide.

Catalytic efficiency of the metal carbene complexes is much higher than of the benzimidazolium salt **10**. Comparison of TON and TOF for the catalysts **11**, **14**, **17a**,**b**, **20** at concentrations of 0.1 mol% showed that efficiency of the nickel complex **14** is noticeably lower than that of the copper complex **11** and the nickel and palladium chelate complexes **17a**,**b** (compound **14** was partially decomposed with formation of a metallic nickel in the course of reaction). Palladium complex **20** efficiently catalyzes the reaction during first minutes of the process. A complete catalyst deactivation occurred at approximately 75% conversion.

For highly catalytically effective compounds **11**, **17a**,**b**, **22,** it was possible to perform a comparison of the TON and TOF values at a lower concentration (0.01 mol%). For the monocarbene complex **11** and chelate complexes **17a,b** the indexes TON and TOF were close, but the most effective was the palladium chelate complex **17b**. copper(1) biscarbene complex **13** and the polymeric carbene complex **22** were even more effective .

TON and TOF values are maximum for compounds **13** and **22** at concentrations of 0.001 mol%, whereas for the polymeric catalyst **22** (Exp. No. 19) these values are slightly higher than for the complex **13** (Exp. No. 18). For the most active rhodium(III) carbene complex **9** they were noticeably increased in both cases in reaction with the related benzophenone (TON 10580, TOF 441 h^{-1}). TON value for the complex **9** is lower than that for compounds **13**, **22**, but the difference in TOF values is especially high due to the long reaction time using the known catalyst **9** (up to 24 h) with yields not higher than 86%. Almost quantitative yields of the compound **25** (Exp. No. 14, 17) were observed in case of catalysis with complexes **13**, **22** during 2 hour of the reaction time.

Benzophenone **24** at the catalyst concentration of 0.001 mol% was reduced analogously with formation of benzhydrol **26** with high TON and TOF values comparable with those for the ketone **23** reaction.

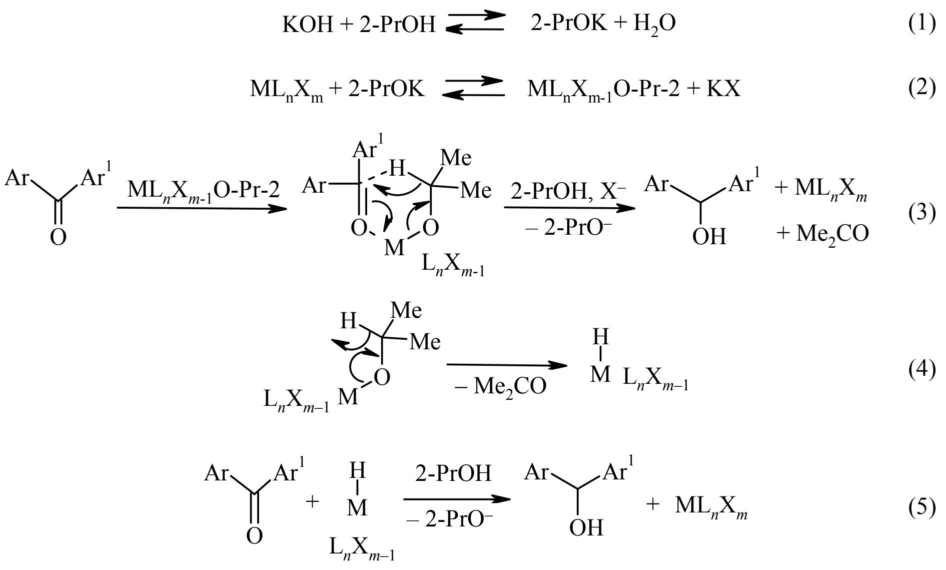
It should be noted that the inorganic copper halogenides (CuCl, CuI) are considerably less active than their heterocyclic carbene complexes. Reaction completion in these cases could not be reached even using 10 mol% catalyst concentrations.

The probable mechanisms of the ketone catalytic reduction with 2-propanol in the presence of potassium hydroxide are presented below (Scheme 7).

Mechanism of the reduction of carbonyl compounds with alcohols catalyzed by metal carbene complexes is evidently similar to the effect of aluminum isopropoxide in the Meerwein-Ponndorf-Verley reaction. Moreover, for the carbene complexes, first a halogen ion exchange for an alkoxide ion probably happens, whereas the alkoxide ion is formed in equilibrium from potassium hydroxide and isopropanol (Equation 1), with formation of a metal complex alkoxide (Equation 2). Further, analogously to the Meerwein-Ponndorf-Verley reduction, an interaction of the carbonyl compound with the vacant *d*-orbital of the metal and a hydride transfer from alcoholate group to the carbonyl carbon atom in a cyclic transition state occurs (Equation 3).

Similarly, in chelate complexes **17a**,**b,** a displacement of phenolate ion from the metal coordination sphere with subsequent restoration of the chelate structure and acetone formation may occur. However, another way is also possible, proposed earlier in [31], where a metal hydride acts as an intermediate (Equation 4), which reduces the multiple carbonyl bond (Equation 5). This reaction direction was confirmed by transition metal hydrides isolation in some cases [3].

Scheme 7



L - carbene ligand, X other ligands (e.g., halide, etc)

Thus three classes of catalysts of the hydride transfer from 2-propanol to ketones have been found – carbene complexes of copper(I), nickel, and palladium, and also carbenes, which are, however, less effective. It is essential that copper (I) complexes are substantially more effective than the known rhodium, iridium and ruthenium complexes. The most effective catalyst proved to be the copper(I) carbene polymeric complex. Copper(I) biscarbene monomeric complex was of the similar efficiency.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on Gemini 200 and Bruker Avance II 400 spectrometers with TMS as internal standard. Purity of substances was monitored by TLC on Silufol plates with a 10:1 $CHCl_3$–MeOH mixture.

Molecular properties of polymer **22** were studied on the measurement complex for Du Pont liquid chromatography, fitted with bimodal Zorbax PSM-100 and 1000 columns, each of which can be linearly calibrated in molecular mass from 10^2-10^6. Chromatograph was calibrated using Du Pont PS polysterene standard with molecular masses of M_w 1000, 50000 and $M_w/M_n = 1.01$. Oligomer coming out of the column was detected by an ultraviolet detector set to 282 nm wave length. DMF purified and dried according to the standard methods was used as eluent. Analyses temperature was 25°C and the flow rate was 0.7 ml/min. System pressure was equal to 53–55 bar. Error of the retention time detection was ±1%. To determine the amount of high- and low-molecular mass fractions, after the sample coming out from the column and signal recording using MO Spectra Physics software program the peak area ratios were calculated for peaks which correspond to each component with certain average molecular mass. Molecular properties of the polymer **22** were calculated using Chrom I Insoftus software program [32]. The method was used for molecular mass determination of polar substances, including polyelectrolites [32–35]. Elemental analysis for metal content was carried out along with carbon, hydrogen and halogen contents measurement using dry oxides residue after sample combustion.

(1,3-Dibenzylbenzimidazol-2-ylidene)copper(I) Chloride (11). A mixture of 1,3-dibenzylbenzimidazolium chloride (**10**) (1.0 g, 3.0 mmol) and copper(I) chloride (0.3 g, 3.0 mmol) was dissolved in dry MeCN (15 ml), Et_3N (0.5 ml, 3.6 mmol) was added, and the mixture was boiled for 2 h. Then more Et_3N (0.5 ml, 3.6 mmol) was added, and refluxing was continued for 30 min. The reaction product was precipitated with water, filtered off, washed with a 1:3 2-PrOH–petroleum ether mixture, and dried over KOH. Product **11** (1.05

g, 84%) was recrystallized from MeCN. Yield 0.7 g (56%); mp 175-177°C. ^1H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 5.76 (4H, s, $2CH_2N$), 7.24-7.54 (14H, m, H Ar). ^{13}C NMR spectrum (50 MHz, $CDCl_3$), δ, ppm: 51.2 (CH_2N); 111.8, 123.4, 127.3, 127.7, 128.5 (C Ar); 133.4, 136.3 (*i*-C Ar); 188.6 (C-2). Found, %: C 63.61; H 4.64; Cl 8.59; Cu 15.92; N 7.24. $C_{21}H_{18}ClCuN_2$. Calculated, %: C 63.47; H 4.57; Cl 8.92; Cu 15.99; N 7.05.

Bis(1,3-dimethylbenzimidazol-2-ylidene)copper(I) Iodide (13). A mixture of 2-cyanomethyl-1,3-dimethyl-2*H*-benzimidazoline (**12**) (2.55g, 13.6 mmol) and copper(I) iodide (1.30 g, 6.8 mmol) in MeCN (5 ml) was refluxed for 2 h. The precipitate was filtered off, washed with a small amount of MeCN, and dried. Yield 2.20 g (67%); mp. 220-221°C (MeCN). ^1H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 4.06 (12H, s, $4CH_3$); 7.40 (4H, m, H Ar); 7.65 (4H, m, H Ar). ^{13}C NMR spectrum (50 MHz, DMSO-d_6), δ, ppm: 34.3 (CH_3); 110.9 (C-4,7); 123.0 (C-5,6); 134.0 (*i*-C Ar); 190.7 (C-2). Found, %: C 44.53; H 4.14; Cu 13.38; I 26.51; N 11.44. $C_{18}H_{20}CuIN_4$. Calculated, %: C 44.78; H 4.18; Cu 13.16; I 26.28; N 11.60.

Bis(1,3-dimethylbenzimidazol-2-ylidene)nickel Dichloride (14). 2-Cyanomethyl-1,3-dimethyl-2*H*-benzimidazoline (**12**) (0.95 g, 5.08 mmol) in MeCN (6 ml) was added to a suspension of $NiCl_2(PPh_3)_2$ (1.66 g, 2.54 mmol) in MeCN (4 ml) and the mixture was refluxed for 2 h. The precipitate was filtered off, washed with ether, and dried. Yield 1.07 g (100%); mp 275-278°C (MeCN). ^1H NMR spectrum (200 MHz, DMSO-d_6+Py-d_5), δ, ppm: 4.47 (12H, s, $4CH_3$), 7.30-7.78 (8H, m, H Ar). ^{13}C NMR spectrum (200 MHz, DMSO-d_6+Py-d_5), δ, ppm: 35.7 (CH_3); 110.4, 123.8 (C Ar); 134.9, 144.2 (*i*-C Ar); 180.6 (C-2). Found, %: C 51.35; H 4.76; Cl 16.67; N 13.15; Ni 14.07. $C_{18}H_{20}Cl_2N_4Ni$. Calculated, %: C 51.23; H 4.78; Cl 16.80; N 13.28; Ni 13.91.

Bis-(1-*tert*-butyl-2-(2-oxidophenyl)-3-phenyl-1,2,4-triazol-5-ylidene)palladium (17b). The salt **15b** (0.23 g, 0.62 mmol) and $Pd(OAc)_2$ (0.07 g, 0.31 mmol) were dissolved in a mixture of THF (10 ml) and DMSO (0.5 ml), heated at 50°C and stirred for 2 h. MeOH (10 ml) and Na_2CO_3 (0.26 g, 2.48 mmol) were added and the mixture stirred for 1 h. The reaction mixture was poured into water (50 ml). The precipitate was filtered off and dried. The precipitate was dissolved in CH_2Cl_2 (10 ml) and filtered through a thin layer of silica gel. The solution was evaporated to dryness. Yield 0.13 g (62%); mp 140°C (PhMe). ^1H NMR spectrum (200 MHz, $CDCl_3$), δ, ppm: 1.60 (18H, s, $2(CH_3)_3C$); 7.31-7.56 (18H, m, H Ar). ^{13}C NMR spectrum (100 MHz, $CDCl_3$), δ, ppm: 30.8 (CH_3); 62.6 ($(CH_3)_3\underline{C}$); 114.6, 121.4, 124.4, 128.5, 128.6, 129.4, 130.2 (C Ar); 126.9 (*i*-C Ph); 148.2 (*i*-C 2-oxydophenyl); 153.0 (C-3); 161.7 (C–O); 171.1 (C-2). Found, %: C 62.72; H 5.07; N 12.39; Pd 15.24. $C_{36}H_{36}N_6O_2Pd$. Calculated, %: C 62.56; H 5.25; N 12.16; Pd 15.40.

Bis[4-(4-bromophenyl)-1-*tert*-butyl-3-phenyl-1,2,4-triazol-5-ylidene]palladium Dichloride (20). 4 (4-Bromophenyl)-1-*tert*-butyl-3-phenyl-1,2,4-triazol-5-ylidene (**19**) [29] (0.20 g, 0.56 mmol) in THF (1 ml) was added to a suspension of palladium chloride (0.05 g, 0.28 mmol) in MeCN (1 ml) and stirred for 30 min. The precipitate was filtered off and dried to give compound **20** (0.15 g); a further 0.1 g of complex **20** was obtained from the mother liquor by evaporation. Overall yield 0.25 g (100%); mp 160-163°C (MeCN, subl.). ^1H NMR spectrum (200 MHz, DMSO-d_6), δ, ppm: 1.64 (18H, s, $2(CH_3)_3C$); 7.26-7.67 (18H, m, H Ar). ^{13}C NMR spectrum (50 MHz, DMSO-d_6), δ, ppm: 30.1 (CH_3); 62.9 ($(CH_3)_3\underline{C}$); 127.8, 128.6, 128.7, 129.1, 130.4, 131.6, 132.4, 132.9 (C Ar); 143.2 (*i*-C Ar); 151.4 (C-3); 171.0 (C-2). Found, %: C 48.61; H 3.96; Br 18.26; Cl 8.05; N 9.37; Pd 11.75. $C_{36}H_{36}Br_2Cl_2N_6Pd$. Calculated, %: C 48.59; H 4.08; Br 17.96; Cl 7.97; N 9.44; Pd 11.96.

Polymer of 1,1',3,3'-Bis(3-oxa-1,5-pentylene)bis(benzimidazole-2-ylidene)copper(I) Iodide (22). Copper(I) iodide (0.66 g, 3.4 mmol) in absolute MeCN (15 ml) was added dropwise with constant stirring in an atmosphere of nitrogen at room temperature to a solution of 1,1',3,3'-bis(3-oxa-1,5-pentylene)bisbenzimidazolinium diacetylacetonate (**21**) [30] (2.00 g, 3.4 mmol) in absolute MeCN (30 ml). The reaction product began to crystallize from the solution. After addition of all of the copper(I) iodide, the mixture was kept at room temperature for 40 min. The precipitate was filtered off and washed on the filter with ether in an atmosphere of nitrogen. The crystals of complex were greenish in appearance. Yield 1.60 g (82%); mp 164-165°C. ^1H NMR spectrum (400 MHz, DMSO-d_6), δ, ppm: 3.82 (8H, s, $4CH_2O$); 4.30-4.70 (8H, m, $4CH_2N$); 6.60-7.95 (8H, m, H Ar). ^{13}C NMR spectrum (100 MHz, in solid state), δ, ppm: 48.3 (CH_2O); 69.4 (CH_2N); 112.0, 123.9, 130.5, 134.0 (C Ar); 142.8 (*i*-C Ar); 154.8, 164.9 (C-2). LC: M_w 43700; M_n 42400 (M_w/M_n =1.03). Found, %: C 46.89; H 4.31; Cu 11.34; I 22.42; N 9.44. $C_{22}H_{24}CuIN_4O_2$. Calculated, %: C 46.61; H 4.27; Cu 11.21; I 22.39; N 9.88.

General Method for the Reduction of Compounds 23, 24 and Control of the Reaction of. 0.1 M KOH solution (10 mmol) in 2-PrOH and a small amount of a catalyst (Table 1) were added to ketone **23** or **24** (2 mmol). The reaction mixture was refluxed and monitored by TLC. Quantitative analysis of the starting material and the reduction product during the reaction time was carried out as follows: 2-PrOH was evaporated until crystallization of the remaining starting material began (a volume of about 3 ml), cooled, and the residue was filtered off. Because of the very low solubility of the ketone in alkaline solution, the ketone did not remain in the mother liquor (TLC monitoring). Water (12 ml) was added to the mother liquor, and the precipitate of the carbinol **25** or **26** was filtered off, dried, and the yield of product determined. Estimation of the purity of the compound isolated was determined TLC and ^{1}H NMR spectroscopy.

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REFERENCES

1. W. A. Herrmann, *Angew. Chem, Int. Ed.,* **41**, 1290 (2002).
2. J. W. Herndon, *Coord. Chem. Rev.,* **206/207**, 237 (2000).
3. S. Nolan (editor), *N-Heterocyclic Carbenes in Synthesis.* Wiley-VCH, Weinheim, 2006, p.304.
4. D. Enders, O. Niemeier, and A. Henseler, *Chem. Rev.,* **107**, 5606 (2007).
5. M. Albrecht, R. H. Crabtree, J. Mata, and E. Peris, *Chem. Commun.,* 32 (2002).
6. H. Seo, B. Y. Kim, J. H. Lee, H.-J. Park, S. U. Son, and Y. K. Chung, *Organometallics*, **22**, 4783 (2003).
7. M. Poyatos, E. Mas-Marza, J. A. Mata, M. Sanau, and E, Peris, *Eur. J. Inorg. Chem.,* 1215 (2003).

8 J. R. Miecznikowski and R. H. Crabtree, *Organometallics*, **23**, 629 (2004).

9. F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, and L. A. Oro, *Organometallics,* **24**, 2203 (2005).
10. E. Mas-Marza, M. Sanau, and E. Peris, *Inorg. Chem.,* **44**, 9961 (2005).
11. C.-Y. Wang, C.-F. Fu, Y.-H. Liu, S. M. Peng, and S. T. Liu, *Inorg. Chem.,* **46,** 5779 (2007).
12. H. Turkmen, T. Pape, F. E. Hahn, and B. Cetinkaya, *Organometallics,* **27**, 571 (2008).
13. B. Milani, C. Crotti, and E. Farnetti, *Dalton Trans.,* 4659 (2008).
14. I. Kownacki, M. Kubicki, K. Szubert, and B. Marciniec, *J. Organomet. Chem.,* **693,** 321 (2008).
15. Y.-H. Chang, C.-F. Fu, Y.-H. Liu, S.-M. Peng, J.-T. Chen, and S.-T. Liu, *Dalton Trans.,*861 (2009).
16. Y. Cheng, H.-J. Xu, J.-F. Sun, Y.-Z. Li, X.-T. Chen, and Z.-L. Xue, *Dalton Trans.,* 7132 (2009).
17. A. Sinha, S. M. W. Rahaman, M. Sarkar, B. Saha, P. Daw, and J. K. Bera, *Inorg. Chem,* (Washington, D.C., U.S.), **48**, 11114 (2009).

18 J.-F. Sun, F. Chen, B. A. Dougan, H.-J. Xu, Y. Cheng, Y.-Z. Li, X.-T. Chen, and Z. I. Xue, *J. Organomet. Chem.,* **694,** 2096 (2009).

19. D. Gnanamgari, E. L. O. Sauer, N. D. Schley, C. Butler, C. D. Incarvito, and R. H. Crabtree, *Organometallics,* **28,** 321 (2009).
20. Y. Cheng, J.-F. Sun, H.-L. Yang, H.-J. Xu, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, *Organometallics,* **28**, 819 (2009).
21. W. N. O. Wylie, A. J. Lough, and R. H. Morris, *Organometallics,* **28**, 6755 (2009).
22. N. Ding, and T. S. A. Hor, *Dalton Trans.,* 10179 (2010).

23 Y. Cheng, X.-Y. Liu, H.-J. Xu, Y.-Z. Li, X.-T. Chen, and Z.-L. Xue, *Inorg. Chim. Acta,* **363**, 430 (2010).

24. S. Gulcemal, J.-C. Daran, and B. Cetinkaya, *Inorg. Chim. Acta,* **365**, 264 (2011).
25. A. V. Kiselev. Dis. Cand. Khim. Nauk, Donetsk (2008).

26. M. I. Korotkikh, A. V. Kiselyov, T. M. Pekhtereva, O. P. Shvaĭka, A. G. Kayli, and J. N. Johns, *Dop. NAN Ukraine,* 150 (2005).
27. N. I Korotkikh, O. P. Shvaika, G. F. Rayenko, A. V. Kiselyov, A. V. Knishevitsky, A. N. Cowley, J. N. Jones, and C. L. B Macdonald, *ARKIVOC*, **8**, 10 (2005).
28. A. J. Boydston, J. D. Rice, M. D. Sanderson, O. L. Dykhno, and C. W. Bielawski, *Organometallics,* **25**, 6087 (2006).
29. N. I. Korotklikh, N. V. Glinyanaya, A. H. Cowley, J. A. Moore, A.V. Knishevitsky, T. M. Pekhtereva, and O. P. Shvaika, *ARKIVOC,***16**, 156 (2007)
30. M. I. Korotkikh, K. O. Marichev, A. V. Kiselyov, and O. P. Shvaika, *Ukr. Biorg. Acta,* **6,** 22 (2008).
31. V. Jurkauskas, J. P. Sadighi, and J. Buchwald, *Org. Lett.,* **5**, 2417 (2003).
32. L. R. Snyder and J. J. Kirkland, *Introduction to Modern Liquid Chromatography.* 2nd Ed., Wiley-Interscience, New York, 1979.
33. T. Xie, J. Penelle and M. Verraver, *Polymer,* **43,** 3973 (2002).
34. O. B. Rudakov, I. A. Vostrov, S. V. Fedorov, A. A. Filippov, V. F. Semenev, and A. A. Pridantseva, *Hand Book of Chromatography. Methods of Liquid Chromatography* [in Russian], Vodolei, Voronezh (2004).
35. A. Khenshen, X.-P. Kupe, F. Lotshpaik, and V. Velter, *High Performance Liquid Chromatography in Biochemistry* [Russian translation], Mir, Moscow (1988).