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Spontaneous Generation and Stereoselective Coupling of $Co_2(CO)_6$-Complexed Propargyl Radicals

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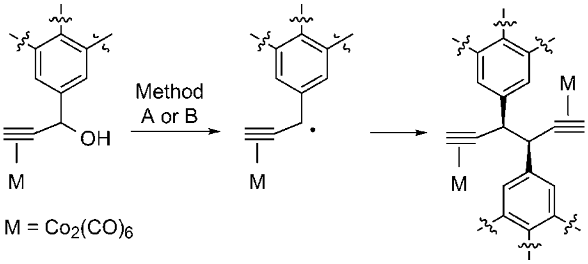
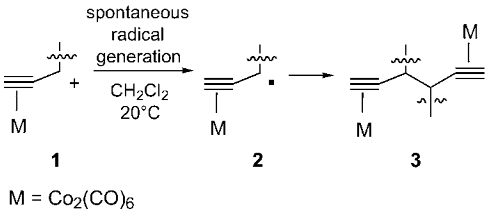
ABSTRACT



The spontaneous generation and stereoselective coupling of $Co_2(CO)_6$-complexed propargyl radicals have been discovered. One- and two-step complementary methods (Method A: (1) HBF_4; (2) CH_2Cl_2, 20 °C; Method B: Tf_2O, CH_2Cl_2, 20 °C) provided an easy access to synthetically useful d,l-3,4-diaryl-1,5-alkadiynes (de 74–98%).

Scheme 1



We discovered that cobalt-complexed propargyl cations **1** undergo spontaneous conversion to respective radicals **2** followed by an intermolecular coupling and formation of 1,5-hexadiynes **3** (Scheme 1). The reaction represents the newest example of generation of ligand-based organometallic radicals with an unpaired electron α to the metal core.[1,2] In contrast to their cationic counterparts,[3] cobalt-complexed propargyl radicals remain scarcely investigated, although the synthetic potential discovered so far is truly remarkable.[2,4] The parent reaction involves treatment of propargyl alcohol **4** ($R^1 = R^2 = H$) with HBF_4 and isolation of cationic species **5**, stable at low temperatures in a solid form (Scheme 2). Dissolving **5** in CH_2Cl_2 and exposing it to ambient temper-

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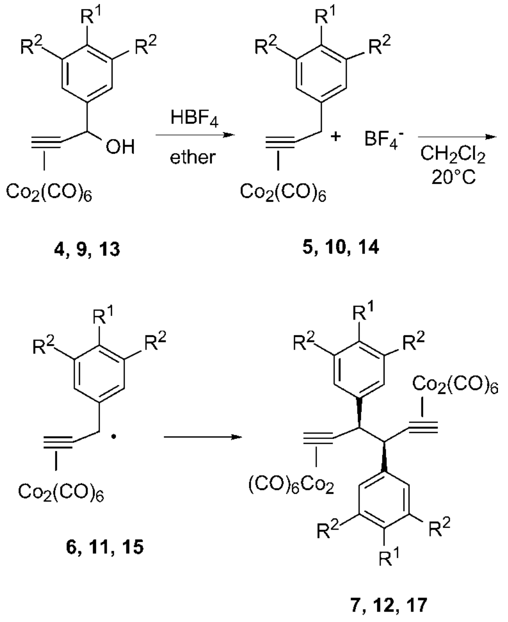
Scheme 2



4 - **7** $R^1 = R^2$ = H; **9** - **12** R^1 = OMe, R^2 = H;
13 - **15**, **17** $R^1 = R^2$ = OMe.

atures for 9 h (TLC/^{1}H NMR) resulted in its spontaneous conversion to propargyl radical **6** which, in turn, intermolecularly dimerized to D,L-dimer **7** (80%)[4c] with a diastereoselectivity of 88%. The reaction exhibits excellent chemoselectivity: (1) only "head-to-head" coupling was observed since the protection of triple bond with a metal cluster precludes an acetylene−allene rearrangement[5a] and (2) minute quantities of H-atom abstraction product, $(HC{\equiv}CCH_2Ph)Co_2(CO)_6$ (**8**), were detected, by NMR, in the crude mixture (2%). An incorporation of *p*-methoxy group into an aromatic nucleus appears to noticeably affect the reaction rate: derived from alcohol **9** (R^1 = OMe; R^2 = H), propargyl cation **10** achieves a full conversion in 13 h (TLC /^{1}H NMR). The retardation most probably occurs due to a slower generation of radical **11** since the dimerization step itself is known to be a diffusion-controlled process.[5b] D,L-Dimer **12** was isolated, as a pure stereoisomer,[4g] in a high yield (79.6%); also higher diastereo- (de 94%) and chemoselectivities were observed since the formation of the respective H-atom abstraction product, an analogue of hydrocarbon **8**, did not take place at all. To further test if the spontaneous cation-to-radical conversion is, in fact, dependent upon the nature of p-substituent, 3,4,5-trisubstituted substrate **13** ($R^1 = R^2$ = OMe) was probed. While the generation of cation **14** readily occurred, its conversion to the respective dimeric product, via radical **15**, was further retarded. After 25 h, upon treatment with MeOH, which converts any unreacted cationic species to $[HC{\equiv}CCH(OMe)\text{-}3,4,5\text{-}C_6H_4(OMe)_3]Co_2(CO)_6$ (**16**), the ratio of D,L-**17**:meso-**17**:**16** was equal to 51:8:41 (de 74%). A complete conversion was achieved with zinc (10 equiv, 20 °C, 20 h) acting as a reducing agent: an inseparable mixture of D,L-**17** and meso-**17** was isolated in a combined yield of 69.1% (de 74%). These data indicate that an increased π-donation from multiple MeO groups, via an aromatic ring, upon a cationic center, is rather inhibitory for the radical process (Figure 1). The "radicalization" of cation might occur by a single-electron transfer (SET) from a metal core toward a π-bonded propargyl ligand, an intramolecular *cluster-to-ligand reduction* (Scheme 3). Such a conversion might take place either via bonds or through the space (*spin−orbital interaction*), since, according to X-ray crystallographic data,[6] the α-carbon atom in cobalt-complexed propargyl cation is noticeably shifted toward one of two cobalt atoms (2.81 Å). An oxidized metal cluster (35 e$^-$) in radical **18** could then be reduced by a second molecule of cation **5** containing a 36 e$^-$ metal core. The suggested *cluster-to-cluster reduction* between electronically diverse transition metal species is well documented.[7]

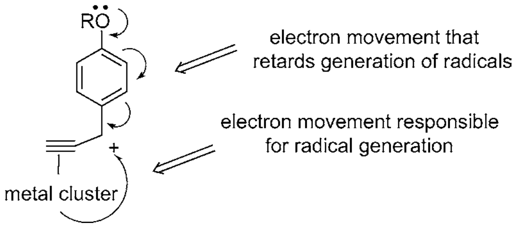
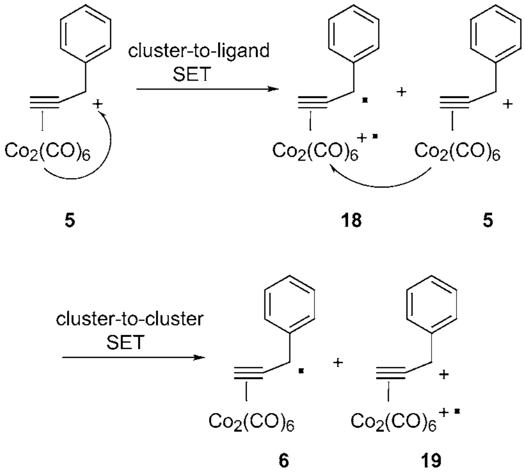


Figure 1.

Scheme 3



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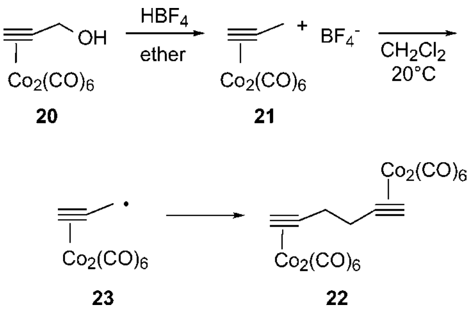
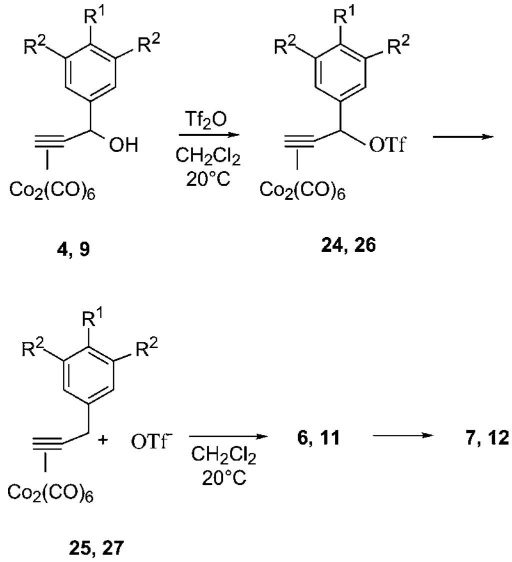
The radical **6** thus formed would give rise to D,L-dimers, while the highly electron-deficient species **19** would, most probably, undergo gross decomposition.[8] While an excessive stabilization of cationic centers proved to be inefficient for spontaneous radical generation, the stabilization provided by a phenyl group is rather crucial for the process. Derived from primary alcohol **20**, cation **21** afforded dimer **22** in a low yield (36.6%). The quenching with methanol did not derive the respective solvolysis product, an analogue of **16**, indicating that although the spontaneous generation of radical **23** did take place, a prolonged exposure of primary cation **21** to ambient temperatures might have caused its thermal decomposition (Scheme 4).

Scheme 4



Besides two-step spontaneous dimerization reaction, we also developed its *one-step variant* that precludes the very isolation of cobalt-complexed propargyl cations (Scheme 5). The treatment of propargyl alcohol **4** with a 2-fold excess of triflic anhydride afforded D,L-**7**:meso-**7** in a ratio of 92:8 (41.5%). It is most conceivable that mixed ester **24** is formed in situ, followed by a spontaneous C−O bond heterolysis and “radicalization” of cation **25**. The reaction is more efficient with a *p*-MeO group present: under analogous conditions, propargyl alcohol **9** gives rise to respective dimers, D,L-**12**:meso-**12**, in a ratio of 99:1. The higher isolated yield of D,L-**12** (67.6%) suggests more facile cleavage of intermediate ester **26** yielding cation **27**.

Scheme 5



4, **6**, **7**, **24**, **25** $R^1 = R^2 = H$;
9, **11**, **12**, **26**, **27** $R^1 = OMe$, $R^2 = H$.

The dimerization reaction thus found represents the *first reported case* of *spontaneous generation of radicals in a cobalt-alkyne series*.[1−3,7] It is noteworthy that the level of stereocontrol achieved in these reactions (up to 98% D,L-) is rather unprecedented both for organic[9] and organometallic[1,2] radical dimerizations. Besides its synthetic utility, the novel reaction might be of practical importance converting diamagnetic propargyl cations into paramagnetic radical species at various and substituent-dependent rates. This is conceptually precedented by the spontaneous formation of ferrocenyl radicals:[10] so-called *redox tautomerism* occurs under anaerobic conditions affording the respective bis-ferrocenyl dimeric products.[10a] Consistent with our findings is the fact that “too stable” ferrocenyl cations do not convert into their respective radicals[11] or undergo only partial conversion over an extended period of time.[10b]

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Supporting Information Available: Experimental procedures and full characterization for compounds DL- and meso-**7**, **12**, **17**, and **22**. This material is available free of charge via the Internet at http://pubs.acs.org.

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