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Fritz E. Kühn[a]; Dirk Schön[b]; Guofang Zhang[a]; Oskar Nuyken[b]
[a] Anorganisch-chemisches Institut der, Technischen Universität München, Garching bei München, Germany [b] Lehrstuhl für Makromolekulare Stoffe der, Technischen Universität München, Garching bei München, Germany

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MONOMETALLIC SOLVENT STABILIZED TRANSITION METAL CATIONS AS INITIATORS FOR CYCLOPENTADIENE POLYMERIZATION

Fritz E. Kühn,[1,†] **Dirk Schön,**[2] **Guofang Zhang,**[1] **and Oskar Nuyken**[2,*]

[1]Anorganisch-chemisches Institut der
Technischen Universität München
Lichtenbergstraße 4
D-85747 Garching bei München, Germany

[2]Lehrstuhl für Makromolekulare Stoffe der
Technischen Universität München
Lichtenbergstraße 4
D-85747 Garching bei München, Germany

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ABSTRACT

Several mononuclear transition metal cations stabilized by acetonitrile molecules act as initiators for the polymerization of cyclopentadiene. The highest yield is reached with Cr, Mn, Fe, and Zn complexes, all of them in the oxidation state +II. The analogous V and Ni complexes, however, are completely or nearly inactive. In general, the observed activity of the examined monomeric complexes correlates well with the ligand field stabi-

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[†] Listed as second major author. Tel: 0049 (0)89 289 13105; Fax: 0049 (0)89 289 13473; E-mail: fritz.kuehn@ch.tum.de

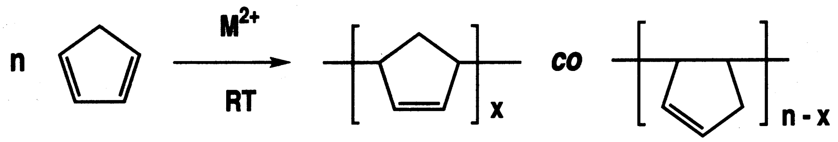
[*] Author to whom correspondence should be addressed. Tel: 0049 (0)89 289 13571; Fax: 0049 (0)89 289 13562; E-mail: oskar.nuyken@ch.tum.de

lization energy as a function of the number of d electrons for octahedrally coordinated transition metals in the oxidation state +II. The counter ions have a pronounced influ-ence on the catalytic activity: the less coordinating they are, the higher is the activity of the cations. The reaction temperature also has a significant influence: above 50°C the complex activity is on decline, possibly due to initiator decomposition or com-petitive inhibition by dicyclopentadiene.

INTRODUCTION

Some dimeric solvent stabilized transition metal complexes, namely $[Mo_2(NCCH_3)_9][BF_4]_4$ and $[Mo_2Ac_2(NCCH_3)_6][BF_4]_2$ [1–5], show activity both in homogeneous and heterogeneous phase in ROMP, alkine-polymerization and cyclopentadiene-polymerization [6–12]. Recently, we have shown that these catalytic applications are not limited to $[Mo_2]^{2+}$ complexes coordinated by acetonitrile and acetato ligands [13]. Several other dimeric systems containing molybdenum and rhodium central atoms are active initiators for the polymerization of cyclopentadiene at room temperature. Crucial for the catalytic activity are the coordination sites at equatorial positions occupied by very weakly coordinating solvent molecules, e. g. acetonitrile. It has also been found that at least two monomeric complexes, namely $[Cr(NCCH_3)_4][BF_4]_2$ [14] and $[Pd(NCCH_3)_4]$-$[BF_4]_2$ [15] are also active as initiators in the diene polymerization [13].

We demonstrate in this paper that the above mentioned compounds are not isolated cases concerning their catalytic application. A broad variety of easily accessible mononuclear transition metal complexes show excellent activities as initiators in the cationic polymerization, as exemplified on the polymerization of cyclopentadiene [16–23] (Equation 1).



(1)

EXPERIMENTAL

Synthesis of Catalysts

All examined complexes have been prepared according to literature procedures. Compounds **1** and **3-10** were prepared according to Reference [25], complex **2** as described in Reference [14], compound **3b** according to Reference [34]. The identity of all complexes has been proven by elementary analyses, Raman- and IR spectroscopy. The received data have in all cases been identical with the data given in the literature. The depicted structural formulae are in agreement with the X-ray data of the particular complexes, in all cases examined by this method.

Polymerization Experiments

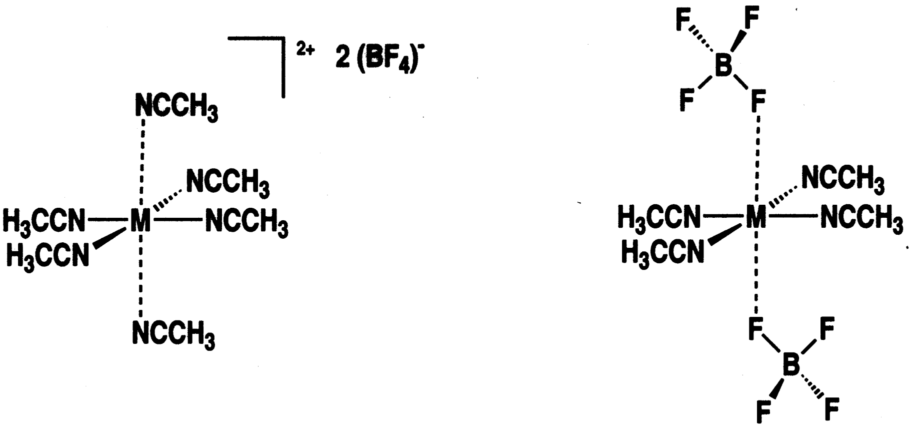
In a dry round bottom flask under argon atmosphere (glove box) 40 mL of a solution of dry cyclopentadiene (c(cyclopentadiene) = 2.27 mol/L) in dry methylene chloride (drying agent = CaH_2) was added to 0.05 mmol (if not stated otherwise, see Table 1) of a M(II) complex compound (**1-10**) under vigorous stirring at room temperature. After 16 hours reaction time 3 mL of methanol were added to stop the reaction. The solvent was removed in oil pump *vacuo* (10 Pa). The yield was determined gravimetrically after drying in a drying oven (5d, 2000 Pa, 20°C). Because of the sensitivity of the polycyclopentadiene to radical induced crosslinking all work up steps were performed under O_2-exclusion.

The NMR experiments have been performed with a Bruker-ARX 300 spectrometer. The GPC has been carried out with the following equipment: Waters 510 pump, columns: Waters Ultrastyragel 500, 1000, 10000, 100000 Å, RI-detector: Waters 410, eluent: THF, flow rate: 0.5 mL/min, calibration standard: polystyrene.

RESULTS AND DISCUSSION

The polymerization of cyclopentadiene initiated by the complexes **1-10** at room temperature with an initiator:monomer ratio of usually ca. 1:1800 or 1:3600, respectively, has been examined. $[Co(NCCH_3)_4][BF_4]_2$ (**5**) was selected as an example to examine the reaction conditions in more detail. The obtained results were compared with data already available from the literature [13] and are summarized in Table 1 and Figures 1 and 2.

The preparation of the initiators has been performed according to modified literature procedures as described in the Experimental part. It can be assumed that the examined complexes exist as $[M(NCCH_3)_6]^{2+}$ cations in solution [14, 24–28]. In most of the cases, two of the acetonitrile ligands can be removed very easily in oil pump vacuum according to elemental analyses and thermogravimetry (TG) [28] examinations. However, even upon prolongated drying



M = V(II) (1)

M = Cr(II) (2), Mn(II) (3), Fe(II) (4), Co(II) (5), Ni(II) (6), Pd(II) (7), Cu(II) (9), Zn(II) (10)

Complexes 1–10.

(days) in oil pump vacuum the removal of more than two acetonitrile ligands is nearly impossible. The elemental analyses that were obtained after drying the samples in oil pump vacuum for several hours usually show complexes of the composition $[M(NCCH_3)_4](BF_4)_2$. Only in the case of the vanadium complex **1** the composition $[M(NCCH_3)_6](BF_4)_2$ remained unchanged even after prolongated drying in oil pump vacuum at room temperature.

The solvent- and initiator concentration dependence of the yield is in the case of the compounds **1-10** very similar to that of the bimetallic solvent stabilized transition metal compounds which we examined recently [13]. Polar non coordinating solvents e. g. CH_2Cl_2 are the most useful solvents in order to obtain good product yields. The steric bulk of the coordinating nitrile ligands seems to have no significant influence on the polymerization, as it was observed in the case of the bimetallic complexes which have been examined recently [13]. Acetonitrile, pivalonitrile, and benzonitrile ligands coordinated to a $M(II)^{2+}$ center do not change the product yield significantly. We kept the initiator:substrate ratio on a level (usually ca. 1:1800) on which only the most active systems reached 100% conversion. In order to get a closer insight into their activity differences the most active systems (Mn^{2+}, Fe^{2+}, Co^{2+}) were examined with initiator:substrate ratios in the range of ca. 1:3600–1:36000 (Table 1).

TABLE 1. Overview on the Catalytic Results Gained by Utilizing Complexes **1–10** as Initiators for the Cyclopentadiene Polymerization (Reaction Time = 16h, Temperature = 25°C, Solvent = CH_2Cl_2, Reaction Volume = 40 ml).

No.	Complex[a]	c(Init.) [mol/L]	c_0(Cp) [mol/L]	C_I/C_{Cp}	Yield [%]	M_n (GPC)[b]	M_w (GPC)[b]	M_w/M_n	1,2-prod. [%][c]	TOF[d] [10^{-2} s^{-1}]
1	$[V(AN)_6][BF_4]_2$	0.00125	2.27	1:1816	0	0	0	-	-	0
2	$[Cr(AN)_4][BF_4]_2$	0.00125	2.27	1:1816	92	14800	33400	2.25	44	2.9
3	$[Mn(AN)_4][BF_4]_2$	0.000625	2.27	1:3632	100	24800	67000	2.70	43	6.3
3	$[Mn(AN)_4][BF_4]_2$	0.000313	2.27	1:7264	67	-[e]	-[e]	-	-[e]	8.5
3a	$[Mn(AN)_4][BPh_4]_2$	0.000625	2.27	1:3632	10	-[f]	-[f]	-	-[e]	0.6
3b	$[Mn(AN)_6][BTFMPB]_2$	0.000063	2.27	1:36320	100	-[e]	-[e]	-	-[e]	63
4	$[Fe(AN)_4][BF_4]_2$	0.000625	2.27	1:3632	94	4600	11200	2.43	42	5.9
4a	$[Fe(AN)_4][BPh_4]_2$	0.000625	2.27	1:3632	< 5	-[f]	-[f]	-	-[e]	< 0.3
5	$[Co(AN)_{4.5}][BF_4]_2$	0.000625	2.27	1:3632	76	36800	170000	4.62	45	4.8
6	$[Ni(AN)_4][BF_4]_2$	0.00125	2.27	1:1816	15	-[f]	-[f]	-	-[e]	0.5
7	$[Pd(AN)_4][BF_4]_2$	0.00125	2.27	1:1816	66	G	g	-	-[e]	2.1
8	$[Cu(AN)_4][BF_4]$	0.00125	2.27	1:1816	0	0	0	-	-	0
9	$[Cu(AN)_4][BF_4]_2$	0.00125	2.27	1:1816	91	18800	41900	2.23	38	2.9
10	$[Zn(AN)_4][BF_4]_2$	0.00125	2.27	1:1816	100	29900	73500	2.46	43	3.2

[a] AN = acetonitrile; [b] determined by RI-detector, calibration standard polystyrene; [c] the remaining amount is 1,4-product; [d] Mol monomer per Mol catalyst per sec; [e] not determined; [f] oily, oligomeric products were obtained; [g] high gelation

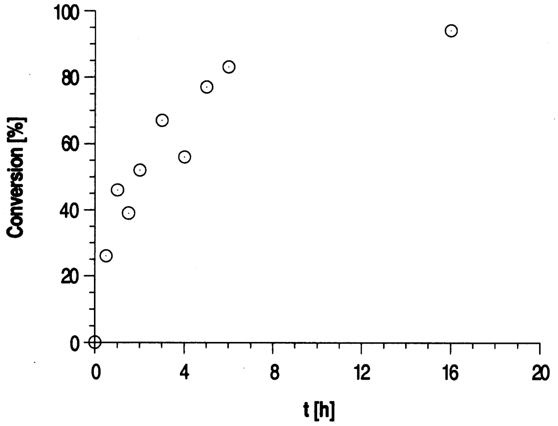


Figure 1. Dependence of the conversion of cyclopentadiene ($c_{Co(0)}$ = 2.27 mol/L^{-3}) on the reaction time (initiator: [Co(NCCH$_3$)$_4$][BF$_4$]$_2$ (**5**), c_1 = 0.000625 mol/L; T = 25°C; solvent: CH$_2$Cl$_2$).

While [V(NCCH$_3$)$_6$][BF$_4$]$_2$ is completely inactive as initiator in the cyclopentadiene polymerization and [Ni(NCCH$_3$)$_4$][BF$_4$]$_2$ shows only very little activity, most of the other [M(NCCH$_3$)$_4$][BF$_4$]$_2$ complexes are of comparable or even higher activity than the dimeric [M$_2$(NCCH$_3$)$_{10}$][BF$_4$]$_4$ compounds (M =

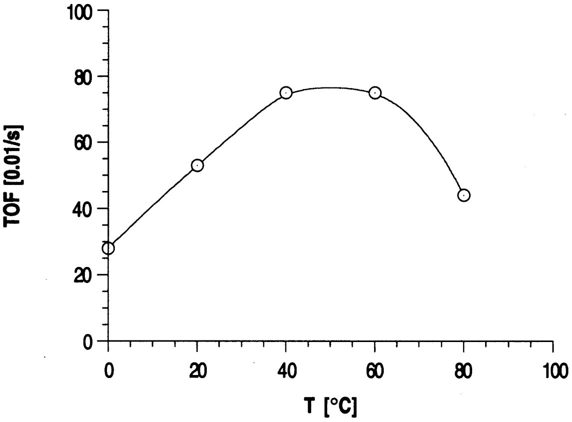


Figure 2. Polymerization of cyclopentadiene - dependence of the turnover frequencies (TOFs, calculated after 16 hours reaction time) on the reaction temperature (initiator: [Co(NCCH$_3$)$_4$][BF$_4$]$_4$ (**5**)). Exp. conditions: see Table 1.

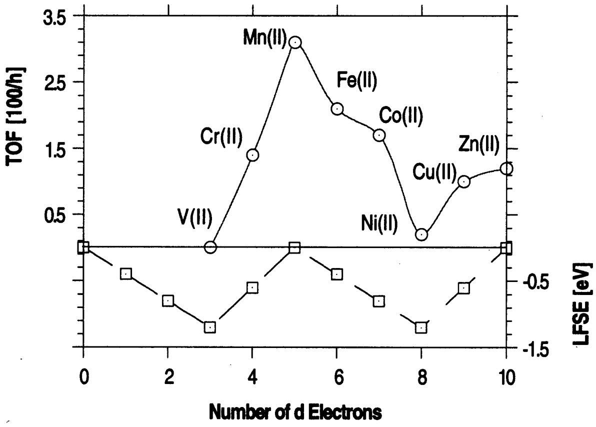


Figure 3. Polymerization of cyclopentadiene - turnover frequencies (TOFs) and predicted ligand field stabilization energies (LFSEs) [30] as a function of the number of d electrons for octahedrally coordinated transition metal cations.

Mo, Rh) which were examined previously [13]. The activity of the monomeric complexes, described by the TOFs (TOF = Turn Over Frequency) correlates very well with the predicted ligand field stabilization energy of octahedral cations (Figure 3) [29, 30]. A low ligand field stabilization energy indicates a weak metal-ligand interaction and therefore allows an easy exchange of the original ligands.

This stabilization energy should be highest for the V^{2+} and Ni^{2+}-complexes and smallest for the Mn^{2+} and Zn^{2+}-complexes (no stabilization). Consistently the Mn^{2+}-complexes **3** and **3b** are the most active ones (depending also on the coordination ability of the counter anion, see below), the Ni^{2+}-complex **6** and the V^{2+} complex **1** show (nearly) no initiator activity. This correlation shows that the complexes with the weakest metal-nitrile interaction are the most active initiators. The easier it is to replace the acetonitrile-ligands by substrate molecules the faster the reaction can proceed. Therefore the rate determining step of the reaction seems likely to be the replacement of a nitrile ligand by a cyclopentadiene molecule.

The initiator activity is also in good accord with the thermal stability regarding nitrile ligand loss of the initiator complexes. $Ni(II)^{2+}$ and $V(II)^{2+}$-complexes have been found to be the most (thermally) stable complexes [28]. Despite the observed differences are rather small (only ca. 15 K between the thermal decomposition onset of the most and the least stable complex), the readiness of the M^{2+}-complexes for exchanging ligands surely has a crucial influence on the catalytic performance. We assume that the replacement of one of the original ligands by a cyclopentadiene molecule is probably the initial step for the cyclopentadiene polymerization.

This view is supported by the influence of the counter ion on the reaction rate. While more strongly coordinating counter ions e. g. BPh_4^- in complex **3a** clearly hamper the polymerization, non coordinating counter ions such as $TFPB^-$ ($TFPB^-$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate) in **3b** accelerate the reaction significantly. Despite all TOFs summarized in Table 1 refer to 16 hours reaction time we observed the reaction to be virtually complete after significantly less than 1 hours using derivative **3b** as initiator. This rises the "real TOF" by at least one order of magnitude in comparison to the TOF given in Table 1. The TOF of complex **3b** is therefore, at least two orders of magnitude higher than that of complex **3**, containing BF_4^- as the counter ion and three orders of magnitude in comparison to the BPh_4—compound **3a**.

A more detailed examination of the reaction behavior of the Co^{2+}-complex **5** shows no obvious induction period (see Figure 1). The conversion is very quick within the first hours and then slows down as most of the substrate is consumed. The TOFs given in Table 1 can therefore, be regarded as lower limits for the real turnover frequencies, which must be considerably higher.

The initiator activity is also dependent on the reaction temperature. At 0°C the activity is low. An optimum is reached above room temperature at ca. 40°C. At this temperature, the ligand exchange velocity in solution is very high as NMR-measurements of closely related diamagnetic complexes indicate [2, 5, 14, 31-33]. Below room temperature the ligand-metal interaction is increasingly stronger and exchange reactions are being hindered. Above 50°C the activity starts already to decline, possibly due to beginning initiator decomposition (Figure 2). An additional explanation for the lower activity can be a competition between substrate and dicyclopentadiene for free coordination sites. Dicyclopentadiene is formed by a Diels-Alder reaction at higher temperatures. Experiments have shown that dicyclopentadiene acts as efficient inhibitor for the polymerization of cyclopentadiene.

Polymerization of cyclopentadiene initiated by low concentrations of less active transition metal complexes lead to white air sensitive plastics which are soluble in THF. Higher concentrations of the same initiator compounds or the use of compounds of higher activity as initiators usually leads to crosslinking and accordingly to insoluble products. A comparison of the products derived by the classical cationic polymerization pathway (Et_2AlCl/H_3C-C_6H_4-CH_2Cl, *n*-

hexane, -80°C) to the polymers derived by polymerization with transition metal complex cations shows that the latter cases produce a significantly higher percentage of 1,2- cyclopentadiene units in comparison to 1,4 units (^{1}H-NMR). Indications for the appearance of 1,3-cyclopentadiene units or other byproducts have not been found. This can be due to the stronger ion pair separation at the active chain end [16 – 18]. In the examined case the weaker ion pair separation is due to the weaker coordination capability of the BF_4^- in comparison to $AlEt_2Cl_2^-$, the stronger solvent polarity of methylene chloride in comparison to *n*-hexane, and especially the higher reaction temperature.

CONCLUSION

Monometallic transition metal cations in the oxidation state +II can act as efficient initiators of the cyclopentadiene polymerization. The activity of these complexes is in good correlation to their predicted ligand field stabilization energy as a function of the number of d electrons available. As we have already assumed in a previous paper [13] the results obtained with monometallic complexes prove that the initiation of the polymerization reaction is not dependent on the presence of a metal metal multiple bond interaction. The interaction of the substrate with the metal center probably starts by an attack of the substrate on a free coordination site at the metal center or by replacement of one of the weakly coordinated ligands. Non coordinating anions can significantly improve the TOFs of the polymerization reaction. More work to clearify the mechanism of the polymerization reaction is currently under way in our laboratories. In this context it will be of special interest to examine whether only the highly reactive cyclopentadiene can be polymerized or whether other monomers can also be utilized for homo- and copolymerization reactions with $[M(NCCH_3)_4]^{2+}$-type initiators.

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