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Polymer synthesis in the presence of bis(cyclopentadienyl) derivatives of Group IV—VI transition metal dichlorides: a quantum chemical study of particular reaction stages*

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Key pathways of interaction between growing radicals of vinyl monomers and bis(cyclopentadienyl) derivatives of Group IV—VI transition metal dichlorides were studied by the BP86/6-31G(d) and B3LYP/LanL2DZ quantum chemical methods. Prospects for use of these organometallic compounds as chain growth regulators in controlled polymerization were assessed. The character of the interaction of the compounds studied with the growing radicals is mainly determined by the metal atom.

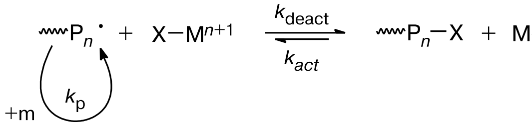
Key words: bis(cyclopentadienyl) metal compounds, quantum chemical modeling, BP86/6-31G(d) and B3LYP/LanL2DZ methods, polymer synthesis.

Recently, organic compounds of transition metals have found wide application not only as catalysts of coordination polymerization of olefins and dienes,[1] but also as regulators of radical polymerization of vinyl monomers.[2] Increased interest in the use of organometallic compounds in polymer synthesis is, in particular, associated with the development of the concept of atom transfer radical polymerization (ATRP),[3,4] one of the most promising methods of "living" chain polymerization. In this type of processes, the growth of the polymer chain is controlled using various metal (copper, cobalt, iron, *etc.*) complexes.[2—4]

The ATRP mechanism is based on the interaction between transition metal halides, where the metals are in the lowest oxidation state, and alkyl halides. This reaction, known as the Kharasch reaction[5] in organic chemistry, occurs at temperatures above 100 °C and results in alkyl radicals $R^{\bullet}$ capable of initiating polymerization. This is accompanied by reversible oxidation of the transition metal. Carrying out the reaction in a vinyl monomer medium permitted practical implementation of fragment-by-fragment growth of the polymer chain, *i.e.*, "living" chain polymerization. The process can be described by Scheme 1.

Earlier,[6—11] bis(cyclopentadieny)titanium dichloride (Cp_2TiCl_2) as well as bis(cyclopentadienyl)niobium and -tungsten dichlorides (Cp_2NbCl_2 and Cp_2WCl_2, respectively) were proposed as chain growth regulators in styrene and methyl methacrylate (MMA) polymerization. Introduction of these additives significantly affects the kinetic parameters of MMA and styrene polymerization in the presence of azoisobutyric acid dinitrile (initiator) and, in particular, leads to considerable suppression of the gel effect.[6,7] The M_n values of the polymers synthesized using these compounds are linearly related to the monomer conversion. Based on the experimental data,[6] we suggested controlled chain growth in the system. The action mechanism of Cp_2TiCl_2 in styrene and MMA polymerization was established using modern quantum chemical methods.[7,8]

Scheme 1



$\sim P_n^{\bullet}$ is the polymer radical; X—M^{n+1} is the transition metal halide, where the metal is in the highest oxidation state; ~P—X is the adduct of the interaction of the macroradical containing the carbon—halogen bond; M^{n+} is the metal in the lowest oxidation state; k_{act}, k_{deact}, and k_p are the rate constants for activation, deactivation, and chain propagation, respectively; and m is monomer.

In this connection it was quite interesting and promising, from the practical standpoint, to study the interaction between growing radicals of vinyl monomers and bis(cyclopentadienyl) derivatives of other Group IV—VI

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transition metals using quantum chemistry methods and to assess the effect of the metal atom in the organometallic compound molecule on the reactivity of the growing radicals.

Calculation Procedure

All quantum chemical calculations were carried out with the Gaussian-98 program[12] in the framework of the density functional theory.[13,14] The starting molecular geometry parameters of the organometallic compounds under study were set equal to those obtained by X-ray analysis. If different spin states were possible, calculations were performed for the most energetically favorable one. For all molecules and radicals studied, we located potential energy minima; the stationary points were characterized by vibrational frequency calculations. Radical systems were investigated using the unrestricted wave function formalism.

Density functional calculations were carried out with the Becke 1988 nonlocal exchange functional,[15] the Perdew correlation functional (BP86),[16] and the Lee—Yang—Parr correlation functional (B3LYP).[17,18] Organotitanium compounds and reactions involving them were calculated with the 6-31G(d) basis set. Due to the lack of complete 6-31G basis set, organometallic compounds containing other transition metal atoms were calculated using the conventional LanL2DZ basis set where the inner electron shells of the metal and chlorine atoms were replaced by the Los Alamos ECP core potential.[19—21] BP86/6-31G(d) and B3LYP/LanL2DZ calculations of organotitanium compounds give consistent results. According to published data for related systems,[7,8,22—24] the results obtained by the methods employed here differ from experimental data by at most 5 kcal mol^{-1}.

In some cases, preliminary search for stationary points was done using a specific basis set composed of 6-31G for C, 3-21G for H, and 6-31G(d) for Cl atoms.

The results of quantum chemical calculations were visualized using the Moltran 2.5 program.[25]

Results and Discussion

Based on the results of analysis of the structure and general reactivity of organometallic compounds, three probable pathways of the interaction between organometallic compounds formed by Group IV—VI transition metals and growing radicals were considered.

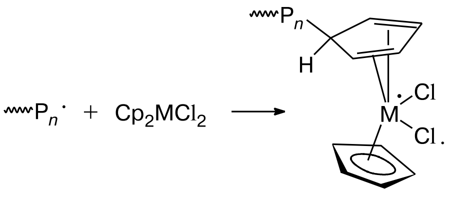
1. Interaction of the growing radical ($\sim P_n^{\bullet}$) with the organometallic compound resulting in the formation of a new M—C bond:

$$\sim P_n^{\bullet} + Cp_2MCl_2 \longrightarrow \sim P_n{-}\overset{\bullet}{M}Cp_2Cl_2. \qquad (1)$$

2. Chlorine abstraction from the Cp_2MCl_2 molecule by the macroradical with reduction of the oxidation state of the metal:

$$\sim P_n^{\bullet} + Cp_2MCl_2 \longrightarrow \sim P_n{-}Cl + Cp_2\overset{\bullet}{M}Cl. \qquad (2)$$

3. Addition of the polymer radical ($\sim P_n^{\bullet}$) to the cyclopentadienyl ring:



(3)

The results of calculations for model radicals, namely, styrene $MeCH^{\bullet}Ph$ (**1**) and MMA $MeC^{\bullet}MeCOOMe$ (**2**) are listed in Table 1.

Bis(cyclopentadienyl)metal dichlorides containing Group IV and Group VI transition metal atoms have 16- and 18-electron outer shells, respectively. In the former case the metal atom has an unfilled orbital, whereas in the latter case it has a nonbonding electron pair. No stable complexes corresponding to the interaction between the radical and organometallic compound resulting in the formation of a metal—carbon bond were located in both cases. Unlike the Group IV and Group VI metal compounds, the Group V transition metal compounds have 17-electron outer shells including one unpaired electron. Potentially, this group of compounds can form a new M—C bond in the interaction with radicals and thus complete the outer electron shell to a 18-electron one. According to our quantum chemical calculations (see Table 1), in this case the formation of an M—C bond is possible, but not energetically favorable. This is probably due to (i) bulkiness of the radicals in question and (ii) steric hindrance in the coordination spheres of the metal atoms.

Table 1. Energy changes ($\Delta_r E$/kJ mol^{-1}) in reactions (1)—(3) obtained from B3LYP/LANL2DZ calculations.

Metal	Reaction (1)		Reaction (2)		Reaction (3)	
	1	**2**	**1**	**2**	**1**	**2**
Ti*	—	—	28.9	36.4	−4.2	−2.9
Zr	—	—	123.8	137.7	33.7	36.8
Hf	—	—	154.4	168.2	39.3	42.3
V	—	—	6.3	20.1	−1.9	−2.1
Nb	72.4	106.3	50.6	64.4	−47.7	−47.7
Ta	47.2	78.3	79.9	93.7	−73.3	−73.7
Cr	—	—	−128.4	−114.6	−134.8	−135.4
Mo	—	—	−10.9	2.9	−96.2	−94.6
W	—	—	29.7	43.5	−92.5	−91.2

* Reactions with the organotitanium compound were calculated by the BP86/6-31G(d) method.

Reaction (2) involving abstraction of a chlorine atom from Cp_2MCl_2 is expected to occur more readily on going from Ti to V and Cr due to a decrease in the M—Cl bond energy with an increase in the atomic number within the rows. This is accompanied by elongation of the M—Cl bond (Table 2, Fig. 1) and by a decrease in the angle between the two bonds formed by the metal atom with the chlorine atoms. For the same-group metals, abstraction of a chlorine atom from Cp_2MCl_2 becomes more difficult as the atomic number increases. This trend is consistent with the corresponding changes in the metal electronegativities.[26] Therefore, an increase in the metal electronegativities causes the M—Cl bond to weaken. It should be noted that bis(cyclopentadienyl)chromium dichloride

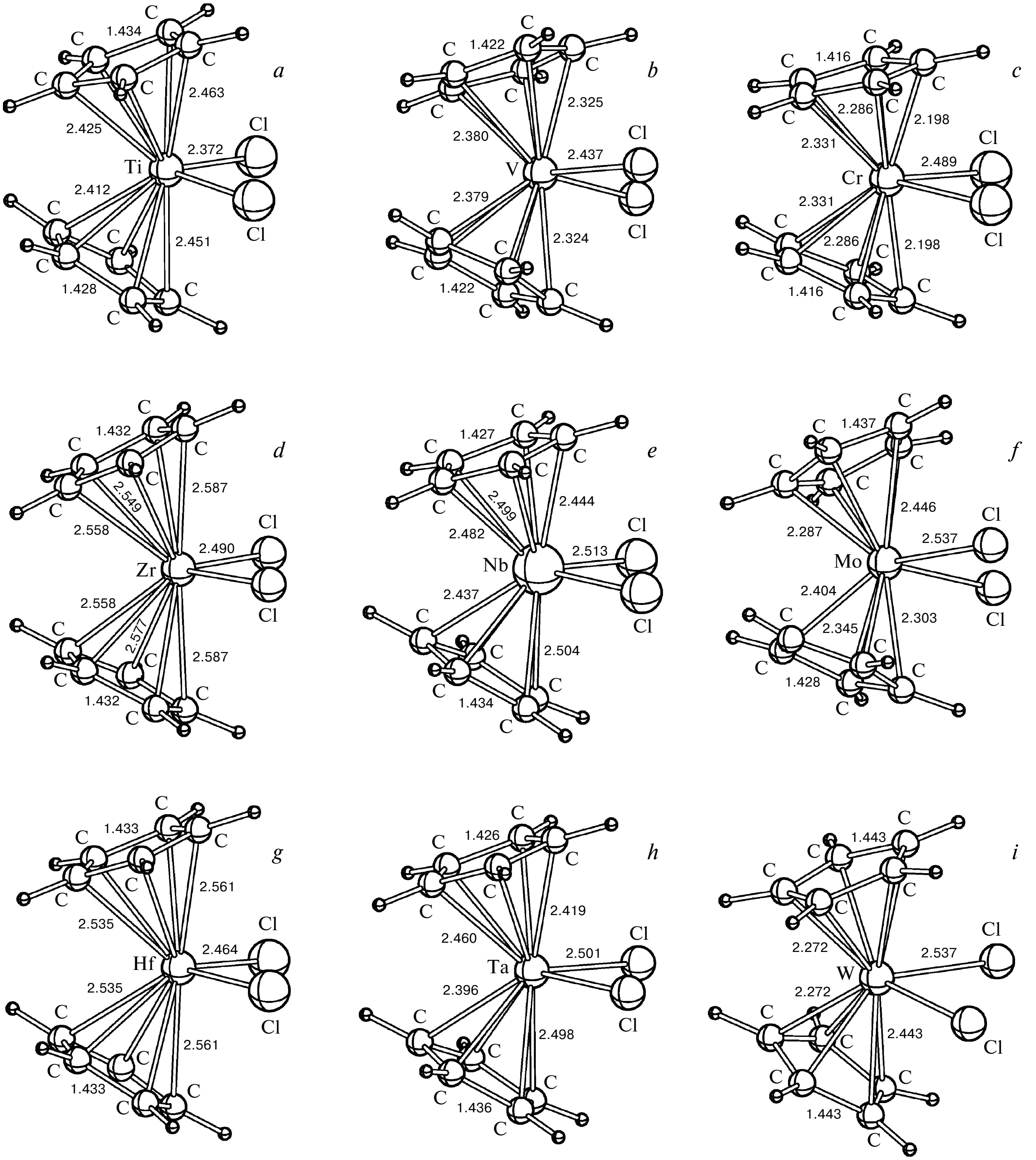


Fig. 1. Molecular structures of bis(cyclopentadienyl) derivatives of Group IV—VI metals dichlorides: Ti (*a*), V (*b*), Cr (*c*), Zn (*d*), Nb (*e*), Mo (*f*), Hf (*g*), Ta (*h*), and W (*i*). All geometries optimized at the B3LYP/LANL2DZ level.

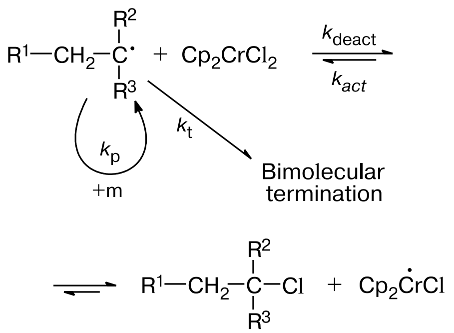
Table 2. Geometric parameters of bis(cyclopentadienyl) derivatives of Group IV—VI metals dichlorides obtained from B3LYP/LANL2DZ calculations

Metal	Bond length/nm		Angle/deg Cl—M—Cl
	d(M—C)	*d*(Met—Cl)	
Ti	0.243	0.237	96.5
V	0.237	0.244	88.6
Cr	0.229	0.249	84.3
Zr	0.257	0.249	100.2
Nb	0.248	0.251	89.1
Mo	0.237	0.254	83.1
Hf	0.255	0.246	98.7
Ta	0.246	0.250	87.7
W	0.236	0.254	82.2

Cp_2CrCl_2 is a relatively unstable compound. It is logical to assume that if the equilibrium in reaction (2) is shifted to the left, the organometallic compound can be used as chain growth regulator in ATRP (see Scheme 1).

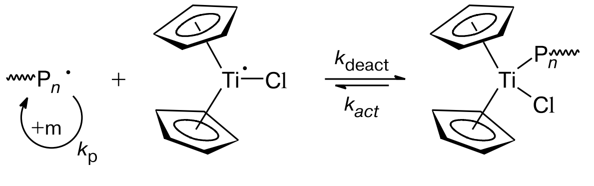
Thus, the results of our quantum chemical calculations suggest that, among the compounds studied, complex Cp_2CrCl_2 is expected to be the most efficient in controlled reverse ATRP, the efficiency of complex Cp_2MoCl_2 being somewhat lower (Scheme 2).

Scheme 2



At the same time a small positive energy effect of this reaction does not preclude the reduction of the organometallic compound by the growing radicals to the metal complexes Cp_2MCl, which in turn can act as reversible inhibition agents similar to the Ti^{III} compound (Scheme 3).

Scheme 3



Similar prerequisites were found for compounds of all metals studied except zirconium and hafnium, for which the energy change in the chlorine abstraction reaction is ~130 and 160 kJ mol^{-1}, respectively.

Reaction (3), that is, addition of the growing radicals to the cyclopentadienyl ring, is energetically more favorable than the chlorine abstraction reaction (2). In this case the addition is expected to occur more easily with an increase in the atomic number of the metal in the row. For diamagnetic compounds of Group IV and Group VI metals the "ease" of addition decreases on going from Ti to Hf and from Cr to W. At the same time, the reverse was found for paramagnetic compounds of the Group V metals. Namely, the energy effect of the reaction of radical addition to the cyclopentadienyl ring increases on going from V to Nb and Ta.

Compounds of the first-row transition metals, *i.e.*, Ti and V (but not Cr !) are characterized by nearly equal energy effects of reactions (2) and (3). However, a study[8] of the titanium compound showed that the activation energy for reaction (2) is somewhat lower than for reaction (4). Thus, for these metals abstraction of a halogen atom and reduction of the organometallic compound to Cp_2MCl are more preferable than addition of organic radical to the cyclopentadienyl ring and subsequent reduction of the organometallic compound to $CpMCl_2$. This was experimentally confirmed taking Cp_2TiCl_2 as an example; compound $Cp_2Ti^{\bullet}Cl$ was detected by EPR spectroscopy in the reaction medium in the course of MMA polymerization in the presence of Cp_2TiCl_2 (see Ref. 7).

From the data in Table 1 it follows that the interaction of cyclopentadienyl derivatives of the second- and third-row Group IV—VI transition metals with the growing radicals more probably involves the addition to the cyclopentadienyl ring with the formation of $Cp(\eta^4\text{-}C_5H_5R)MCl_2$ rather than chlorine abstraction. The geometry of the complex formed is shown in Fig. 2 taking the organoniobium compound as an example.

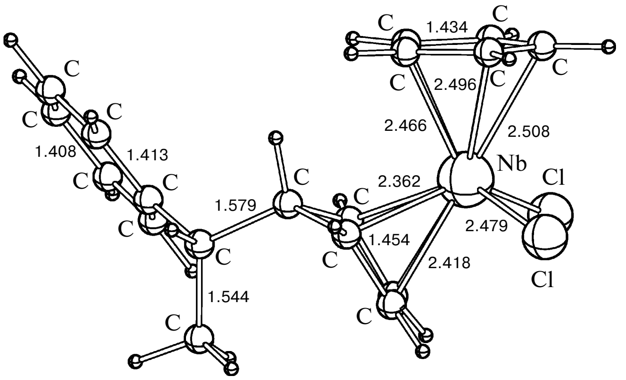


Fig. 2. Complex formed in the interaction of 1-phenylethyl radical and Cp_2NbCl_2. Geometry optimized at the B3LYP/LANL2DZ level.

A study of the organotitanium compound showed that the η^4-bond formed in this case is relatively weak (35—38 kJ mol^{-1}) and can be cleaved with ease under the experimental conditions. Therefore, compounds formed by these metals can be reduced to $CpMCl_2$ by organic radicals. The coordinatively unsaturated compounds thus formed can in turn act as chain growth regulators in radical polymerization of vinyl monomers.

Thus, the results of quantum chemical modeling indicate that the cyclopentadienyl derivatives of Group IV—VI transition metals can interact with growing radicals and that the reaction pathway is mainly determined by the metal atom. The interaction of the metal complexes with the growing radicals causes their reactivity to change and thus can immediately affect the kinetic parameters of polymerization and the molecular weight characteristics of the polymers being synthesized.

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