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A novel approach to the synthesis of azobenzene using dicobalt carbonyl†

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Reaction of $Co_2(CO)_8$ with $HC{\equiv}CC_6H_4NH_2$ in THF at 55 °C for 4 hours gave an unusual complex $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]C_6H_4N{=}\}_2$ 2 in reasonable yield; the crystal structure of 2 reveals that it can be regarded as two alkyne-bridged dicobalt fragments joined by a diazene-based ligand; a mechanism for the formation of 2 is proposed.

It has been shown previously that an unusual carbonylation of primary amine takes place at room temperature when using $Co_2(CO)_8$ as catalyst (Scheme 1).[1] Complex **1**, $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]CH_2NH\}_2C{=}O$, can be seen as two propargylamine-bridged dicobalt complexes coupled by a carbonyl group. Noticeably, carbonylation,[2] linking two propargylamine-bridged dicobalt complexes, takes place during the reaction. To the best of our knowledge, there is no prior example of the preparation of an azobenzene derivative from two primary amines through a cobalt-mediated reaction.[3] We report herein a one-pot reaction of the formation of an azobenzene compound, a potential liquid crystal raw material,[4] from 4-ethynylaniline *via* a cobalt-assisted coupling reaction.

Treatment of $Co_2(CO)_8$ with one molar equivalent of $HC{\equiv}CC_6H_4NH_2$ in THF at 55 °C for 4 hours gave an unusual complex, $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]C_6H_4N{=}\}_2$ (**2**; 18.3%) (Scheme 1).‡ The yield of **2** can be up to 38.4% by appropriate adjustment of the molar ratios of the two reactants (Table 1).

Suitable crystals of **2** were obtained on recrystallisation from CH_2Cl_2–hexanes (1 : 1) at 4 °C and its structure was determined by an X-ray diffraction method.§ The structure of **2** (Fig. 1) can be viewed as two alkyne-bridged dicobalt fragments linked by a diphenyldiazene. Alternatively, it can be seen as two dicobalt fragments, $Co_2(CO)_6$, coordinated to $HC{\equiv}C{-}C_6H_4{-}N{=}N{-}C_6H_4{-}C{\equiv}CH$. It is interesting that the azo-like compound **2** was observed rather than the expected type **1** compound (Scheme 1). The bond length of N–N(0A) is 1.240(5) Å, a typical N=N bond. It is 1.340(4) Å for C(7)–C(8), which is a typical C=C bond. The interatomic distance of Co(1)–Co(2), at 2.4724(5) Å, falls within the normal range for a Co–Co single bond.[5] The bond angle of N(0A)–N–C(12) is 113.0(3)°, is consistent with normal sp^2 hybridization of the nitrogen atom. The existence of an N=N bond is also confirmed by an absorption at 1402 cm^{-1}, characteristic of an azo-group, in the infrared spectrum. Noticeably, the parallel reaction of $HC{\equiv}CC_6H_4NH_2$ with $Ru_3(CO)_{12}$ was previously shown to result in the formation of the acetylide derivative $[(\mu\text{-}H)Ru_3(CO)_9(\mu_3\text{-}C{\equiv}CC_6H_4NH_2)]$ *via* C–H bond activation.[6]

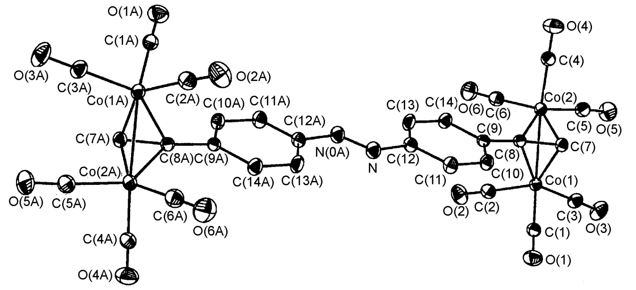
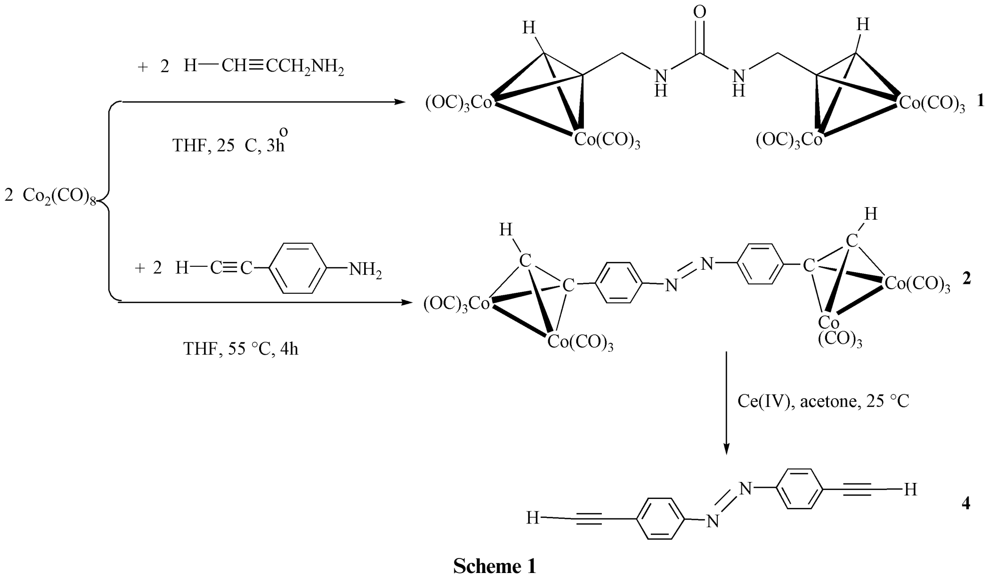


Fig. 1 The molecular structure of $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]C_6H_4N{=}\}_2$ **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°) for **2**: N–N(0A) 1.240(5), N–C(12) 1.442(3), C(7)–C(8) 1.340(4), Co(1)–Co(2) 2.4724(5); C(7)–C(8)–C(9) 142.7(3), C(12)–N–N(0A) 113.0(3).

The reactions of $Co_2(CO)_8$ with 4-ethynylaniline under various reaction conditions were carried out and the results are listed in Table 1. Several observations are noteworthy. Firstly, the yield of **2** was maximized for a molar ratio of $Co_2(CO)_8$ to



Scheme 1

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† Electronic supplementary information (ESI) available: proposed mechanism for the formation of **1** and **2**; DFT studies on intermediates **Va** and **Vb**. See http://www.rsc.org/suppdata/dt/b2/b204881g/

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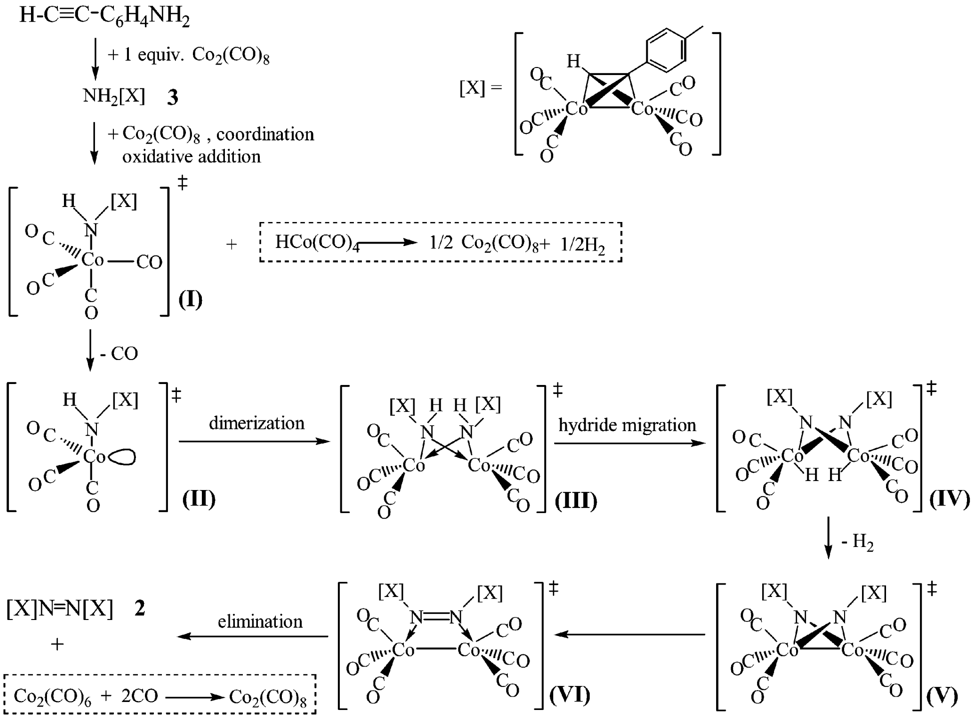

Fig. 2 Proposed mechanism for the formation of **2**.

Table 1 The reaction of $Co_2(CO)_8$ with 4-ethynylaniline[a]

Entry	[M] : [EA] : [NEt$_3$][b]	CO/psi	Yield of **2** (%)
1[c]	1.0 : 1.0 : 0	—	13.6
2	1.0 : 1.0 : 0	—	18.3
3	1.5 : 1.0 : 0	—	31.9
4	1.75 : 1.0 : 0	—	38.4
5	2.0 : 1.0 : 0	—	36.3
6	1.0 : 1.0 : 2.0	—	16.6
7	1.0 : 1.0 : 0	14.7	14.3
8	1.0 : 1.5 : 0	—	9.9
9	1.0 : 1.0 : 0	500	5.3

[a] All of the above reactions, except Entry 1, were carried out at 55 °C for 4 hours. [b] [M]: $Co_2(CO)_8$; [EA]: 4-ethynylaniline. [c] The reaction was carried out at 25 °C for 4 hours.

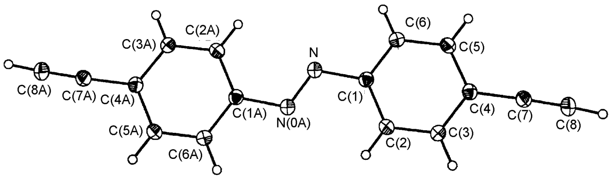

Fig. 3 The molecular structure of $HC{\equiv}CC_6H_4N{=}NC_6H_4C{\equiv}CH$ **4**. Selected bond lengths (Å) and bond angles (°) for **4**: N–N(0A) 1.247(2), C(7)–C(8) 1.180(2), C(8)–C(7)–C(4) 177.90(15), C(1)–N–N(0A) is 114.66(13).

4-ethynylaniline of about 1.75 : 1. Secondly, the yield of **2** was reduced under one atmosphere of carbon monoxide. Third, the yield of **2** was found to decrease in the presence of NEt_3.

The reaction mechanism proposed for formation of **2** is shown in Fig. 2. First, the triple bond of 4-ethynylaniline is bridged by a dicobalt hexacarbonyl fragment to form $Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_4NH_2)$ **3** followed by the coordination of **3** to another molar equivalent of $Co_2(CO)_8$ through its amine site. Presumably, a splitting of two uni-cobalt complexes, $[Co_2(CO)_6(\mu\text{-}HC{\equiv}CC_6H_4NH)Co(CO)_4]$ (**I**) and $HCo(CO)_4$ takes place after an oxidative addition process. Then, the first step involves loss of CO from **I**, forming the activated complex **II**, which subsequently dimerizes to yield **III**. Subsequent processes including hydride migration, hydrogen elimination, and N=N bond formation are attributed to formation of intermediates **IV**, **V** and **VI**, respectively. The product **2** results from reductive elimination of **VI**. Based on computational studies by the density functional theory (B3LYP) method,[7] we believe that the reason for the formation of **2** rather than type **1** compounds rests on the characteristics of intermediate **V**.

The organic moiety, $HC{\equiv}CC_6H_4N{=}NC_6H_4C{\equiv}CH$ **4**, was obtained by treatment of **2** with oxidant, Ce(IV),[8] and work-up (Scheme 1).¶ The structure of **4** (Fig. 3) was determined by an X-ray diffraction method.‖ The bond length of N–N(0A) is 1.247(2) Å, a typical N=N bond. It is 1.180(2) Å for C(7)–C(8), which is a typical C≡C bond. The bond angle of C(1)–N–N(0A) is 114.66(13)°, which is close to that of **2** and also indicates that the two nitrogen atoms exist at almost sp^2 hybridization. This strong yellow colored compound is also evidenced by the absorption at 451.6 nm in the UV-VIS spectrum.

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Notes and references

‡ Synthesis of **2**: A solution of $Co_2(CO)_8$ (0.6000 g, 1.750 mmol) and 4-ethynylaniline (0.2100 g, 1.790 mmol) in 20 cm^3 of THF was frozen and degassed. The solution was then allowed to warm up to room temperature and stirred for 4 hours. Subsequently the resulting red solution was filtered through silica gel and purified using centrifugal thin-layer chromatography (CTLC). The first orange–red band of the title compound, $\{[Co_2(CO)_6(\mu\text{-}HC{\equiv}C)]C_6H_4N{=}\}_2$ **2**, was eluted with CH_2Cl_2–hexanes (1 : 1) and the solvent was removed *in vacuo* to yield **2** (13.6%, 0.0956 g, 0.1190 mmol). The optimized yield of **2**, 38.4%, was achieved when the molar ratio of $Co_2(CO)_8$ to 4-ethynylaniline was 1.75 : 1 and the reaction was carried out at 55 °C for 4 hours (see Table 1). Selected spectroscopic data for **2**: IR (CH_2Cl_2/cm^{-1}) ν1402.1 (N=N), 2097.8 (CO), 2058.1 (CO), 2021.6 (CO); ^{1}H NMR ($CDCl_3$): δ 7.89 (d, J_{H-H} = 8.20 Hz, 2H, arene), 7.66 (d, J_{H-H} = 8.40 Hz, 2H, arene), 6.435 (s, 1H, ≡CH); ^{13}C NMR ($CDCl_3$): δ 199.11 (CO), 152.08 (1C, *ipso*-arene), 141.11 (1C, *p*-arene), 130.95 (2C, *o*-arene), 123.49 (2C, *m*-arene), 88.41 (1C, ≡C), 72.82 (1C, ≡CH); FAB mass spectrum of **2**, *m*/*z*: 804.7 [M$^+$]; Elemental analysis: calc. for **2** C 41.93, H 1.26, N 3.49; Found: C 39.35, H 1.39, N 3.90%.

§ Crystal data for **2**: $C_{14}H_5Co_2NO_6$, $M = 401.05$, triclinic, space group $P\bar{1}$, $a = 8.2979(6)$, $b = 9.6328(8)$, $c = 9.7840(8)$ Å, $\alpha = 78.950(2)$, $\beta = 75.756(2)$, $\gamma = 88.829(2)°$, $V = 743.67(10)$ Å^3, $Z = 2$, $D_c = 1.791$ Mg m^{-3}, $\mu = 2.259$ mm^{-1}, $F(000) = 396$, $T = 293(2)$ K, $R_1 = 0.0363$, $wR_2 = 0.1026$. Suitable crystals of **2** were sealed in thin-walled glass capillaries under a nitrogen atmosphere and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The space group determination was based on a check of the Laue symmetry and systematic absences, and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package.[9] All non-H atoms were located from successive Fourier maps and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. CCDC reference number 186204.

¶ Preparation of **4**: Complex **2** (0.5299 g, 0.66 mmol) was placed in 20 cm^3 of acetone in a 100 cm^3 flask and 1.5 molar equivalents of $Ce(NH_4)_2(NO_3)_6$ (0.5000 g, 0.9120 mmol) was added. The solution was stirred at 25 °C for 10 minutes. Saturated NaCl solution was added several times to wash the solution and the organic phase was collected and washed with 30 cm^3 of diethyl ether. Subsequently the resulting orange solution was filtered through silica gel and purified using centrifugal thin-layer chromatography (CTLC). The first orange band of the title compound, $HC{\equiv}CC_6H_4N{=}NC_6H_4C{\equiv}CH$ **4**, was eluted with CH_2Cl_2–hexanes (1 : 1) and the solvent was removed *in vacuo* to yield **4** (78.0%, 0.1186 g, 0.5150 mmol). Selected spectroscopic data for **4**: IR (CH_2Cl_2/cm^{-1}) ν 1403.7 (N=N); ^{1}H NMR ($CDCl_3$): δ 7.86 (d, J_{H-H} = 7.61 Hz, 2H, arene), 7.64 (d, J_{H-H} = 7.21 Hz, 2H, arene), 3.24 (s, 1H, ≡CH); ^{13}C NMR ($CDCl_3$): δ 152.07 (1C, *p*-arene), 133.01 (2C, *m*-arene), 125.01 (1C, *ipso*-arene), 122.93 (2C, *o*-arene), 83.20 (1C, ≡C), 79.69 (1C, ≡CH); EI mass spectrum of **4**, *m*/*z*: 230 [M$^+$]; Elemental analysis: calc. for **4** C 83.38, H 4.38, N 12.16; Found: C 81.81, H 4.40, N 11.87%.

‖ Crystal data for **4**: $C_{16}H_{10}N_2$, $M = 230.26$, monoclinic, space group $P2(1)/n$, $a = 3.9108(5)$, $b = 5.9654(8)$, $c = 25.640(3)$Å, $\beta = 92.214(3)°$, $V = 597.72(13)$ Å^3, $Z = 2$, $D_c = 1.279$ Mg m^{-3}, $\mu = 0.077$ mm^{-1}, $F(000) = 240$, $T = 293(2)$ K, $R_1 = 0.0416$, $wR_2 = 0.1249$. CCDC reference number 186202. See http://www.rsc.org/suppdata/dt/b2/b204881g/ for crystallographic data in CIF or other electronic format.

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