



## High-temperature reaction of a $\text{Co}_2(\text{CO})_6$ -complexed propargyl cation

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### ABSTRACT

The novel high-temperature reaction of  $\text{Co}_2(\text{CO})_6$ -complexed propargyl cations, occurring in the spontaneous and stereoselective (90–97% *d,l*-) manner and yielding the radical dimers, *d,l*-3,4-diaryl-1,5-hexadiynes (**2**, **11**, **14**), is described. Despite the alleged thermal lability and delicate nature of the requisite  $\text{Co}_2(\text{CO})_6$ -complexed propargyl cations, the reaction temperature can be elevated from 20 °C to 147 °C, shortening the reaction time from 660 min to less than 1 min. Isotopic enrichment experiments detected (MS TOF/ESI/APCI) an incorporation of upto eight  $^{13}\text{C}$  ligands into the metal core, suggesting a single electron, cluster-to-cluster reduction along the reaction coordinate. The reaction kinetics is found to be sensitive toward the electronic nature of the substituents (H, OMe) and to the substitution pattern (0-, 4-, 3,4,5-) on the periphery of the aromatic ring. Calculation data suggest that the spontaneous transfer of a single electron from the metal cluster, onto a  $\pi$ -bonded propargyl moiety, is dependent upon the negative charge on aromatic  $\text{C}_\alpha$  carbon atom, located alpha to the cationic center. The spontaneous conversion of diamagnetic species (propargyl cation) to paramagnetic counterparts (propargyl radical) indicates that the  $\pi$ -bonded organometallic cations can act as the prototypes for transition metal-based thermal sensors. Their application in photochemical research, electronic devices, molecular electronics, and biomedical fields can also be envisioned.

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### 1. Introduction

Transition metals  $\pi$ -bonded to the unsaturated organic carbocations significantly stabilize them [1] relative to their organic counterparts [2] and allow for isolation and complete structural characterization ( $^1\text{H}/^{13}\text{C}$  NMR, X-ray) [1,3,4]. *Ionic reactions* represent the bulk of the experimental material reported with the O-, N-, C-, P-, S-, H-nucleophiles adding to the  $\alpha$ -located cationic centers and converting transition metal-stabilized cations to their neutral counterparts [5]. Given the delicate nature of these species, it is a common practice to carry out the reactions under the mildest conditions possible, typically, within the range of  $-78^\circ$  to  $+20^\circ\text{C}$  [1,5]. *Radical reactions* involving transition metals, as a  $\pi$ -bonded auxiliary, have given a new impetus to the development of the field of *organometallic radical chemistry* [6]. Metal cores are shown to immobilize the unsaturated units susceptible to rearrangements, such as a triple bond, thus improving the chemoselectivity of radical reactions, a common deficiency in the purely organic environment. Another benefit of having a metal core in a close proximity to the radical center is an enhanced stereoselectivity, stemming from the bulkiness of mono- and dinuclear clusters, a key parameter that can be varied, at will, by fine-tuning the ligand substitution reactions [7]. Although the field of organometallic radical chemistry, involving organic ligands  $\pi$ -bonded to the transition metals, is

inferior, by its degree of exploration, to that of ionic reactions, it has nevertheless made a notable contribution to synthetic organic chemistry [6,8,9].

As a part of the systematic studies on the behavior of organic radicals altered, both sterically and electronically, by the complexation with  $\text{Co}_2(\text{CO})_6$ -core, we reported on the diastereoselectivity of homo- and cross-, inter- and intramolecular coupling reactions, as well as novel methods for radical generation [10]. Among those are conceptually related, complementary protocols involving the spontaneous and THF-mediated radical coupling reactions [10f,10g]. The former describes the *room temperature* conversion of cobalt-complexed propargyl cations to the respective radicals and subsequent intermolecular dimerization [10f]. Herein, we report that despite an alleged thermal lability of cobalt-complexed propargyl cations, the temperature of the spontaneous reaction can be elevated to 147 °C, without any significant decline in either the yields of radical dimers, or the level of diastereoselectivity (90–97% *d,l*-). Most remarkably, kinetic studies indicated that by increasing the reaction temperature, from 20 °C to 147 °C, the reaction could come to completion in less than 1 min, instead of 660 min. Furthermore, kinetic studies revealed that the reaction rate is, unexpectedly, dependent upon the substituents on the periphery of the aromatic ring. The mechanistic hypothesis derived from computational analysis suggests that the negative charge alpha to the cationic center is essential to the rate of the spontaneous transfer of a single electron from the metal cluster, onto a  $\pi$ -bonded propargyl moiety. For *neutral cobalt-alkyne complexes*, only

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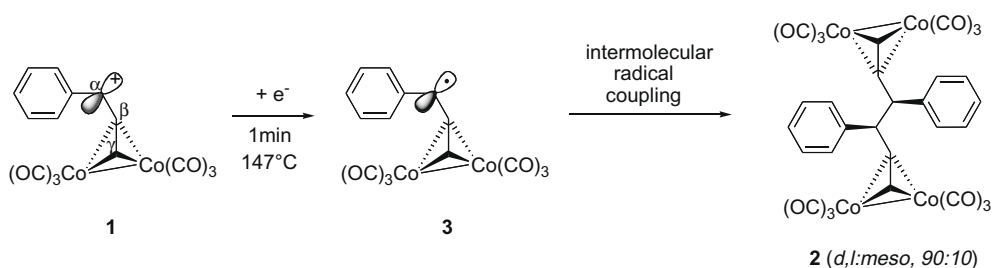
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two reactions are known to occur at elevated temperatures: (1) *ligand substitution* reaction [7] converting  $\text{Co}_2(\text{CO})_6$ -complexes to axially, or equatorially, substituted  $\text{Co}_2(\text{CO})_5\text{L}$  and  $\text{Co}_2(\text{CO})_4\text{L}_2$  complexes (50–80 °C); and (2) the *Pauson–Khand* reaction [11] which transforms cobalt–alkyne complexes to cyclopentenones within a wide temperature range (20–150 °C). To the best of our knowledge, for *cationic cobalt–alkyne complexes*, this account represents the only case of a synthetically viable reaction, either in ionic or radical chemistry. Among attractive features of the high-temperature radical reaction of the cobalt-complexed propargyl cations is a high level of diastereoselection (90–97% *d,l*) that is unprecedented both for organic and organometallic, intermolecular radical coupling reactions [8,12]. In a broader sense, the reaction might be of interest from a practical standpoint since it represents the spontaneous conversion of diamagnetic species (propargyl cation) to paramagnetic counterparts (propargyl radical) with the rates being strongly dependent upon temperature (*valence tautomerism*).

## 2. Results and discussion

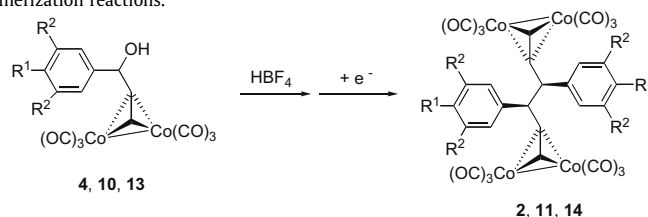
Cobalt-complexed propargyl cation **1** [10f] was dissolved in 1,1,2,2-tetrachloroethane and immersed, for 1 min, into a pre-heated bath (147 °C) to yield 1,5-hexadiyne **2** in high yield (84.0%) and excellent *d,l*-diastereoselectivity (*d,l:meso*, 90:10) (Scheme 1 and Table 1). The reaction supposedly involves a spontaneous conversion of cation **1** to radical **3**, and subsequent intermolecular radical self-coupling. At 20 °C, under analogous conditions, dimer **2** was previously isolated in 80% yield, as a dia-

stereomeric mixture (*d,l:meso*, 94:6) [10f]. In an attempt to shed some light upon the mechanism of the reaction, in particular its dependence upon the temperature and topology of the substrate, kinetic studies were carried out at 20 °C and 40 °C (Table 1, entries 1,2). Alcohol **4** was treated with  $\text{HBF}_4$  [10f] to yield the cation **1** which was dissolved in  $\text{CH}_2\text{Cl}_2$  and then sampled to generate the respective concentration curves (Fig. 1). The standard protocol included quenching the aliquots with MeOH, thus converting an unreacted cation **1** to  $[\text{HC}\equiv\text{CCH}(\text{OMe})\text{Ph}]\text{Co}_2(\text{CO})_6$  (**5**), and determining, by  $^1\text{H}$  NMR, the ratio of dimer **2**:Me-ether **5**. As concentration curves indicate (Fig. 1), at 20 °C, the reaction was relatively slow, at 660 min, while in refluxing  $\text{CH}_2\text{Cl}_2$ , it came to completion much faster, in 100 min. The degree of conversion, after 60 min, as quantified by the concentration of dimer **2**, was equal to 24.5% and 86.0%, respectively. A high *d,l*-diastereoselectivity observed at 20 °C (*d,l:meso*, 94:6) remained unchanged with an increase in temperature (Table 1, entries 1,2). Preparative studies, under optimized conditions (40 °C, 100 min), afforded dimer **2** in high yield (93.0%) and an excellent *d,l*-diastereoselectivity (*d,l:meso*, 94:6; Table 1, entry 3). Further increase in temperature, to 83 °C, by using 1,2-dichloroethane as a solvent, allowed to effect even a faster reaction (6 min), without significantly compromising either yield (88.0%), or diastereoselectivity (*d,l-2:meso-2*, 92:8; Table 1, entry 4). In summary, alcohol **4** can be converted, in two steps (cation isolation – spontaneous dimerization), at various temperatures (20 °C, 40 °C, 83 °C, 147 °C), to dimer **2**, with the reaction times dropping from 660 min, via 100 min and 6 min, to an astonishing 1 min!



Scheme 1.

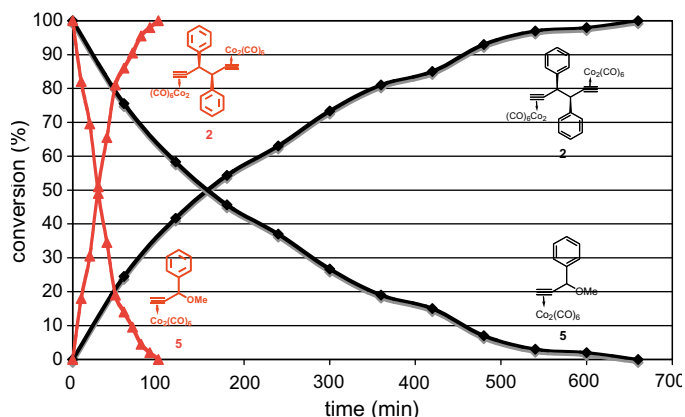
**Table 1**  
Cobalt-core mediated, spontaneous radical dimerization reactions.



	Substrates	Substitution pattern	T (°C)	Reaction products mode <sup>a</sup>	Products	Reaction time (min)	<i>d,l:meso</i> crude	Yield <sup>b</sup> (%)	<i>d,l:meso</i> isolated
1.	<b>4</b> ( $\text{R}^1 = \text{R}^2 = \text{H}$ )	0-	20	A	<b>2</b> ( $\text{R}^1 = \text{R}^2 = \text{H}$ )	660	94:6		
2.			40	A		100	94:6		
3.			40	B		100	94:6	93.0	95:5
4.			83	B		6	92:8	88.0	93:7
5.			147	B		1	90:10	84.0	91:9
6.	<b>10</b> ( $\text{R}^1 = \text{OMe}$ , $\text{R}^2 = \text{H}$ )	4-	40	A	<b>11</b> ( $\text{R}^1 = \text{OMe}$ , $\text{R}^2 = \text{H}$ )	270	96:4		
7.			40	B		270	96:4	87.2	97:3
8.			147	B		1	95:5	80.2	97:3
9.	<b>13</b> ( $\text{R}^1 = \text{R}^2 = \text{OMe}$ )	3,4,5-	40	A	<b>14</b> ( $\text{R}^1 = \text{R}^2 = \text{OMe}$ )	180	97:3		
10.			40	B		180	97:3	55.7	100:0

<sup>a</sup> Reaction modes: A – kinetic studies; B – preparative studies.

<sup>b</sup> The yields are calculated on the basis of the reaction stoichiometry that requires two equivalents of propargyl cations to form an equivalent of respective radicals.

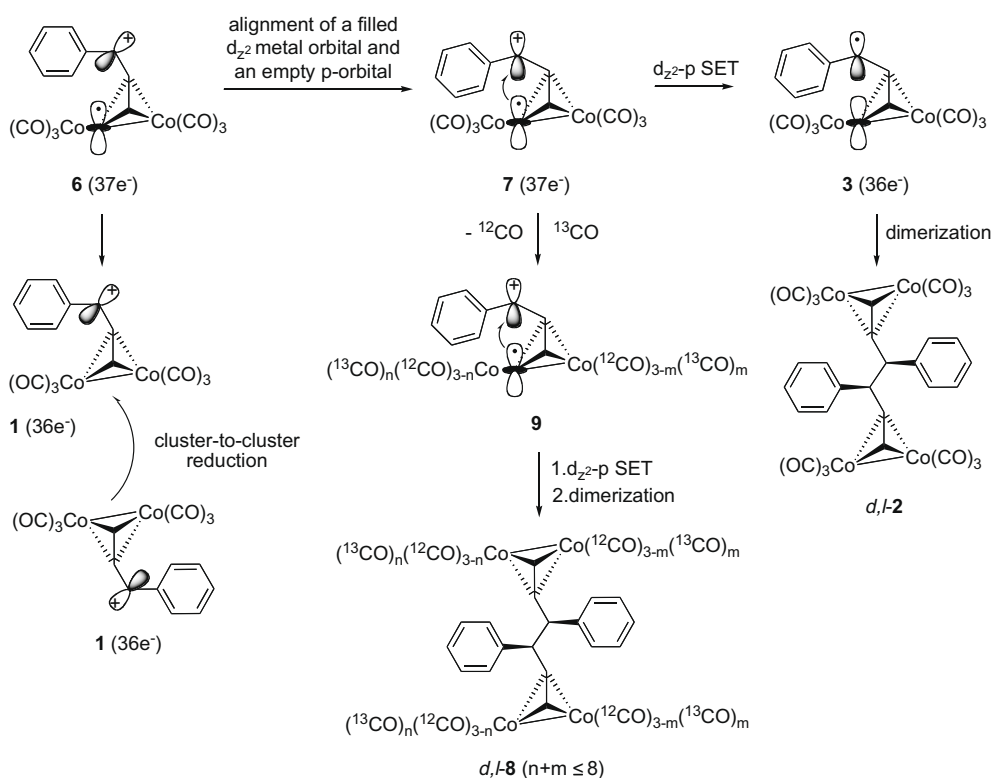


**Fig. 1.** The concentration curves for spontaneous coupling reaction of alcohol **4** at 20 °C (◆; reaction time 660 min) and 40 °C (▲; reaction time 100 min).

The proposed mechanism of the spontaneous reaction is depicted in Scheme 2. In the absence of the reducing agent, two identical cationic clusters **1** could interact with each other, with one of them acting as a reducing agent and donating an electron toward the second cluster (*cluster-to-cluster reduction*) [13]. The recipient moiety could be either the cluster itself, or an  $\alpha$ -cationic center. The experimental evidence points to the metal cluster to be a single electron recipient, generating the  $37e^-$  species **6**. A  $d_{z^2}$  orbital is arbitrarily chosen to act as a carrier for an incoming electron. The next step includes an alignment of a  $d_{z^2}$  orbital of the metal atom and an empty p-orbital of the carbocationic center, implying that an axial overlap of two orbitals – according to the main tenet of the theory on chemical bonding [14] – will provide the most efficient conditions for a cluster-to-ligand electron transfer. The suggested level of flexibility is in line with an amply demonstrated

ability of organometallic and coordination complexes to undergo conformational changes [15]. Rearranged species **7** could undergo an alleged  $d_{z^2}$ -p single electron transfer (SET), relieving the metal cluster of an extra electron and converting the cationic species into requisite radical **3**, subsequently dimerizing to *d,l*-1,5-hexadiyne **2**.

To prove that a  $36e^-$ -species **1** does undergo a cluster-to-cluster reduction along the reaction coordinate, the spontaneous reaction was carried out in  $^{13}\text{C}$ O atmosphere. Dimer **8** was isolated by PTLC and analyzed by MS TOF/ESI/APCI and  $^{13}\text{C}$  NMR spectroscopic methods. In cluster redox chemistry, the mono- and polynuclear metal cores are known to undergo one-electron transfer reactions, to act as electron reservoirs, and also to be reduced, and oxidized, either by chemical or electrochemical means [13,16]. If the hypothesis is correct, then the formation of the reduced metal clusters **6** could be detected by a *ligand substitution reaction* [7]: the  $19e^-$  species – generated by reduction of the polynuclear metal carbonyls with Na/Ph<sub>2</sub>CO, or electrochemically – are reported to undergo an accelerated – by a factor of  $>10^6$  – ligand displacement at ambient temperatures [17]. By analogy, following the cluster-to-cluster reduction and  $d_{z^2}$ -p alignment, species **7** would undergo a ligand exchange with heavy  $^{13}\text{C}$ O molecules, replacing  $^{12}\text{C}$ O counterparts and forming an isotopically enriched radical **9**. Subsequent  $d_{z^2}$ -p SET and radical coupling would afford dimer **8**. The comparison of MS TOF/ESI/APCI data for *d,l*-**2** and *d,l*-**8** revealed an incorporation of up to eight molecules of  $^{13}\text{C}$ O, with the major species containing two to three “heavy” ligands (*d,l*-**2** [M+OMe]<sup>+</sup> 832.7965; *d,l*-**8** 832.7975, 833.7980, 834.8017, 835.8044, 836.8076, 837.8119, 838.8145, 839.8178, 840.8249) (Fig. 2). Analogously, *meso*-**2** and *meso*-**8** strikingly differ in the isotopic distribution with the latter undergoing a ligand exchange reaction with up to eight molecules of  $^{13}\text{C}$ O (*meso*-**2** [M+OMe]<sup>+</sup> 832.8006; *meso*-**8** 832.8111, 833.8050, 834.8080, 835.8097, 836.8140, 837.8159, 838.8199, 839.8240, 840.8300 (Fig. 3). The configuration of diastereomers – *d,l* vs. *meso* – does not seem to affect the level of  $^{13}\text{C}$ O



**Scheme 2.**

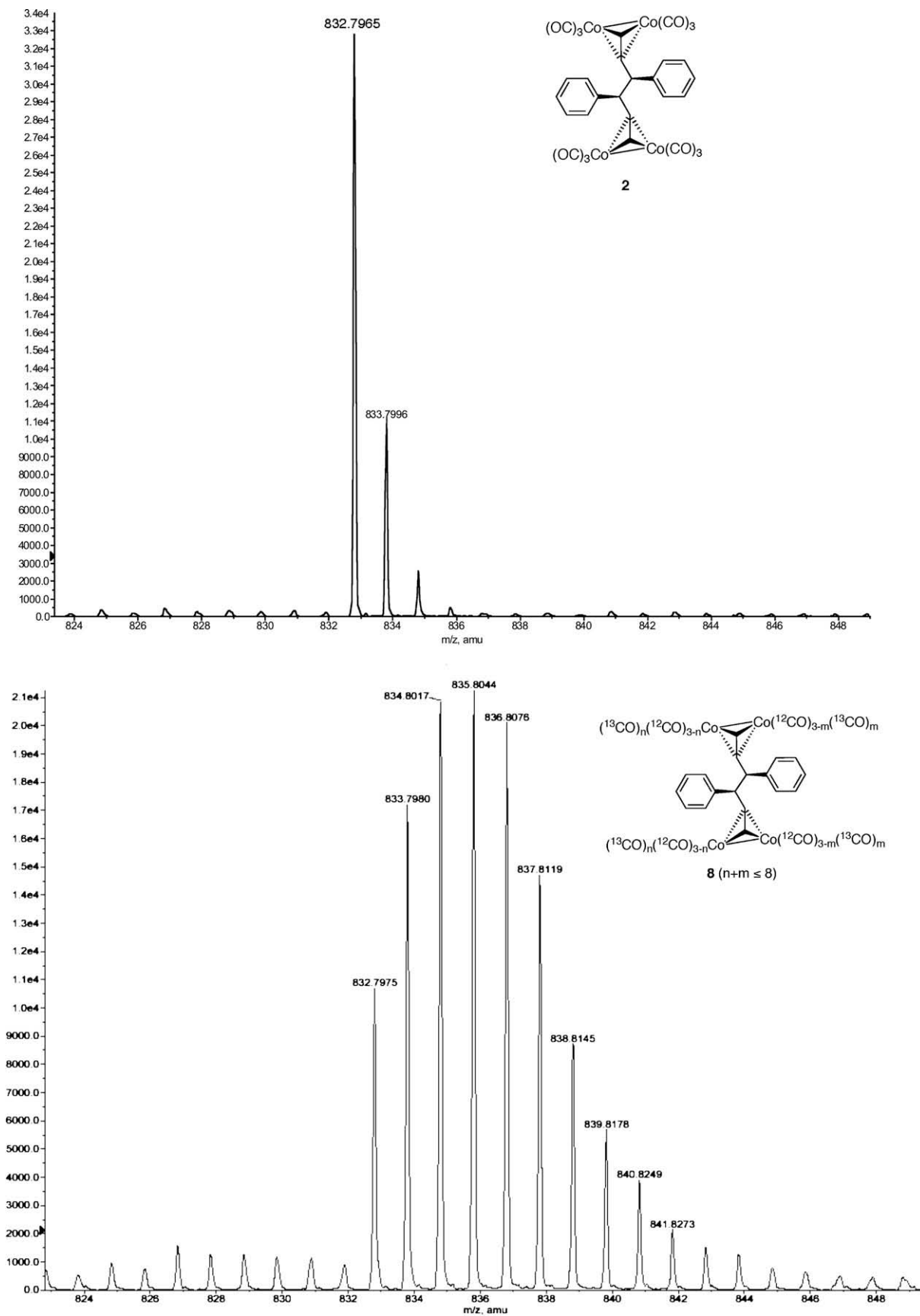


Fig. 2. The MS TOF/ESI/APCI spectra of *d,l*-**2** and  $^{13}\text{C}$ -labelled *d,l*-**8**.

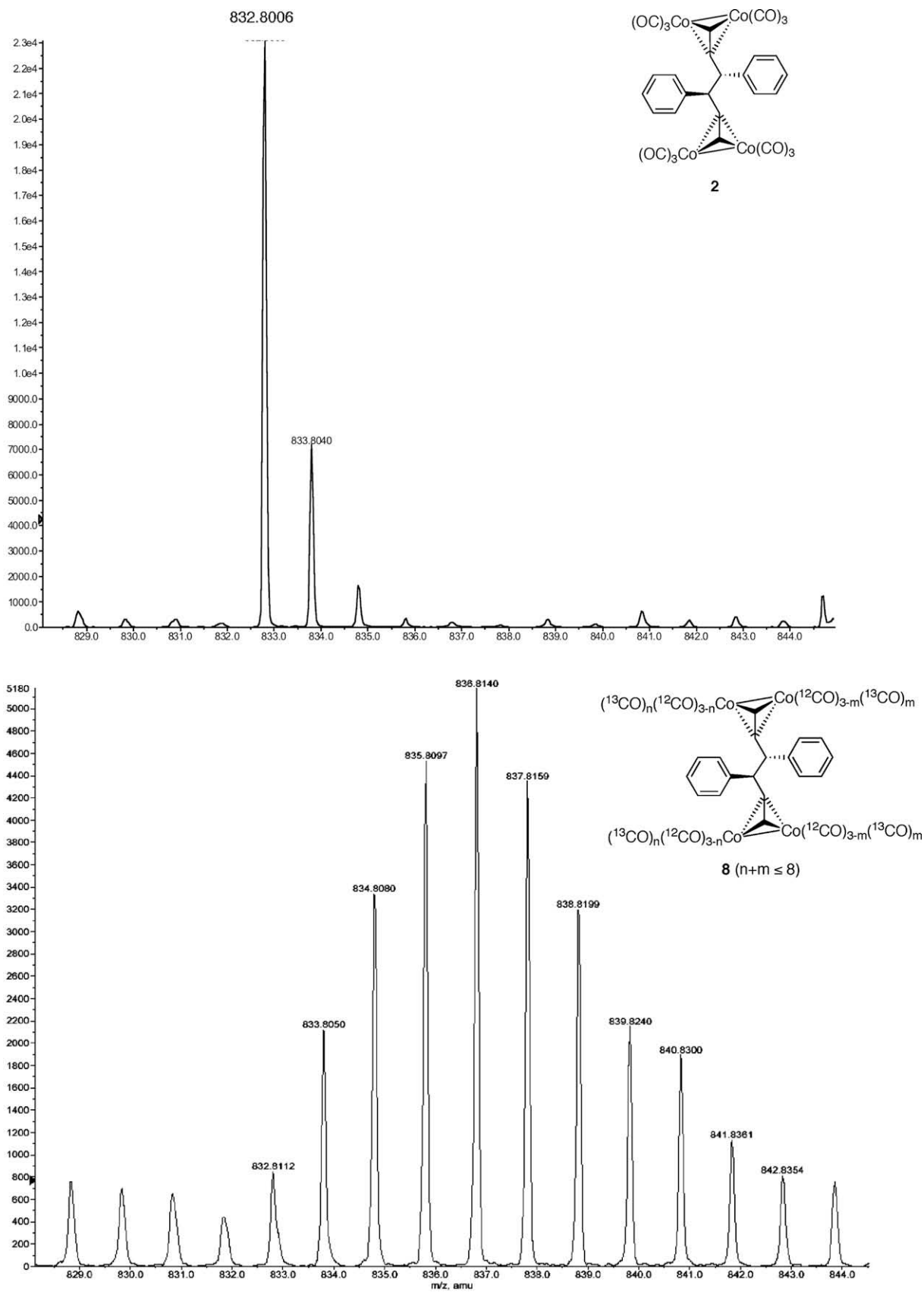


Fig. 3. The MS TOF/ESI/APCI spectra of meso-2 and <sup>13</sup>C-labelled meso-8.

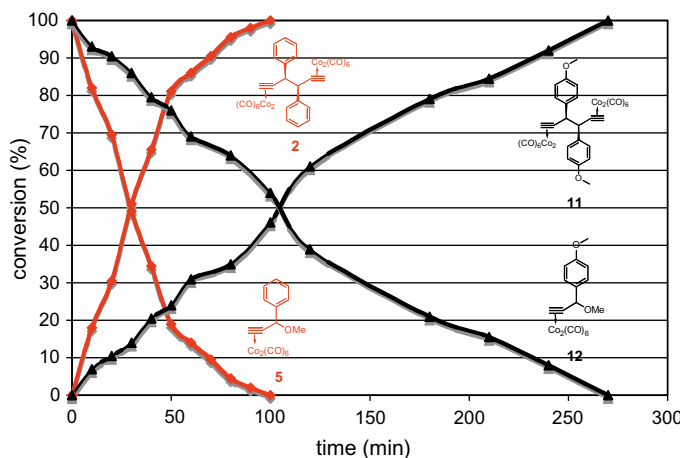


Fig. 4. The concentration curves for spontaneous coupling reaction (40 °C) of alcohols **4** (♦; reaction time 100 min) and **10** (▲; reaction time 270 min).

incorporation, although the intensity of the molecular ion is much higher for *d,l*-**8**, relative to that in *meso*-**8** (832.7975 vs. 832.8111, respectively; Figs. 2 and 3). The  $^{13}\text{C}$  NMR analysis revealed a sharp increase in the peak intensity of cobalt-coordinated  $^{13}\text{CO}$  signals (199.1, 200.4 ppm) indicating an incorporation of “heavy” carbon monoxide into the dimeric product.

To assess the impact of a donating 4-OMe group on the kinetic profile of the spontaneous reaction, alcohol **10** was converted to the respective cation and then heated at 40 °C in  $\text{CH}_2\text{Cl}_2$ . The aliquots were treated with methanol and the progress was quantified by the NMR ratio of dimer **11** and respective Me-ether, i.e.  $[\text{HC}\equiv\text{CCH}(\text{OMe})\text{C}_6\text{H}_4(4\text{-OMe})]\text{Co}_2(\text{CO})_6$  (**12**). As concentration curves indicate (Fig. 4), the reaction suffered a significant retardation, arriving to completion in 270 min (Table 1, entry 6). In preparative studies, under optimized conditions (40 °C, 270 min), dimer **11** was isolated in high yield (87.2%), as a diastereomeric mixture (*d,l*:*meso*, 96:4; Table 1, entry 7). Further increase of the reaction temperature, to 147 °C, afforded, in 1 min, dimeric product **11** with high yield and *d,l*-stereoselectivity (80.2%; *d,l*:*meso*, 95:5; Table 1, entry 8). The incorporation of additional methoxy groups, in the 3,4,5-positions of the aromatic ring, unexpectedly, resulted in an acceleration of the spontaneous reaction. Thus, at 40 °C, alcohol **13** converted to dimer **14** in 180min[18] forming *d,l*-/*meso*-diastereomers in the ratio of 97:3 (Fig. 5; Table 1, entry 9). In the preparative setting (40 °C, 180 min), *d,l*-**14** was isolated, as a pure diastereomer, in 55.7% yield (Table 1, entry 10).

The key intermediates – carbocations **1**, **16**, **17** – generated from cobalt complexes **4**, **13**, and **10**, respectively, are arranged in order of decreasing reactivity (Fig. 6). This arrangement is somewhat counterintuitive since, contrary to the expectations, the aromatic substituents do not exhibit an accumulative property, i.e. kinetic parameters do not alter concurrently with the number of methoxy groups employed. An increase in the reaction time (**1** 100 min; **16**

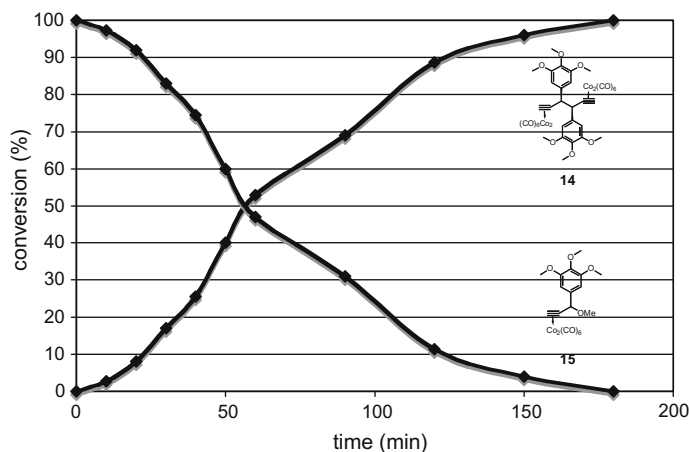


Fig. 5. The concentration curves for spontaneous coupling reaction of alcohol **13** at 40 °C (reaction time 180 min).

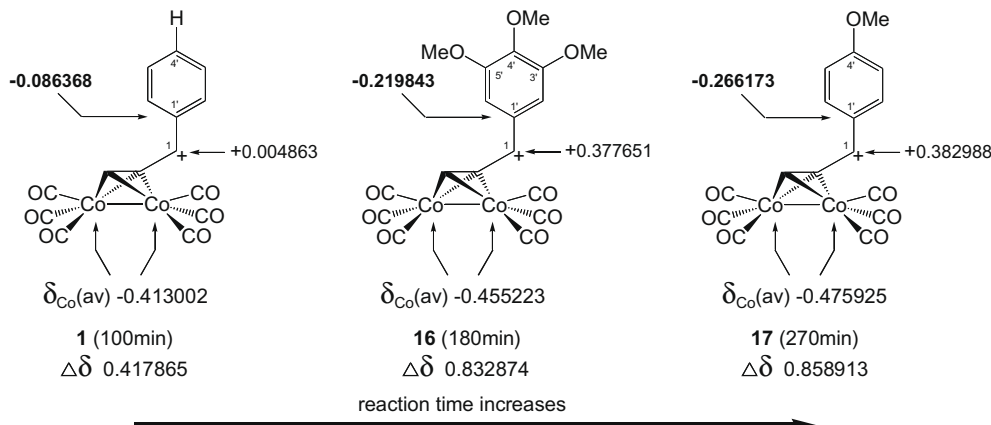


Fig. 6. Charge distribution in  $\text{Co}_2(\text{CO})_6$ -complexed propargyl carbocations derived from PM3 calculations.



180 min; **17** 270 min) is accompanied, as expected, by a drop in the reaction rates quantified by two kinetic parameters. Thus, for cations **1**, **16** and **17**, at 30 min, conversions were equal to 51%, 17% and 14%, and landmark conversions of ~50% were achieved after 30, 60 and 100 min, respectively.

To interpret the observed relative rates of the spontaneous reaction, the charge distribution in cations **1**, **16** and **17** was obtained from PM3 calculation data [19] (Fig. 6). It is conceivable that the rate of the cluster-to-ligand SET would be directly proportional either to the positive charge of the recipient carbocationic center ( $C_1$ -atom), or to the negative charge of the cobalt atoms, or to a charge difference between the cationic center and cobalt atoms. The higher the said values, the stronger the driving force should be, thus accelerating an electron transfer from an electron-rich transition metal toward a  $\pi$ -bonded organic ligand. Computation reveals that there is no correlation between the parameters in question and the rate of the spontaneous reaction. If the positive charge was at work, as the main kinetic determinant, then the fastest reaction would have been observed for cation **17** bearing 4-OMe substituent, since the charge on the  $C_1$ -atom (+0.382988) is the highest among the cationic species under consideration (**1** +0.004863; **16** +0.377651). An average negative charge over the cobalt atoms –  $\delta_{Co(av)}$  – is also the highest in cation **17**, thus suggesting the fastest reaction among three competitors. A combined parameter – charge separation between the metal core and the cationic center,  $\Delta\delta$ , calculated by subtracting an average charge of the cobalt atoms,  $\delta_{Co(av)}$ , from that of the respective  $C_1$ -atoms – also is found to be inconsistent with the experimental observations: the lowest  $\Delta\delta$  value (0.417865) is obtained for cation **1**, the fastest reacting species (Fig. 6). To the contrary, the highest charge difference is observed for the cation **17** (0.858913), the species reacting at the lowest rate. It is worthy to mention that the calculation data allowed us to exclude an alternative mechanism that includes, first, an *intramolecular* reduction (cluster-to-ligand SET), followed by an *intermolecular*, cluster-to-cluster SET. If the cluster-to-cluster reduction were to be preceded by the transfer of a single electron from the cobalt atom, onto a cationic center, then the cation **17** should have been the fastest, not the slowest, reacting species due to the largest charge difference between cobalt atom and  $C_1$  carbon atom ( $\Delta\delta$  0.858913). Analogously, cation **1** should not have been reacting the fastest since the critical charge separation has the smallest numerical value ( $\Delta\delta$  0.417865).

Further consideration of the calculation data allowed us to conclude that the only electronic parameter consistent with the experimental data is the negative charge at the  $C_{1'}$  carbon atom located at the bottom of the aromatic hexagon, alpha to the cationic center. Thus, the lowest charge is found in the fast-reacting cation **1** (–0.086368, Fig. 6), while an incorporation of methoxy groups in 3,4,5- and 4-positions of the aromatic ring causes polarization of the aromatic ring with the lower part of it acquiring an additional negative charge ( $C_{1'}$  **16** –0.219843; **17** –0.266173). A transfer of electron, from the metal cluster, onto a  $\pi$ -bonded cationic center ( $C_1$ ), could, in fact, be sensitive towards a negative charge developing on the  $C_{1'}$  atom. By the virtue of electronic repulsion, a higher negative charge on the  $C_{1'}$  atom would retard the process, while, to the contrary, lowering it would accelerate a transfer of electron thus increasing the reaction rate.

The current hypothesis –  $C_1$ – $C_{1'}$  repulsion as a main kinetic determinant – is based solely on the *electronic factor* and needs to be further corroborated by computational and experimental studies. At the same time, one could not ignore a *conformational factor* that could also be a contributing parameter. According to the suggested mechanism (Scheme 2), an electron transfer is preceded by a conformational change that aligns the participating

p–d orbitals. It is conceivable that the significant differences in the charge distribution could make the cations conformationally different with the cation **1** being positioned the best for the alignment of donor-acceptor orbitals, and cation **17**, on the opposite end, with the highest charge separation, being the least favorable for an orbital–orbital (p–d) interaction, thus retarding the overall process of the radical generation.

### 3. Conclusions

A novel, high-temperature radical reaction represents the spontaneous conversion of diamagnetic species (propargyl cation) to paramagnetic counterparts (propargyl radical). Among its attractive features are a rapid rate of conversion (1 min / 147 °C) and high degree of diastereoselection (90–97% *d,l*) unprecedented both for intermolecular organic and organometallic radical coupling reactions [8,12]. The process is conceptually preceded by the formation of ferrocenyl radicals: so-called *redox tautomerism* can be detected by NMR and occurs under anaerobic conditions, affording the respective bis-ferrocenyl dimeric products [20]. The proposed transfer of a single electron from the reduced metal cluster, onto a  $\pi$ -bonded organic cation, will allow us to design a novel type of radical reactions in which the transition metal cluster acts as a conduit between a reducing agent and cationic center, while positively influencing the stereochemistry of the process due to its bulkiness and proximity to the newly formed stereocenters. Besides the synthetic and fundamental points of view, the spontaneous generation of radicals in cobalt-complexed propargyl cations could also be of interest from the practical standpoint. There has been a longstanding interest in molecular assemblies that could exist in different electronic states (*magnetic or molecular bistability*) and convert into each other within a given range of standard parameters, such as temperature, pressure, electric and magnetic fields (*valence tautomerism*) [21]. In the cobalt–alkyne series, the reaction rate is shown to be temperature-dependent (from 660 min/20 °C to 1 min/147 °C), thus the organometallic cations can act as the *prototypes for transition metal-based thermal sensors*. The practicality of it is further enhanced by the fact that the cobalt-complexed propargyl cations can be structurally tuned to become both water- and air-resistant, as well as persistent in nature [4d]. Their application in photochemical research, electronic devices, molecular electronics, and biomedical fields can also be envisioned.

### 4. Experimental

All manipulations of air-sensitive materials were carried out in flame-dried Schlenk-type glassware on a dual-manifold Schlenk line interfaced to a vacuum line. Argon and nitrogen (Airgas, ultra-high purity) were dried by passing through a Drierite tube (Hammond). All solvents were distilled before use under dry nitrogen over appropriate drying agents (ether, from sodium benzophenone ketyl;  $CH_2Cl_2$ , from  $CaH_2$ ). All reagents were purchased from Sigma–Aldrich and Acros and used as received.  $Co_2(CO)_8$  was purchased from Strem. NMR solvents were supplied by Cambridge Isotope Laboratories.  $^1H$  and  $^{13}C$  NMR spectra were recorded on Bruker DRX-400 ( $^1H$ , 400 MHz) spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to tetramethylsilane. Spin-spin coupling constants ( $J$ ) are given in hertz. Silica Gel Standard Grade (63–200 mm; Sorbent Technologies) was used for flash column chromatography. Analytical and preparative TLC analysis (PTLC) were conducted on Silica gel 60 F<sub>254</sub> (EM Science; aluminum sheets) and Silica Gel 60 PF<sub>254</sub> (EM Science; w/gypsum; 20 × 20 cm), respectively. Eluents are ether (E), petroleum ether (PE), and pentane (P). Mass spectra were run

at the Regional Center on Mass-Spectroscopy, UC Riverside, Riverside, CA (Agilent model 6210 TOF mass spectrometer operating in multimode).

#### 4.1. *d,l*- and *meso*- $\mu$ - $\eta^2$ -(3,4-Diphenyl-1,5-hexadiyne)bis(dicobalthexacarbonyl) (**2**). Kinetic studies at 20 °C

Under an atmosphere of nitrogen, alcohol **4** (105 mg, 0.25 mmol) was transferred to a flame-dried flask and dissolved in diethyl ether (15 mL). The solution was cooled to –20 °C and  $\text{HBF}_4 \cdot \text{Me}_2\text{O}$  (168 mg, 1.25 mmol) was added dropwise. After stirring for 1 h, the ethereal layer was removed and the cation **1** was washed with diethyl ether ( $3 \times 15$  mL) at –20 °C. Residual amount of ether was stripped under reduced pressure (–20 °C) to afford the cation **1** as a dark red solid. Methylene chloride was added (5 mL), and the reaction mixture was warmed to 20 °C. Aliquots of the solution (0.1 mL) were withdrawn every hour (reaction time 660 min), via syringe, and dispersed in methanol (2 mL) at 20 °C. The sample was diluted with  $\text{H}_2\text{O}$  (2 mL) and then extracted with ether (2 mL). The solvent was evaporated under vacuum, and the crude mixture was analyzed by  $^1\text{H}$  NMR to determine the ratio of dimer **2** and Me-ether **5** (*d,l*-**2**, 4.37 and 6.32 ppm; *meso*-**2**, 4.98 ppm; Me-ether **5**, 5.28 ppm). The concentration curves (Fig. 1) were derived from  $^1\text{H}$  NMR spectra; numerical data presented are the average values for three consecutive runs. Upon the reaction completion (660 min), the ratio of *d,l*- and *meso*-**2** was equal to 94:6 (NMR; de 88%). Both diastereomers were fully characterized in the previous account [10g].

#### 4.2. Kinetic studies at 40 °C

Analogous to the experiment conducted at 20 °C, the cation **1** was synthesized and dissolved in dry methylene chloride (5 mL). The reaction mixture was refluxed at 40 °C, the aliquots of the solution (0.1 mL) were withdrawn every 10 min (reaction time 100 min), via syringe, and dispersed in methanol (2 mL) at 20 °C. The sample was diluted with  $\text{H}_2\text{O}$  (2 mL) and then extracted with ether (2 mL). The solvent was evaporated under vacuum, and the crude mixture was analyzed by  $^1\text{H}$  NMR to determine the ratio of dimer **2** and Me-ether **5** (*d,l*-**2**, 4.37 and 6.32 ppm; *meso*-**2**, 4.98 ppm; Me-ether **5**, 5.28 ppm). The concentration curves (Figs. 1 and 6) were derived from  $^1\text{H}$  NMR spectra; numerical data presented are the average values for two consecutive runs. Upon the reaction completion (100 min), the ratio of *d,l*- and *meso*-**2** was equal to 94:6 (NMR; de 88%).

#### 4.3. Preparative studies at 40 °C

Analogous to the experiment conducted at 20 °C, the cation **1** was synthesized and dissolved in dry methylene chloride (5 mL). The reaction mixture was refluxed at 40 °C for 100 min. The solvents were stripped under reduced pressure (NMR: *d,l*-**2:meso**-**2**, 94:6), and the crude mixture was fractionated on preparative TLC plate (P) to afford *d,l*- and *meso*-**2** (46.5 mg, 93.0%; *d,l*-**2:meso**-**2**, 95:5, de 90%).

#### 4.4. Preparative studies at 83 °C

Analogous to the experiment conducted at 20 °C, the cation **1** was synthesized and dissolved in dry 1,2-dichloroethane (5 mL). The reaction mixture was refluxed for 6 min at 83 °C (TLC control), the solvent was removed under reduced pressure, and the residue (NMR: *d,l*-**2:meso**-**2**, 92:8) was fractionated on preparative TLC plate (PE). Obtained were *d,l*- and *meso*-**2** (44 mg, 88.0%; *d,l*-**2:meso**-**2**, 93:7, de 86%).

#### 4.5. Preparative studies at 147 °C

Analogous to the experiment conducted at 20 °C, the cation **1** was synthesized and dissolved in dry 1,1,2,2-tetrachloroethane (5 mL). The reaction mixture was refluxed for 1 min at 147 °C (TLC control), the solvent was removed under reduced pressure, and the residue (NMR: *d,l*-**2:meso**-**2**, 90:10) was fractionated on preparative TLC plate (PE). Obtained were *d,l*- and *meso*-**2** (42 mg, 84.0%; *d,l*-**2:meso**-**2**, 91:9, de 82%).

#### 4.6. Isotopically enriched *d,l*- and *meso*- $\mu$ - $\eta^2$ -(3,4-diphenyl-1,5-hexadiyne)bis(dicobalthexacarbonyl) (**8**). $^{13}\text{C}$ Incorporation experiment

Under an atmosphere of nitrogen, alcohol **4** (105 mg, 0.25 mmol) was placed in a flame-dried flask and dissolved in diethyl ether (15 mL). The solution was cooled (–20 °C) and treated with  $\text{HBF}_4 \cdot \text{Me}_2\text{O}$  (168 mg, 1.25 mmol). After stirring for 1 h at –20 °C, an ethereal layer was removed, and cation **1** was washed with diethyl ether ( $3 \times 15$  mL) at –20 °C. Residual amount of ether was stripped under reduced pressure (–20 °C), the cation **1** was dissolved in  $\text{CH}_2\text{Cl}_2$  (5 mL), and a  $^{13}\text{C}$  atmosphere was introduced. The reaction mixture was heated at 40 °C (30 min), quenched with water (1 mL), and extracted with ether (10 mL). An organic layer was separated, volatile organic solvents were evaporated under reduced pressure, and the crude mixture was fractionated by the preparative TLC (P) to yield *d,l*-**8** (5 runs) and *meso*-**8** (1 run). *d,l*-**8**  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  54.8, 77.6, 102.1, 127.4, 128.5, 129.1, 143.6, 199.1, 200.4 (high intensity). The spectrum contains an extra, low-intensity signal at 113.5 ppm. *d,l*-**2** MS TOF/ESI/APCI contained  $[\text{M}+\text{OMe}]^+$  signals of the normal isotopic distribution at 832.7965, 833.7996 (Fig. 2). *d,l*-**8** MS TOF/ESI/APCI contained  $[\text{M}+\text{OMe}]^+$  signals at 832.7975, 833.7980 ( $^{13}\text{C}$  incorporated), 834.8017 ( $^{213}\text{C}$ ), 835.8044 ( $^{313}\text{C}$ ), 836.8076 ( $^{413}\text{C}$ ), 837.8119 ( $^{513}\text{C}$ ), 838.8145 ( $^{613}\text{C}$ ), 839.8178 ( $^{713}\text{C}$ ), 840.8249 ( $^{813}\text{C}$ ) (Fig. 2). *meso*-**2** MS TOF/ESI/APCI contained  $[\text{M}+\text{OMe}]^+$  signals of the normal isotopic distribution at 832.8006, 833.8040 (Fig. 3). *meso*-**8** MS TOF/ESI/APCI contained  $[\text{M}+\text{OMe}]^+$  signals at 832.8111, 833.8050 ( $^{13}\text{C}$  incorporated), 834.8080 ( $^{213}\text{C}$ ), 835.8097 ( $^{313}\text{C}$ ), 836.8140 ( $^{413}\text{C}$ ), 837.8159 ( $^{513}\text{C}$ ), 838.8199 ( $^{613}\text{C}$ ), 839.8240 ( $^{713}\text{C}$ ), 840.8300 ( $^{813}\text{C}$ ) (Fig. 3).

#### 4.7. *d,l*- and *meso*- $\mu$ - $\eta^2$ -[3,4-Di(4'-methoxyphenyl)-1,5-hexadiyne]bis(dicobalthexacarbonyl) (**11**). Kinetic studies at 40 °C

Under an atmosphere of nitrogen, alcohol **10** (112 mg, 0.25 mmol) was transferred to a flame-dried flask and dissolved in diethyl ether (15 mL). The solution was cooled to –20 °C and  $\text{HBF}_4 \cdot \text{Me}_2\text{O}$  (168 mg, 1.25 mmol) was added dropwise. After stirring for 1 h, the ethereal layer was removed, and the cation **17** was washed with diethyl ether ( $3 \times 15$  mL) at –20 °C. Residual amount of ether was stripped under reduced pressure (–20 °C) to afford the cation **17** as a dark red solid. Methylene chloride was added (5 mL), and the reaction mixture was refluxed at 40 °C. The aliquots (14; 0.1 mL) were sampled (sampled up to 5 h; reaction time 270 min), via syringe, and dispersed in methanol (2 mL) at 20 °C. The sample was diluted with  $\text{H}_2\text{O}$  (2 mL) and then extracted with ether (2 mL). The solvent was evaporated under vacuum, and the crude mixture was analyzed by  $^1\text{H}$  NMR to determine the ratio of dimer **11** and Me-ether **12** (*d,l*-**11**, 4.31 and 6.30 ppm; *meso*-**11**, 4.34 ppm; Me-ether **12**, 6.04 ppm). The concentration curves (Fig. 4) were derived from  $^1\text{H}$  NMR data; numerical data presented are the average values from two consecutive runs. Upon the reaction completion, the ratio of *d,l*- and *meso*-**11**



was equal to 96:4 (NMR; de 92%). Both diastereomers were fully characterized in the previous account [10e].

#### 4.8. Preparative studies at 40 °C

Analogous to the experiment conducted at 40 °C, the cation **17** was synthesized and dissolved in dry methylene chloride (5 mL). The reaction mixture was refluxed at 40 °C for 270 min. The solvents were stripped under reduced pressure, and the diastereomeric ratio was determined by NMR (*d,l*-**11**:*meso*-**11**, 96:4). The crude mixture was fractionated by column chromatography (Florisil, 20 g; PE) to afford *d,l*- and *meso*-**11** (47 mg, 87.2%) in the ratio of 97:3 (de 94%).

#### 4.9. Preparative studies at 147 °C

Analogous to the experiment conducted at 40 °C, the cation **17** was synthesized and dissolved in dry 1,1,2,2-tetrachloroethane (5 mL). The reaction mixture was refluxed at 147 °C for 1 min. The solvents were stripped under reduced pressure, and the diastereomeric ratio was determined by NMR (*d,l*-**11**:*meso*-**11**, 95:5). The crude mixture was fractionated by column chromatography (Florisil, 20 g; PE:E, 10:1) to afford *d,l*- and *meso*-**11** (43 mg, 80.2%) in the ratio of 97:3 (de 94%).

#### 4.10. *d,l*- and *meso*- $\mu$ - $\eta^2$ -[3,4-Di(3',4',5'-trimethoxyphenyl)-1,5-hexadiene]bis(dicobalthexacarbonyl) (**14**). Kinetic studies at 40 °C.

Under an atmosphere of nitrogen, alcohol **13** (127 mg, 0.25 mmol) was transferred to a flame-dried flask and dissolved in diethyl ether (15 mL). The solution was cooled to –20 °C and  $\text{HBF}_4 \cdot \text{Me}_2\text{O}$  (168 mg, 1.25 mmol) was added dropwise. After stirring for 1 h, the ethereal layer was removed, and the cation **16** was washed with diethyl ether (3 × 15 mL) at –20 °C. Residual amount of ether was stripped under reduced pressure (–20 °C) to afford the cation **16** as a dark red solid. Methylene chloride was added (5 mL), and the reaction mixture was refluxed at 40 °C. The aliquots (8; 0.1 mL) were extracted (up to 3 h; reaction time 180 min), via syringe, and dispersed in methanol (2 mL) at 20 °C. The sample was diluted with  $\text{H}_2\text{O}$  (2 mL) and then extracted with ether (2 mL). The solvent was evaporated under vacuum, and the crude mixture was analyzed by  $^1\text{H}$  NMR to determine the ratio of dimer **14** and Me-ether **15** (*d,l*-**14**, 4.26 ppm; *meso*-**14**, 4.28 ppm; Me-ether **15**, 6.03 ppm). The concentration curves (Fig. 5) were derived from  $^1\text{H}$  NMR data; numerical data presented are the average values from two consecutive runs. Upon the reaction completion the ratio of *d,l*- and *meso*-**14** was equal to 97:3 (NMR; de 94%). Both diastereomers were fully characterized in the previous account [10f].

#### 4.11. Preparative studies at 40 °C

Analogous to the experiment conducted at 40 °C, the cation **16** was synthesized and dissolved in dry methylene chloride (5 mL). The reaction mixture was refluxed at 40 °C for 180 min. The solvents were stripped under reduced pressure (NMR: *d,l*-**14**:*meso*-**14**, 97:3). The crude mixture was fractionated on Florisil column (20 g; PE) to yield *d,l*-**14** as a single diastereomer (34 mg, 55.7%).

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