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Cobalt-templated radical processes: inter- and intramolecular coupling of propargyl radicals

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Abstract

A novel method for radical C–C bond formation in the α-position to $Co_2(CO)_6$-clusters has been elaborated. The two-dimensional exploration of the process resulted in the discovery of structurally diverse O- and S-containing organic molecules capable of acting as efficient mediators in reductive coupling reactions, and in the elaboration of the preparative synthesis of 3,4-disubstituted 1,5-alkadiynes and carbocycles with eight- and nine-membered rings. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Propargyl cation; Propargyl radical; Cobalt complex; 1,5-Cycloalkadiyne; Crystal structure

1. Introduction

The chemistry of carbon-centered radicals π-bonded to transition metals is an emerging area at the interface of radical organic and organometallic chemistry. While the mode of interaction of an unpaired electron with a metal cluster is poorly understood, as well as the configurational and conformational specifics involved, the novel methods for radical generation and some useful C–C bond forming reactions have been reported [1]. Our interest in this area stems from manganese-initiated radical reactions of conjugated enynes [2] with chemoselectivity refined by complexation of the triple bond with a $Co_2(CO)_6$-protecting group [1l], as well as from facile, regioselective reduction of Co-complexed propargyl chloride [3], providing perhaps experimental evidence for the stabilizing effect of a metal core upon intermediate radical. In continuation of our program on the chemistry of transition-metal-altered reactive intermediates [1l–n,4], we reported recently on the inter- and intramolecular reductive coupling of Co-complexed propargyl cations mediated by zinc [1m,n]. While readily soluble cationic intermediates afford dimeric products in good yields, the experimental protocols are less feasible for monocations with lower solubility in CH_2Cl_2 and also for bis-propargyl cations, the starting materials for cyclic 1,5-alkadiynes. The main reason is the *heterogeneity of the reducing agent* that results in prolonged reaction times and substantially compromises the chemoselectivity of the process. Partial success was achieved with benzophenone ketyl in benzene [1n], although attendant with the latter are substantial experimental inconveniences. We report herein a novel experimental method for inter- and intramolecular radical C–C bond formation in the α-position to a Co-cluster which is mediated by a variety of *homogeneous agents*, O- and S-containing organic molecules.

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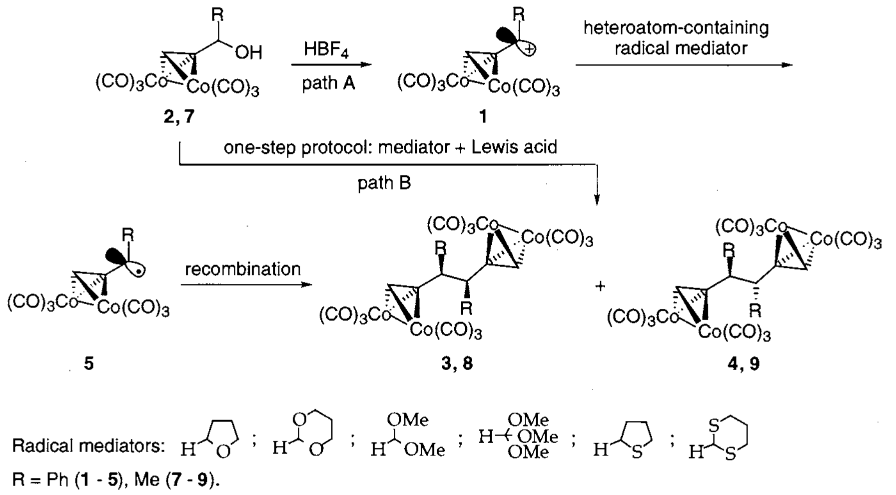


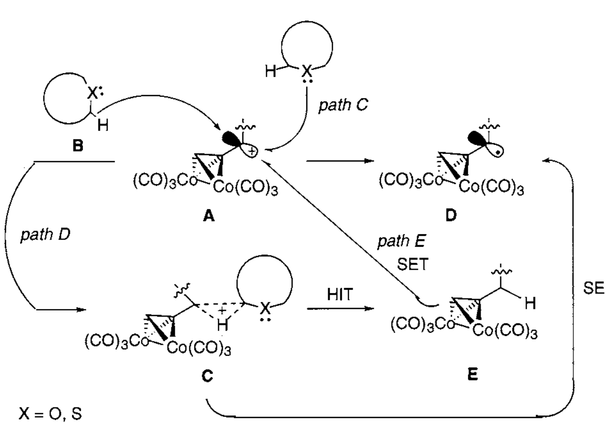
Scheme 1.

2. Results and discussion

We found that treatment of the cation **1**, derived from Co-complexed propargyl alcohol **2** [5], with topologically diverse O- and S-containing compounds affords isomeric bis-clusters **3** and **4** (Scheme 1, path A). The propargyl radical **5** is the most plausible precursor to the latter, indicating that cation **1** undergoes a one-electron reduction along the reaction coordinate. A variety of structures triggering reductive dimerization is exhibited in Scheme 1 comprising the five- and six-membered cyclic compounds (tetrahydrofuran, 1,3-dioxolane, tetrahydrothiophene, 1,3-dithiane) and their acyclic analogs with up to three heteroatoms (formaldehyde dimethyl acetal, trimethyl orthoformate). The standard protocol includes isolation of cation **1** [6] and subsequent treatment with a twofold excess of radical mediators at ambient temperature. The *diastereoselectivity* is remarkably high and varies in the range of 68–94%, with the D, L-isomer **3** as a major product. These results exceed by far the highest selectivity of 50% reported for Co-propargyl derivatives [1m], as well as for other organometallic species [1]. The *chemoselectivity* is determined by the concentration of the side-product, a hydrocarbon $(HC{\equiv}CCH_2Ph)Co_2(CO)_6$ (**6**), which reaches the highest mark of 14% with tetrahydrothiophene as a radical mediator. Its formation is not practically observed with most of compounds tested ($\leq 1\%$) thus making recombination the major conversion pathway for transient radicals **5**.

The method represents a two-step—heterolysis, one-electron reduction—conversion of propargyl alcohol **2** to dimeric bis-clusters **3** and **4** with high diastereo- and chemoselectivities. A further refinement of the parent procedure resulted in the elaboration of an even more attractive synthetic alternative, a one-step protocol, which allows for a *direct reductive dimerization* of alcohol **2** without a tedious isolation of intermediate cation **1** (Scheme 1, path B). The latter was achieved by a tandem action of equimolar quantities of HBF_4, a Lewis acid, and radical mediators. Among the latter, THF and 1,3-dioxolane exhibited the highest diastereoselectivity of 90%. From the synthetic viewpoint, the most attractive feature of novel protocols is the utilization of *homogeneous* and *easy-to-handle radical mediators* which stands in sharp contrast to the inconveniences associated with choosing heterogeneous [1m] or air-sensitive [1n] reducing agents. The *compatibility* of novel radical mediators with practically every functional group is another positive feature favorably distinguishing them from highly reactive species, such as benzophenone ketyl [1n]. It is noteworthy that the stabilizing effect of the $Co_2(CO)_6$-moiety upon the developing cationic center in **1** is crucial: the reaction does not take place with *uncomplexed* propargyl alcohols due to significant retardation of the heterolysis step.

The mechanism of radical mediation by O- and S-containing compounds, in particular, the genesis of an



Scheme 2.

Table 1
Crystal data and structure refinement for **8**, **9** and **13**

Identification code	**8**	**9**	**13**
Empirical formula	$C_{20}H_{10}Co_4O_{12}$	$C_{20}H_{10}Co_4O_{12}$	$C_{33}H_{18}Co_4O_{12}$
Formula weight	678.00	678.00	842.19
Temperature (K)	173(2)	293(2)	198(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell dimensions			
a (Å)	7.669(4)	6.936(4)	10.043(3)
b (Å)	11.485(3)	7.997(4)	10.229(6)
c (Å)	13.944(3)	11.941(4)	17.515(9)
α (°)	94.68(3)	77.64(3)	95.86(4)
β (°)	91.77(3)	80.57(4)	94.41(3)
γ (°)	101.77(3)	74.16(4)	106.59(4)
Volume (Å^3), Z	1196.9(7), 2	618.5(5), 1	1704.8(14), 2
Density (calc.) (mg m^{-3})	1.881	1.820	1.641
Absorption coefficient (mm^{-1})	2.785	2.695	1.973
F(000)	668	334	840
Crystal size (mm)	$0.43 \times 0.30 \times 0.18$	$0.25 \times 0.20 \times 0.15$	$0.30 \times 0.18 \times 0.10$
θ range for data collection (°)	1.47–24.97	1.76–24.95	1.18–21.98
Limiting indices	$-9 \leq h \leq 9$	$-8 \leq h \leq 8$	$-10 \leq h \leq 10$
	$-13 \leq k \leq 13$	$-9 \leq k \leq 9$	$-10 \leq k \leq 10$
	$-16 \leq l \leq 16$	$-14 \leq l \leq 14$	$-2 \leq l \leq 18$
No. of reflections collected	8850	4356	4427
No. of independent reflections	4197 ($R_{int} = 0.0670$)	2178 ($R_{int} = 0.0882$)	4169 ($R_{int} = 0.0060$)
Absorption correction	ψ	ψ	None
Max and min transmission	0.9996, 0.9304	0.9978, 0.9061	
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4191/0/325	2178/0/163	4168/0/337
Goodness-of-fit on F^2	2.103	1.058	1.197
Final R indices [$I \geq 2\sigma(I)$]	$R_1 = 0.0487$, $wR_2 = 0.1012$	$R_1 = 0.0562$, $wR_2 = 0.1443$	$R_1 = 0.0686$, $wR_2 = 0.1765$
R indices (all data)	$R_1 = 0.0582$, $wR_2 = 0.1212$	$R_1 = 0.0670$, $wR_2 = 0.1633$	$R_1 = 0.0978$, $wR_2 = 0.1985$
Largest difference peak and hole (e Å^{-3})	0.917, −0.635	0.912, −0.697	0.749, −0.521

electron that reduces cation **1**, is not well established [7]. Despite its deceptive simplicity, the two-component composition—cation **1** and radical mediator—provides a number of chemically conceivable pathways which might account for the formation of dimeric products. The most obvious one includes delivery of a single electron from an heteroatom (O, S) towards a cationic center (Scheme 2, path C), which can be ruled out based on several lines of evidence. First, reaction does not occur with diethyl ether as used in the standard isolation procedure [6]; second, the reaction time is different for all four O-containing mediators, ranging from 10 min to 4 h; and third, no acceleration is observed with tetrahydrothiophene relative to tetrahydrofuran (1.5 h vs. 1.5 h), the one that might be expected based on the lower electronegativity of the sulfur atom. It should also be mentioned that the interaction of Co-complexed cations with O-, S-, P- and N-nucleophiles is well documented to produce respective solvolysis products, while formation of dimeric bis-clusters has not been observed [6,8]. An alternative scenario is represented by path D (Scheme 2) with initial attack of an electrophile, a p-orbital in cation A, on the filled bond orbital of α–C–H bond in mediator **B**. Such a coordination is analogous to that postulated for boron–hydrogen bond hydrolysis [9], and was also invoked to interpret the structural features of stable organic cations [10]. The tentative transition state (**C**) might include a cyclic three-membered molecular fragment [10b,11] which could undergo either single-electron transfer (SET) or hydride-ion transfer (HIT, [12]) to radical **D** or hydrocarbon **E**, respectively. The latter itself can act as an electron source because the metal cluster supposedly has a higher electron density compared to that in cation **A** (path **E**). The reaction pathways are not limited to those in Scheme 2; in fact, a number of other interactive modes can be envisioned [13] which are currently under detailed mechanistic investigation [14]. From a practical viewpoint, an understanding of the stoichiometry is important for calculation of the actual yields of dimeric products [15].

The one-step method for reductive dimerization has also been applied to the secondary alcohol **7** which produces a cation with a low solubility in methylene

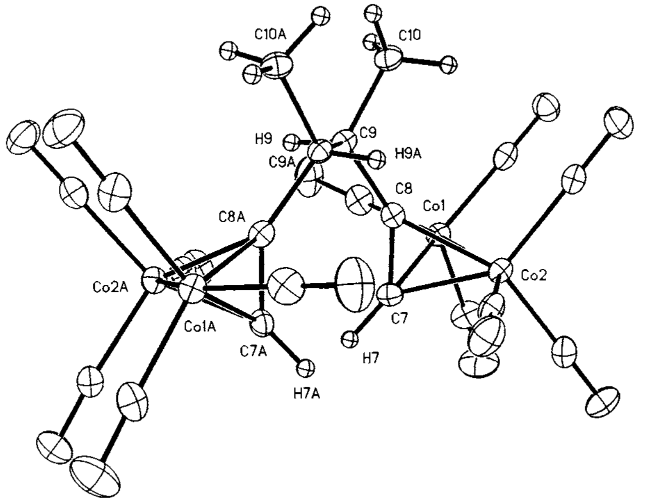


Fig. 1. X-Ray determined molecular structure of D, L-**8** with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (°): C7–C8 1.318(7), Col–Co2 1.769(6), H7–C7–C8 136.0(3), C7–C8–C9 144.1(5), H7A–C7A–C8A 135.9(3), C7A–C8A–C9A 143.6(5), H7A–H7 2.29(1), H7A–C7A–C8A–C9A − 3.4(2), H7–C7–C8–C9 − 4.6(2), H9–C9–C9A–H9A 172.0(5), C10–C9–C9A–C10A 46.1(3), C8A–C9A–C9–C8 − 62.6(3), C8A–C9A–C9–C10 − 172.0(5), C8–C9–C9A–C10A − 171.8(5), C7C8–C7AC8A 11.8(3). The numbering scheme used illustrates the pseudo-C2 geometry and was chosen to facilitate comparison of bond lengths and angles in this molecule.

chloride; this, in turn, results in low conversion (58%) and extended reaction time (17 h) even in the presence of fivefold excess of heterogeneous reducing agent [1m]. Under standard procedure including the treatment of alcohol **7** with twofold excess of HBF$_4$ and tetrahydrofuran, D, L- and *meso*-isomers **8** and **9** were isolated and their structures established by means of X-ray crystallography (Table 1). The former adopts a pseudo-C2 symmetric conformation (Fig. 1) with noticeably distorted *gauche*-orientation of methyl groups (C10–C9–

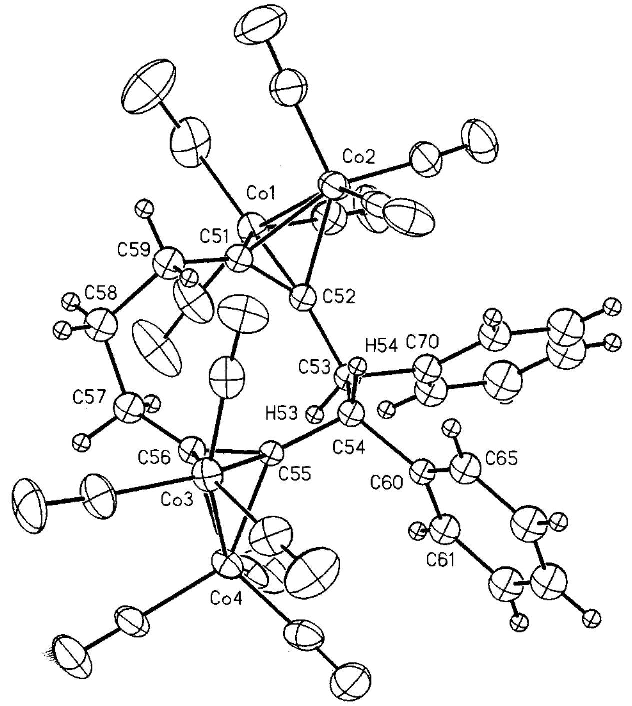


Fig. 3. X-Ray determined molecular structure of D, L-**13** with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (°): C51–C52 1.34(1), C55–C56 1.32(1), Col–Co2 2.464(2), Co3–Co4 2.467(2), C53–Col 3.21(1), C53–Co2 3.20(1), C54–Co3 3.20(1), C54–Co4 3.18(1), C59–Col 3.19(1), C59–Co2 3.11(1), C57–Co3 3.24(1), C57–Co4 3.13(1), C70–C61 3.08(1), C70–C65 4.05(1), C52–C51–C59 145.5(9), C51–C52–C53 143.9(8), C70–C53–C54 116.7(7), C70–C53–H53 106.6(5), C60–C54–C53 114.8(7), C60–C54–H54 107.1(4), C56–C55–C54 143.2(8), C55–C56–C57 143.5(8), C58–C57–C56 118.1(8), C57–C58–C59 116.0(8), C51–C59–C58 115.8(8), H54–C54–C53–H53 − 150.8(4), C70–C53–C54–C60 − 28.5(3), C52–C53–C54–C55 79.6(4), C55–C54–C53–C70 − 153.8(7), C52–C53–C54–C60 − 155.1(6), C53–C52–C51–C59 3.6(3), C54–C55–C56–C57 6.3(3); angle between the bonds: C55–C56 and Co3–Co4 88.7(6), C51–C52 and Col–Co2 90.3(6), Col–Co2 and Co3–Co4 42.6(5), C51–C52 and C55–C56 44.5(5); angle between phenyl rings 60.8(5).

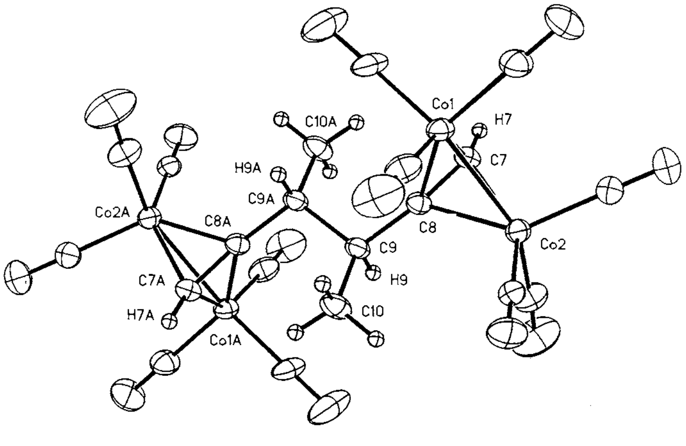
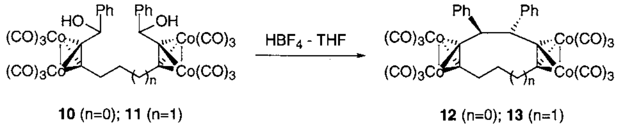


Fig. 2. X-Ray determined molecular structure of *meso*-**9** with 30% probability ellipsoids. Selected interatomic distances (Å) and angles (°): C7–C8 1.323(3), Col–Co2 1.775(2), H7–C7–C8 139.9(1), C7–C8–C9 144.2(2), H7–C7–C8–C9 6.7(1), H9A–C9A–C9–H9 180, C8–C9–C9A–C10A 54.5(1). Molecules of *meso*-**9** contain a center of symmetry utilized and consistent with the special position symmetry of the lattice, e.g. there is only one molecule per unit cell in space group $P\bar{1}(\#2)$ and the molecule sits on the crystallographic center.

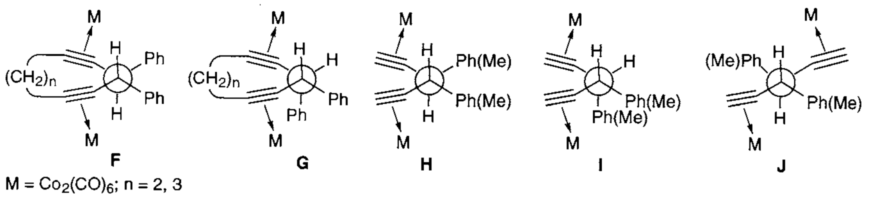


Scheme 3.

C9A–C10A 46.1°) and nearly ideal disposition of Co-alkyne units (C8A–C9A–C9–C8 62.6°). As molecular modeling shows, the repulsion between axial CO-groups pushes the metal clusters away from each other, which in turn brings the C–C triple bonds in close-to-parallel locations (C7C8–C7AC8A 11.8°). Acetylenic hydrogens (H7A, H7) are remarkably proximate to each other with a separation distance of 2.29 Å, less than the sum of the van der Waals radii (about 2.5 Å). Other noteworthy structural features of **8** include: (1) an essentially undistorted planarity of alkyne moieties (H7A–C7A–C8A–C9A −3.4°, H7–C7–C8–C9 −4.6°); (2) a bent geometry for the coordinated alkyne unit (C7–C8–C9 144.1°, C7A–C8A–C9A 143.6°) with substantially smaller angles for acetylenic termini (H7–C7–C8 136.0°, H7A–C7A–C8A 135.9°); and (3) a lengthened coordinated C–C triple bond (1.32–1.33 Å vs. 1.21 Å for free ligand) attendant with complexation to transition metal. The *meso*-complex **9** has C_i-symmetry with the center of symmetry positioned on the C9–C9A bond (Fig. 2). In contrast to the D, L-isomer, the molecule crystallizes in an extended conformation with metal clusters further apart from each other.

The novel synthetic methodology has also been applied for the construction of eight- and nine-membered carbocycles with 1,5-disposition of triple bonds. Synthesized by conventional methods [16], bis-complexes **10** and **11** were exposed to a combined action of HBF_4 and THF in optimized molar ratios of 1:10:10 and 1:4:20, respectively. In situ generation of bis-cationoid species and subsequent double reduction to bis-radicals affords cyclized products **12** and **13**, each represented by a single stereoisomer. Their configurations as D, L- were determined by spectral and chromatographic comparison with an authentic sample (**12**, [1n]), and by means of X-ray diffraction (**13**, Fig. 3). The molecular assembly around carbon atoms bearing phenyl groups (C53, C54) is severely distorted, which is indicated by values of bond angles (C70–C53–C54 116.7°; C60–C54–C53 114.8°) and dihedral angles (H54–C54–C53–H53 −150.8°; C70–C53–C54–C60 −28.5°). The aromatic nuclei are twisted relative to each other forming an angle of 60.8°; in accord with this deviation are the following non-bonding interatomic distances: C70–C61 3.08Å and C70–C65 4.05Å. While cobalt-alkyne units are essentially undistorted with angles of bent triple bonds lying within the expected range (143–145°) and nearly planar π-bonded ligands (3.6°, 6.3°), the nine-membered ring is nevertheless highly strained. It is substantiated by bond angles for sp^3-hybridized ring carbons (C58–C57–C56 118.1°, C57–C58–C59 116.0°, C51–C59–C58 115.8°), and the relative twist of metal cores quantified by the angle between metal–metal vectors (Co1–Co2 and Co3–Co4 42.6°) or C–C triple bonds (C51–C52 and C55–C56 44.5°). It is worthy to mention that the molecule has C_2-symmetry with the C58 atom positioned on the pseudo twofold axis which, in turn, bisects the C53–C54 bond.

The novel approach to the synthesis of 1,5-cycloocta- and 1,5-cyclononadiynes (**12**, **13**) constitutes the major improvement over the existing methods [1m–n,17]. The exclusive D, L-diastereoselectivity can be explained based on conformational analysis of reactive intermediates (Schemes 3 and 4). Diradical **F**, a precursor of D, L-**12** and D, L-**13**, represents the only conformation with anti-disposition of H-atoms and two *gauche* interactions between bulkier substituents. The rotamer **G** has three destabilizing *gauche* interactions which make it kinetically disfavored, and the cyclization process itself highly stereoselective. In intermolecular coupling reactions the steric hindrance is minimized for **H**, an acyclic analog of conformer **F**, which produces D, L-isomers **3** and **8**. The major structural difference between otherwise analogous species **G** and **I** is the tether: sterically hindered intermediates **I** can convert to more stable species **J** which are responsible for the formation of *meso*-isomers **4** and **9**. Such an explanation is substantiated by results of X-ray crystallographic analysis (Figs. 1 and 2) revealing C_2 and C_i-symmetry for D, L-**8** and *meso*-**9**, respectively. The difference in diastereoselectivity for dimerization of alcohols **2** and **7** (68–94% vs. 8% [18]) is likely determined by the larger bulkiness of the phenyl group relative to the methyl (104 Å^3 vs. 33 Å^3) which might result in better kinetic differentiation of the intermediates **H** and **J**.



Scheme 4.

3. Experimental

3.1. Syntheses

3.1.1. D,L- and meso-μ-η^2-(3,4-Diphenyl-1,5-hexadiyne)-bis-dicobalt hexacarbonyl (**3**, **4**) and μ-η^2-(3-phenyl-1-propyne)dicobalt hexacarbonyl (**6**)

3.1.1.1. With isolation of propargyl cation ***1*** *(two-step protocol).* Under a nitrogen atmosphere, complex **2** (105 mg, 0.25 mmol) was placed in a flame-dried flask and dissolved in dry diethyl ether (20 ml). A solution was cooled (-20°C) and treated with $HBF_4 \cdot Et_2O$ (203 mg, 1.25 mmol). After stirring for 30 min, the ethereal layer was removed, and cation **1** was washed with dry ether (3×20 ml) at -20°C. A residual amount of ether was stripped under reduced pressure to afford cation **1** (104 mg, 85%) as a dark-red solid. Methylene chloride (2.5 ml) and radical mediator (0.5 mmol) were added at room temperature, and the reaction was monitored by TLC. The crude mixture was filtered through a short bed of Florisil (60–100 mesh, 700 mg), and the ratio of products **3**:**4**:**6**:**14** [19] was determined by NMR. The isolation of dimers was carried out on an SiO_2-column (70–230 mesh, 10 g, petroleum ether) to afford dark-red crystals which were identical by physico-chemical and spectral (TLC, NMR, FAB) data with authentic samples synthesized according to the known procedure [1m]. Radical mediator, reaction time, ratio of **3**, **4**, **6** and **14** (NMR), yields of **3** + **4** (%), de: *tetrahydrofuran*, 1.5 h, 93:5:1:1, 46 [15], 90; *1,3-dioxolane*, 4 h, 88:5:6:1, 38 [15], 90; *formaldehyde dimethyl acetal*, 2 h, 95:3:0:2 [20a], 32 [15], 94; *trimethyl orthoformate*, 10 min, 92:8:0:0 [20b], 27 [15], 84; *tetrahydrothiophene*, 1.5 h, 70:13:14:3, 37 [15], 68; *1,3-dithiane*, 1 h, 90:5:0:5, 26 [15], 90.

3.1.1.2. Without isolation of propargyl cation 1 (one-step protocol). As described previously [5], a treatment of complex **2** (105 mg, 0.25 mmol) with THF (36 mg, 0.5 mmol) and $HBF_4 \cdot Et_2O$ (81 mg, 0.5 mmol) in CH_2Cl_2 (2.5 ml, 0.1 M) for 4.5 h afforded **3** and **4** (de 90%) with a yield of 47% [15]. Analogous reaction with 1,3-dioxolane (37 mg, 0.5 mmol) in 7 h yields **3**, **4** and **14** in the ratio of 94.9:4.7:0.4 (46% [15], de 90%).

3.1.2. D,L- and meso-μ-η^2-(3,4-Dimethyl-1,5-hexadiyne)-bis-dicobalt hexacarbonyl (**8**, **9**)

Under nitrogen atmosphere, a solution of complex **7** (89 mg, 0.25 mmol) and THF (36 mg, 0.5 mmol) in CH_2Cl_2 (2.5 ml, 0.1 M) was cooled (-5°C) and treated with $HBF_4 \cdot Et_2O$ (81 mg, 0.5 mmol). Reaction mixture was allowed to warm up to room temperature (30 min), stirred for 3 h (TLC control), filtered through Florisil (100–200 mesh, 14 g, pentane) under anaerobic conditions and concentrated. Fractionation by preparative TLC (SiO_2, pentane) afforded **8** and **9** (17 mg, 20% [15]) in the ratio of 54:46 (de 8%). TLC (PE): R_f 0.52. M.p. 50–80°C (decomp. without melting). ^{1}H-NMR (200 MHz, $CDCl_3$): D,L-diastereomer **8** 6.14 (d, 2H, HC≡, $J = 0.4$ Hz), 3.04 (m, 2H, CH), 1.35 (d, 6H, CH_3, $J = 6.7$ Hz); *meso*-diastereomer **9** 6.18 (s, 2H, HC≡), 2.64 (m, 2H, CH), 1.52 (d, 6H, CH_3, $J = 6.2$ Hz). MS-FAB: 678 (M^-, 2%), 622 (M^-–2CO, 4%), 594 (M^-–3CO, 11%), 566 (M^-–4CO, 9%), 538 (M^-–5CO, 5%), 510 (M^-–6CO, 6%), 479 (M^-–5CO–Co, 19%), 451 (M^-–6CO–Co, 8%), 426 (M^-–9CO, 3%). Single crystals suitable for X-ray structure analysis (Figs. 1 and 2) were obtained by methanol vapor diffusion into a solution of Co-complexes D,L-**8** and *meso*-**9** in petroleum ether.

3.1.3. bis-(D,L-3,4-Diphenyl-1,5-cyclooctadiyne)-dicobalt hexacarbonyl (**12**)

Under nitrogen atmosphere, a solution of complex **10** [1k,16] (48 mg, 0.056 mmol) and THF (40 mg, 0.56 mmol) in CH_2Cl_2 (0.56 ml, [**10**] = 0.1 M) was treated with $HBF_4 \cdot Et_2O$ (90 mg, 0.56 mmol) at -5°C. Reaction mixture was warmed up to room temperature and stirred additionally for another 7 h (TLC control). Isolation by preparative TLC (SiO_2, petroleum ether:ether 3:1, 4°C) afforded 15 mg of **12** (39% [15], de 100%, conversion 84%) identical by physico-chemical (m.p., TLC) and spectral (NMR, FAB) data with authentic sample synthesized according to a known procedure [1n].

3.1.4. bis-(D,L-3,4-Diphenyl-1,5-cyclononadiyne)-dicobalt hexacarbonyl (**13**)

Under a nitrogen atmosphere, a solution of complex **11** [16] (98 mg, 0.112 mmol) and THF (161 mg, 2.24 mmol) in CH_2Cl_2 (11.2 ml, [**11**] = 0.01 M) was treated with $HBF_4 \cdot Et_2O$ (73 mg, 0.448 mmol) at -5°C. The reaction mixture was warmed up to room temperature and stirred for 5 h (TLC control). To compensate for minor mono-decomplexation of **13**, the reaction mixture was treated with $Co_2(CO)_8$ (15 mg, 0.044 mmol) for 2 h, concentrated under reduced pressure to 2.5 ml and applied to preparative TLC plate (SiO_2, pentane, 4°C, extraction with THF). Afforded was 41 mg of **13** (43% [15], de 100%) as a dark-red solid. TLC (PE:E 15:1): R_f 0.70. T_{decomp} 40–45°C (without melting). ^{1}H-NMR (200 MHz, C_6D_6): 1.65–1.85 (m, 9 lines, 2H, CH_2), 3.02 (ABX_2 system, 4H, $2CH_2$, $J_{H(A)-H(B)} = 15.1$, $J_{H(A)-H(X)} = 4.5$, $J_{H(B)-H(X)} = 8.6$), 4.62 (s, 2H, CH), 6.70–7.10 (m, 10H, 2Ph). ^{13}C-NMR (50 MHz, C_6D_6): 28.5, 33.0, 55.3, 97.5, 107.9, 127.0, 128.2, 128.3, 129.9, 130.1, 200.1. FAB: 842 (M^+, 3.5%), 814 (M–CO, 5.5%), 786 (M–2CO, 6.7%), 758 (M–3CO, 16.9%), 730 (M–4CO, 8.9%), 702 (M–5CO, 4.0%), 674 (M–6CO, 6.9%), 646 (M–7CO, 5.1%), 615 (M–6CO–Co, 20.4%), 562 (M–10CO, 3.1%), 528 (M–7CO–2Co, 15.9%). HR-FAB: calc. for $C_{33}H_{18}O_{12}Co_4$ M^+ 841.812618, found

841.814800. Single crystals suitable for X-ray structure analysis (Fig. 3) were obtained by methanol vapor diffusion into a solution of **13** in benzene.

3.2. Crystallography

Suitable crystals, each, of D, L-**8**, *meso*-**9** and D, L-**13**, were mounted and placed in a goniometer head on the Enraf-Nonius CAD4 diffractometer, and centered optically. The crystal of D, L-**8** was glued to a glass fiber held in a brass pin, but the crystals of *meso*-**9** and D, L-**13** were coated with Paratone oil and placed on the ends of 3 mm silica rods which had been drawn out to a 0.10 mm fiber and cooled to 173 and 198 K, respectively. Cell parameters and an orientation matrix for data collection were obtained by using the centering program in the CAD 4 system. Details of the crystal data for each compound are given in Table 1. For each crystal, the actual scan range was calculated by scan width = scan range + 0.35 tan θ and backgrounds were measured by using the moving-crystal-moving-counter technique at the beginning and end of each scan. Two representative reflections were monitored every 2 h as a check on instrument and crystal stability. Lorentz, polarization, and decay corrections were applied to all data sets, and an empirical absorption correction, based on a series of ψ scans, was applied to the data for D, L-**8** and *meso*-**9**. The weighting scheme used during refinement was $1/\sigma^2$, based on counting statistics.

The structures were solved by the direct methods using SHELXS-86 [21], which revealed the positions of most of the atoms. All other non-hydrogen atoms were found by successive difference Fourier syntheses. Hydrogen atoms were placed in their expected chemical positions using the HFIX command in SHELXL-93 [22] and all hydrogens were included in the final cycles of least squares with isotropic U_{ij} values related to the atom's ridden upon. All other non-hydrogen atoms were refined anisotropically, except the noncarbonyl carbon atoms in complex **13**.

Scattering factors were taken from the International Tables for X-ray Crystallography [23]. All data processing was carried out on a DEC 3000 AXP computer using the Open MolEN system of programs [24]. Structure solution, refinement and preparation of figures and tables for publication were carried out on PCs using SHELXS-86 [21], SHELXL-93 [22] and XP/PC [25].

4. Supplementary material

Supplementary materials consist of coordinates, thermal parameters, complete bond distances and angles for complexes **8**, **9** and **13**. Crystallographic data has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 102651 for complex **8**, No. 102652 for complex **9**, and No. 102653 for complex **13**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax (int code) + 44 (1223) 336-033, or e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

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[20] (a) Methoxy-group transfer product $[HC{\equiv}CCH(OMe)Ph]Co_2(CO)_6]$ was isolated by column chromatography (SiO_2, petroleum ether:benzene, 2:1) in a yield of 11%. TLC (PE): $R_f = 0.11$. ^{1}H-NMR ($CDCl_3$): 3.46 (s, 3H, OMe), 5.29 (d, 1H, CH, $J = 0.83$ Hz), 6.03 (d, 1H, HC≡, $J = 0.92$ Hz), 7.28–7.42 (m, 5H, Ph). FAB: 432 (M^+, 3%), 348 ($-3CO$, 100%); (b) Yield of $[HC{\equiv}CCH(OMe)Ph]Co_2(CO)_6$ was 60%.

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