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Reactions of $Co_2(CO)_8$ with RC_2R' alkynes Part II ☆. Synthesis of $Co_2(CO)_6(RC_2R')$ complexes; oligomerization or cyclotrimerization reactions of substituted acetylenes

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Abstract

The reactions of $Co_2(CO)_8$ with asymmetrically substituted alkynes lead to complexes $Co_2(CO)_6(RC_2R')$ (**1**). These catalyze the cyclotrimerization of alkynes to substituted benzenes. Here we report on the synthesis and characterization of some new complexes **1** and on their reactivity with an excess of alkynes in relatively mild conditions; the characterization of new intermediate $Co_2(CO)_4(RC_2R')_3$ flyover derivatives (complexes **2**) and the synthesis of some symmetrically and asymmetrically substituted benzenes is reported and commented. In some instances alkyne oligomers instead of cyclotrimers were obtained; the reactions are strongly dependent on the type of catalyst, on the conditions adopted and on the steric and electronic effects of the substituents on the alkynes, as shown also by a comparison of our results with those of analogous reactions on other cobalt and nickel derivatives.

Keywords: Oligomerization; Cyclotrimerization; Cobalt complexes; Alkyne complexes

1. Introduction

The main organometallic products formed in high yields in the reactions of $Co_2(CO)_8$ with alkynes are the well known complexes $Co_2(CO)_6(RC_2R')$ (**1**) [1]; these are useful in organic syntheses [2,3]. The Khand–Pauson reaction [3c,4], the codimerization of alkynes with other synthons to give heterocycles [5,6] and the selective propargylation of amines [7] are some examples of the potentiality of complexes **1** or of their cations. The use of the $Co_2(CO)_6$ moiety as a protecting group [8] or as a marker [9] in organic and biological reactions is also noteworthy.

Complexes **1** bearing RC_2R' asymmetrical alkynes may give rise to chiral complexes, when substituted with Group V^0 donor ligands. We started to explore the synthesis of some new complexes **1** with RC_2R' alkynes and their substitution reactions [10]; during these syntheses in relatively mild conditions, in the presence of excess of acetylenes, we also obtained catalytic cyclotrimerization of alkynes to symmetrically or asymmetrically substituted benzenes and/or to other oligomers. Although the mechanisms of these reactions are reasonably well understood, the type of products obtainable is not easy to predict; we therefore attempted to gain some more evidence about the effect of the reaction conditions and of the alkyne substituents on the nature of the organic products obtainable.

We had already begun a study of the reactions of functionalized acetylenes with nitriles and other alkynes in the presence of iron [11] and cobalt carbonyls [12]; in the presence of $Co_2(CO)_8$ these reactions lead to organic heterocycles via metallacyclic intermediates [6,12,13], or to substituted benzenes, via the flyover complexes $Co_2(CO)_4(RC_2R')_3$ (**2**) [14]. In this paper we report on the synthesis of some new complexes **1** and **2** and on their intermediacy in the formation of

R = H; R' = $CMe_2(OH)$, C(Me)Ph(OH), $C(=CH_2)Me$, $CMe_2NHCOC_6H_9$, CH_2NEt_2. R = Ph; R' = Ph, H, C(=O)Me.

☆ For Part I see Ref. [14].

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organic oligomers; we will compare the results obtained with those reported for other nickel and cobalt catalysts in the same reactions.

2. Experimental

2.1. General experimental details. Materials. Analysis of the products

$Co_2(CO)_8$ (Strem Chemicals) and the alkynes (Aldrich, Fluka, Janssen) were commercial products and were used as received. *N*-(α,α-Dimethylpropargyl)-1-cyclohexen-carboxamide (PAM) was obtained as described in Ref. [15].

All reactions were performed in conventional glassware consisting of three-necked flasks equipped with gas inlet, reflux condenser and mercury check valve; distilled dry toluene was used as a solvent under a dry N_2 atmosphere. The reaction mixtures were filtered under N_2 and brought to small volume under reduced pressure; these were purified on TLC preparative plates (Kieselgel P.F. Merck) with mixtures of light petroleum (40–70°) and diethyl ether as eluants, the volume of diethyl ether (10–50%) varying with the polarity of the alkyne substituents. When possible the products were crystallized from heptane, heptane/$CHCl_3$ or heptane/toluene solutions kept at −20 °C under N_2; sometimes oily products were obtained. These were dried with a rotary pump.

Elemental analyses were performed with an F&M C,H,N analyzer; the metal and phosphorus analyses were performed by F. Pascher Laboratories (Remagen, Germany). IR spectra were measured on a Perkin-Elmer 580 instrument. ^1H and $^{13}C\{^1H\}$ NMR spectra were registered on JEOL JNM 270 FT or EX-400 FT instruments, in $CDCl_3$ solution, at room temperature with external TMS as a standard. The FAB mass spectra were registered on a Kratos MS-80 instrument in nitrobenzyl alcohol matrix; the CI mass spectra were obtained on a Hewlett-Packard HP5989A instrument in the conditions described in Ref. [16].

2.2. Synthesis of the complexes. Reactions of $Co_2(CO)_8$ with alkynes

2.2.1. 2-Methyl-3-butyn-2-ol ($HC_2CMe_2(OH)$, MBO)

We have adopted different conditions with respect to previous reports [17]. Treatment of 1.0 g (2.92 mmol) of $Co_2(CO)_8$ with 2.0 ml (18.8 mmol) of MBO under reflux for 2 min, followed by TLC purification yielded red $Co_2(CO)_6\{HC_2CMe_2(OH)\}$ (**1a**, 25% on cobalt), a yellow organic product (compound **A**, 10%), purple $Co_2(CO)_4\{HC_2CMe_2(OH)\}_3$ (**2a**, 30%) and considerable decomposition. The reaction was repeated in the same conditions for 4 min at reflux; the yield of **1a** was lowered (10%) and that of **2a** increased to about 60%. The reaction solution, dried under reduced pressure, was redissolved in $CHCl_3$ for TLC purification; a considerable amount of a whitish solid, sparingly soluble in chloroform, was left undissolved and filtered apart (compound **B**). Compound **B** was recrystallized from acetone and identified as 1,2,4-substituted benzene (~30% on MBO).

Complexes **1a** and **2a**, containing only traces of impurities, were left for some days at 0 °C and then repurified by TLC prior to NMR analyses. Red **1a** gave three bands: **1a** (50%), yellow **A** (20%) and purple **2a** (30%). Purple **2a** also gave three bands; deep red **3** (20%), yellow **A** (40%) and **2a** (20%) and left undissolved **B** (15%). This behaviour made it difficult to obtain reasonably pure samples for analysis.

We were unable to obtain complex **3** in a direct synthesis.

Complex 1a: $Co_2C_{11}H_8O_7$, MW 370.0. *Anal.* Found: Co, 32.1; C, 36.0; H, 2.2. Calc.: Co, 31.85; C, 35.70; H, 2.18%. IR (ν(CO), C_7H_{16}): 2096vs, 2057vs, 2036–2023vs(b), 2015sh cm^{-1}. ^1H NMR: 6.03s (1H, HC=); 1.77s (1H, OH); 1.58s (6H, CH_3). ^{13}C NMR [1]: 15.0s, 21.2s (CH_3); 32.9s (CMe_2); 65.6s*, 71.4s*, 105.8s (C_{alkyne}); 125.1s (C_{alkyne}); 128.8s*, 199.5s(b) (CO). FAB mass spectrum: $P^+ = 436$ *m/z*; 370 *m/z*, loss of 2 CO, then complex fragmentation.

Complex 2a: $Co_2C_{19}H_{24}O_7$, MW 482.3. *Anal.* Found: Co, 24.2; C, 48.1; H, 5.1. Calc.: Co, 24.44; C, 47.32; H, 5.02%. IR (ν(CO), $C_7H_{16}/CHCl_3$): 2054s, 2022vs, 1993s(b) cm^{-1}. ^1H NMR: 8.75m(b) (2H, HC=); 5.19s (1H, HC=); 3.62s (2H, OH); 3.27s (9H, CH_3); 2.99s, 2.81s (9H, CH_3); 1.48s (1H, OH). ^{13}C NMR: 29.8s, 31.0s, 32.4s, 34.1s, 34.6s (CH_3); 72.2s, 74.0s, 79.1s (CMe_2); 107.8s, 108.7s, 128.1s, 128.9s ($Cq_{flyover}$); 200.9b, 205.1b (CO); 223.1s, 228.2s ($Cq_{flyover}$).

Complex 3: $Co_2C_{15}H_{10}O_7$, MW 420.1. *Anal.* Found: Co, 28.3; C, 43.0; H, 2.5. Calc.: Co, 28.06; C, 42.89; H, 2.40%. IR (C_7H_{16}): 2050vs, 2025vs, 2014sh, 1980vs cm^{-1}. ^1H NMR: 8.10s, 6.40s (2H, HC=); 1.82s (2H, OH); 1.51s (12H, Me). ^{13}C NMR: 15.0s*, 29.1s, 30.8s, 32.2s, 32.7s (CH_3); 65.3s*, 71.6s*, 74.0s, 78.7s (CMe_2); 106.4s, 107.5s ($C_{\beta,\,alkyne}$); 201.0d, 205.4s (CO); 222.7s, 227.8s ($C_{\alpha,\,alkyne}$). FAB mass spectrum: $P^+ = 420$ *m/z*; 402, 392, 364 *m/z* then complex fragmentation.

Compound A. IR (KBr pellet): 3464 (31.7), 2971 (35.0), 1697 (23.2), 1555 (28.4), 1505 (41.7), 1370 (30.3), 1183 (37.8), 771 (42.4), 658 (46.6) cm^{-1} (transmittance in parentheses). Closely comparable spectra were obtained in solution. ^1H NMR: 7.59s (3–4H, HC=); 6.41d (2H, HC=); 4.57s (2H, $=CH_2$?); 3.53s (2H, $=CH_2$?); 2.58s, 2.33s (4H, OH); 1.64s (2OH, CH_3); 1.64s (2OH, CH_3). ^{13}C NMR: 15.1s, 22.7s, 24.5s, 28.2s (CH_3, CH_2);

[1] Signals marked with an asterisk belong to impurities of other derivatives present in the same reaction solution.

65.6s, 71.4s (CMe_2); 117.5s, 119.6s, 122.7s, 128.7s, 130.8s, 133.8s, 154.7s, 157.0s, 162.8s (C, organic system). NICI mass spectrum [2]: $P^+ = 564$ *m/z*; 530, 496, 428, 402, 318, 372, 282, 248, 214, 194, 180, 156 *m/z*. PICI mass spectrum: 262, 232, 215, 163 *m/z*.

Compound B: $C_{15}H_{24}O_3$, MW 252.4. *Anal.* Found: C, 71.6; H, 9.7. Calc.: C, 71.39; H, 9.59%. ^{1}H NMR: 7.50s (1H); 6.73s (2H); 2.17s (2H, OH); 1.72s (3H); 1.59s (6H, CH_3). FAB mass spectrum: 252 *m/z*, complex fragmentation.

2.2.2. 3-Phenyl-1-butyn-3-ol ($HC_2C(Me)Ph(OH)$, PBO)

Treatment of 1.0 g (2.92 mmol) of $Co_2(CO)_8$ with 2.0 g (~11.0 mmol) of PBO under reflux for 2 min, gives a dark red suspension. TLC purification shows the presence of unidentified brown and yellow complexes in trace amounts, purple **2b** (1%, tentative identification), dark red oily $Co_2(CO)_6\{HC_2C(Me)Ph(OH)\}$ (**1b**, 40–70%) and considerable decomposition. After filtration of the suspension, an oily red film remained on the filter paper; drying under air afforded a dark red solid (compound **C**) nearly insoluble in the common solvents and sparingly soluble in acetone. ^{1}H NMR in acetone showed a number of signals for Ph, CH_2, CH_3 and OH groups not unequivocally attributable.

Complex 1b: $Co_2C_{16}H_{10}O_7$, MW 432.1. *Anal.* Found: Co, 27.0; C, 44.7; H, 2.4. Calc.: Co, 27.28; C, 44.47; H, 2.33%. IR (ν(CO), C_7H_{16}): 2093vs, 2060vs, 2034–2023vs(b), 2012sh cm^{-1}. ^{1}H NMR: 7.65–7.26m (5H, Ph); 6.14s (1H, HC=); 2.45s (1H, OH); 1.96s (3H, CH_3). ^{13}C NMR: 33.3s (CH_3); 71.7s (CCH_3); 107.2s (C_{alkyne}); 124.0–132.9m (Ph); 148.3s (C_{alkyne}); 197.7, 198.0, 198.7, 199.4m(b) (CO).

2.2.3. Isopropenylacetylene ($HC_2C(=CH_2)Me$, IPA)

Treatment of 1.0 g (2.92 mmol) of $Co_2(CO)_8$ with 1.0 ml (~12.0 mmol) of IPA under reflux for 3 min yields a clear red solution. After TLC separation, dark red oily $Co_2(CO)_6\{HC_2C(=CH_2)Me\}$ (**1c**, 50%), several unidentified trace complexes and considerable decomposition were observed.

The reaction was repeated in the presence of a greater excess of IPA (36.0 mmol) for 3 min at reflux; once again 50% yields of **1c** were obtained together with traces of an orange, a purple and a grey unidentified compound, about 10% of **D** (see below) and considerable decomposition. Complex **1c** was refluxed for 2 min in toluene with a threefold molar excess of IPA; evaporation of the reaction solution under reduced pressure left a liquid residual. One portion was purified by TLC, which showed the presence of unreacted **1c** (60%), unidentified trace products and considerable decomposition; another portion was distilled [18]. Liquid 1,3,5-isopropenylbenzene (compound **D**, 20%) was collected.

[2] Numbers underlined are the more intense peaks.

Complex 1c: $Co_2C_{11}H_6O_6$, MW 352.0. *Anal.* Found: Co, 33.2; C, 37.7. Calc.: Co, 33.48; C, 37.53%. IR (ν(CO), C_7H_{16}): 2095vs, 2058vs, 2036–2028vs(b), 2016sh cm^{-1}. ^{1}H NMR: 6.19s (1H, HC=); 5.32d (2H, CH_2); 2.07s (3H, CH_3). ^{13}C NMR: 23.9s (CH_3); 73.2s (CH_2); 92.8s (CMe); 117.6s, 141.1s (C_{alkyne}); 199.5s(b) (CO).

Compound D: ^{1}H NMR: 7.46s (ring CH); 5.38m, 5.11m (CH_2); 2.18m (CH_3). FAB mass spectrum: $P^+ = 198$ *m/z*.

2.2.4. N-(α,α-Dimethylpropargyl)-1-cyclohexen-carboxamide ($HC_2CMe_2NH\cdot CO\cdot C_6H_9$, PAM)

A suspension of 1.0 g (2.92 mmol) of $Co_2(CO)_8$ and 1.0 g (3.5 mmol) of PAM was warmed till incipient reflux (14 min). TLC purification showed the presence of purple **4d** (1%, tentative identification), dark red $Co_2(CO)_6\{HC_2CMe_2\cdot NH\cdot CO\cdot C_6H_9\}$ (**1d**, 50%), an unidentified blue compound **5d** (1%) and considerable decomposition.

Complex 1d: $Co_2C_{18}H_{17}O_7N$, MW 477.2. *Anal.* Found: C, 45.5; H, 3.8; Co, 24.9. Calc.: C, 45.31; H, 3.59; Co, 24.70%. IR (ν(CO), C_7H_{16}): 2094s, 2056vs, 2028vs(b), 1660m cm^{-1}. ^{1}H NMR: 7.25s (1H, HC=); 6.6d, 6.22d (2H, HC=CH, C_6H_9); 5.75s (1H, NH); 2.15m (CH_2, C_6H_9); 1.74s (3H, CH_3); 0.86s (3H, CH_3). ^{13}C NMR: 21.4s, 22.1s (CH_3); 24.1s, 24.3s, 31.1s (CH_2, C_6H_9); 55.8s, 74.1s (HC, C_6H_9); 104.5s (Cq, C_6H_9): 133.3s, 167.4s (=C−C, HC=); 199.5s(b) (CO).

Complex 4d: $Co_3C_{21}H_{17}O_{10}N$, MW 620.2. *Anal.* Found: Co, 28.4; C, 40.9; N, 2.3. Calc.: Co, 28.51; C, 40.67; N, 2.26%. IR (ν(CO), C_7H_{16}): 2107m, 2060vs, 2024vs, 1868vs cm^{-1}. FAB mass spectrum: 620 *m/z*, loss of 3 CO, then complex fragmentation.

2.2.5. 3-Diethylamino-1-propyne ($HC_2\cdot CH_2NEt_2$, DAP)

Treatment of 2.0 g (5.84 mmol) of $Co_2(CO)_8$ with 3.0 ml (19.3 mmol) of DAP under reflux for 2 min yielded a red–brown suspension, which, after TLC purification, showed the presence of purple **4e** (1%, tentative identification), deep red oily $Co_2(CO)_6(HC_2\cdot CH_2NEt_2)$ (**1e**, 60%) and considerable decomposition.

Complex 1e: $Co_2C_{13}H_{13}O_6N$, MW 397.1. *Anal.* Found: Co, 29.8; C, 39.4. Calc.: Co, 29.68; C, 39.32%. IR (ν(CO), C_7H_{16}): 2095s, 2056vs, 2029vs(b), 2013sh cm^{-1}. ^{1}H NMR: 6.04s (HC=); 3.95s (2H, CH_2); 2.61s (CH_2/Et); 1.07s (CH_3/Et). ^{13}C NMR: 12.3s (CH_3); 47.0s (CH_2/Et); 55.7s (CCH_2); 73.1s, 91.6s (C_{alkyne}); 199.97s(b) (CO).

Complex 4e: $Co_3C_{18}H_{13}O_9N$, MW 564.1. *Anal.* Found: Co, 31.4; C, 38.5. Calc.: Co, 31.34; C, 38.33%. IR (ν(CO), C_7H_{16}): 2103m, 2055vs, 2040vs, 2021m cm^{-1}.

2.2.6. Phenyl-methyl-acetylene (PhC_2Me, FPOP)

Treatment of 2.0 g (5.84 mmol) of $Co_2(CO)_8$ with 4.0 ml (27.6 mmol) of FPOP till incipient reflux (15 min) yielded a dark brown suspension containing dark

red $Co_2(CO)_6(PhC_2Me)$ (**1f**, 95%) and some decomposition products. Complex **1f** was contaminated by excess of liquid FPOP: attempts at crystallizing it resulted in the formation of considerable amounts of a whitish solid deposit (compound **E**) identified as 1,2,4-substituted benzene.

Complex 1f: $Co_2C_{15}H_8O_6$, MW 402.1. *Anal.* Found: Co, 29.5; C, 45.0. Calc.: Co, 29.31; C, 44.81%. IR (ν(CO), C_7H_{16}): 2094vs, 2057vs, 2030vs(b), 2016sh cm^{-1}. ^1H NMR: 7.50–7.30m (Ph); 1.82s (Me).

Compound E: $C_{27}H_{24}$, MW 348.5. *Anal.* Found: C, 93.0; H, 7.0. Calc.: C, 93.06; H, 6.94%. ^1H NMR: 7.61–7.12m (15H, Ph); 2.21s (6H, CH_3); 1.88s (3H, CH_3). ^{13}C NMR: 18.0s, 18.2s, 19.3s (CH_3); 125.2d, 126.3s, 127.1d, 128.1d, 129.9s, 130.1s, 131.7s, 133.9s (C_{ring}, Ph substituents); 139.0s, 140.5s, 141.4s, 141.5d, 142.3s (C_{ring}). FAB mass spectrum: 346 *m/z*.

2.2.7. Phenylacetylene (HC_2Ph, PA)

Treatment of 1.0 g (2.92 mmol) of $Co_2(CO)_8$ with 4.0 g (39.0 mmol) of PA under reflux for 1 min yielded a brown suspension; TLC purification showed the presence of red $Co_2(CO)_6(HC_2Ph)$ (**1g**, 25%), a unidentified blue compound **5g** (1%), purple **2g** (30%) and a whitish solid (compound **F**, 50% on PA). Complex **2g** and **F** migrate together on the TLC plates; the mixture of compounds was washed twice with heptane. Compound **F** remained undissolved and the purple solution of **2g** was kept at −20 °C overnight; a precipitate of **2g** contaminated by some **F** was obtained. This was dissolved again in heptane and recrystallized: **2g** reasonably pure for analysis was obtained in small yields.

Complex 1g: $Co_2C_{14}H_6O_6$, MW 388.1. *Anal.* Found: C, 43.5; H, 1.6. Calc.: C, 43.33; H, 1.56%. IR (ν(CO), C_7H_{16}): 2096vs, 2060vs, 2027vs(b), 2013sh cm^{-1}. ^1H NMR: 7.50–7.28m (5–7H, Ph); 6.31s (1H, HC=). ^{13}C NMR: 90.1s, 137.3s (C_{alkyne}); 120.8–133.9m (Ph); 199.3s(b) (CO).

Complex 2g: $Co_2C_{28}H_{18}O_4$, MW 536.3. *Anal.* Found: Co, 22.0; C, 63.1. Calc.: Co, 21.98; C, 62.71%. IR (ν(CO), C_7H_{16}): 2071s, 2044vs, 2020s(vb) cm^{-1}. ^1H NMR: 7.81–7.74d, 7.40s(b) (Ph); 6.58s (1H); 6.29s (1H); 6.26s (1H, HC=). ^{13}C NMR: 107.4s, 109.1s ($C_{flyover}$); 126.0–129.8m (Ph); 141.6s, 148.4d ($C_{flyover}$); 200.8s(b), 201.1s(b), 203.3s(b) (CO); 204.3s, 208.0s ($C_{flyover}$).

Compound F: $C_{24}H_{18}$, MW 306.4. *Anal.* Found: C, 94.0; H, 6.0. Calc.: C, 94.08; H, 5.92%. ^1H NMR: 7.74–7.25m (Ph, HC=). ^{13}C NMR: 126.2–131.6m (Ph); 139.6s, 140.4s, 140.6s, 141.0s, 141.1s, 141.5s (C_{ring}). FAB mass spectrum: 306 *m/z*.

2.2.8. Other reactions

A suspension of 2.0 g (3.22 mmol) of $Co_2(CO)_5(PPh_3)(PhC_2Me)$ [10] and 5.0 ml (43.1 mol) of FPOP was refluxed for 5 min; TLC purification showed the presence of **1f** (5%), brown–purple $Co_2(CO)_3(PPh_3)(PhC_2Me)_3$ (**6**, 30%) contaminated by compound **E** (60%) and some decomposition.

Complex 6: $Co_2C_{50}H_{39}O_3P$, MW 836.7. *Anal.* Found: Co, 14.5; C, 72.6; P, 3.76. Calc.: Co, 14.09; C, 71.78; P. 3.70%. ^1H NMR: 7.27–6.98m (Ph); 1.60s, 1.31s, 0.92s (CH_3). ^{31}P NMR ($CDCl_3$, r.t., H_3PO_4): +51.0s. ^{13}C NMR: 14.0s, 18.9s, 22.6s (CH_3); 28.9s, 31.8s, 80.0s, 82.1s, 140.7s ($C_{flyover}$); 124.8–135.2m (Ph); 206.6vb (CO). FAB mass spectrum: 836 *m/z*, loss of 3 CO and complex fragmentation.

3. Results and discussion

The reactions of $Co_2(CO)_8$ with RC_2R' alkynes lead, as expected, to complexes **1**; complexes **2** and cyclotrimers and/or oligomers of the alkynes were also obtained in variable amounts depending on the alkynes.

3.1. Characterization of complexes 1

Complex **1a** had already been synthesized [17]; however, the spectroscopic data reported did not allow a comparison with ours. Complexes **1b–1g** were characterized by elemental analyses and spectroscopic techniques, in particular multinuclear NMR. The IR, ^1H and ^{13}C NMR spectra are consistent with those of other well established and structurally characterized complexes $Co_2(CO)_6(RC{\equiv}CR')$ [1–3,19]: generally, only one broad signal was observed in the ^{13}C NMR for the CO with the exception of **1b** where different although very close, signals could be detected. The ^{13}C NMR signals for the coordinated acetylenic C≡C bond span a large range of values indicating that the substituents may exert a considerable effect; this is also reflected by the type and yields of the products, as discussed below.

Examples of reactions of propargyl alcohols with $Co_2(CO)_8$ and, in particular, the synthesis of the cation of **1a**, an interesting reagent in organic chemistry [20], are known. Propargyl alcohols have also been used in homogeneous organic reactions catalyzed by Pd(II) [21]; in these reactions the alcoholic functionalities are modified.

We have found that propargyl alcohols, amines and amides react with $Co_2(CO)_8$ giving CO substitution with unmodified alkynes to form complexes **1**; only in a second step modification of the ligands takes place. We have also found, however, that complexes **1a** and **2a** give apparently disproportionation–dehydration reactions during attempts at repurification. Acid catalyzed dehydration of propargyl alcohols coordinated on clusters has been reported and two reaction pathways identified: one is the loss of the OH and of the terminal acetylenic hydrogen [22] and the other is the loss of the OH and of one hydrogen from R or R' [23]. In

some instances deoxygenation was also observed [24]. In the present case, we strongly suspect that the observed behaviour of complexes **1a** and **2a** is promoted by the silica of the TLC plates as an example of 'surface organometallic reaction' [25]. Worthy noting is the 'synthesis' of complex **3** in this process.

Depending on their catalytic activities, complexes **1** react further, leading to organic compounds: in some instances, however, this process is slow and the final products observed are complexes **2**, **4** and **5**. This is presumably due to the short reaction times (and relatively mild conditions) used in this work which was aimed at obtaining mostly complexes **1** for further substitution reactions with Group V^0 donors.

The role of complexes **2** is discussed below; complexes **4** have been tentatively identified as $Co_3(CO)_9(\mu_3\text{-CR})$ methylidyne clusters on the basis of the analyses and IR spectra [26] and complexes **5** might be butterfly alkyne-substituted $Co_4(CO)_{10}(RC_2R')$ derivatives, a structural arrangement commonly found for cobalt [27]. Their formation requires metal fragment condensation and is presumably competitive with catalysis.

3.2. Some comments on the role of complexes 2

A reaction mechanism for the synthesis of benzenes starting from $Co_2(CO)_8$ and acetylenic derivatives has been proposed and is generally accepted [2c,14]: this involves complexes **1** as the catalysts, binuclear cobaltacyclopentadienyl complexes **3** [6] and flyover bridged complexes **2** [14] as reaction intermediates, as shown in Fig. 1.

The intermediacy of mononuclear cobaltacyclopentadienylic compounds has also been recently discussed [5e].

We have shown that the dicobaltacyclopentadiene $Co_2(CO)_5[\{HC_2CMe_2\}_2NMe]$ (type **3** structure) is a catalyst for the cyclotrimerization of HC_2Ph to a mixture containing comparable amounts of 1,2,4- and 1,3,5-triphenylbenzenes [6]. In the reactions here described we could isolate a complex **3** only for MBO; moreover,

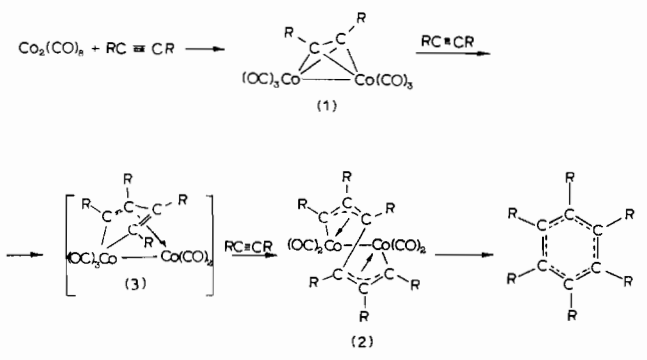

Fig. 1. Proposed mechanism of formation of symmetrically and asymmetrically substituted benzenes, showing the structures and role of complexes **1**, **2** and **3**.

the complex was presumably the result of a silica-mediated disproportionation–dehydration reaction and could not be obtained in a direct synthesis. Thus intermediate complexes **3** remain elusive, and evidence for their role is restricted to a handful of examples.

By contrast, the intermediacy of complexes **2** in the cyclotrimerization reactions is well established both for cobalt [14] and other metals [28] and clusters with alkyne trimers comparable to those in **2** are also known [29].

An attempt at 'trapping' an intermediate **3** by reacting $Co_2(CO)_5(PPh_3)(MeC_2Ph)$ with an excess of MeC_2Ph leads to disproportionation into **1f** and the phosphine-substituted flyover **6** with a structure comparable with that of complexes **2**; considerable amounts of the 1,2,4-cyclotrimer were also found. This indicates that the phosphine-substituted complexes **1** and **2** are also catalysts or intermediates in cyclotrimerization reactions.

3.3. Synthesis and characterization of the organic products. A comparison with other catalytic systems

The identification of the organic products reported in this work was based on spectroscopic data, FAB mass spectrometry and, when possible, on the comparison with literature data; for example compound **B** has been confirmed as the 1,2,4-cyclotrimer because of strong differences between its spectroscopic data and those of the 1,3,5-derivative [30] [3], whose structure is known [31]. Compound **D** was identified as the 1,3,5-cyclotrimer of IPA [30,18,32] because of its physical state and agreement with the NMR data reported in the literature.

It is known that alkynes can be cyclotrimerized either on $Ni(CO)_2(PR_3)_2$ [3b] or on cobalt carbonyl derivatives [2c,3b] [4], the reaction rates depending on the alkyne substituents. In Table 1 we compare the results obtained in this work with those obtained in other reactions with a variety of alkynes and catalysts.

A comparison of the data in Table 1 leads to some considerations: (i) propargyl alcohols are considerably reactive and give either cyclotrimers or (partly dehydrated) oligomers and polymers; (ii) phenylacetylene and other alkynes with Ph substituents tend to give cyclotrimers with preference for 1,2,4-isomers; (iii) the metal of the catalyst plays a role; for example, on nickel a greater tendency to give 1,3,5-cyclotrimers can be noted with respect to cobalt; (iv) the ligands on the catalyst sometimes are responsible for dramatic changes: for example MBO gives 80% of the 1,2,5-cyclotrimer

[3] ^1H NMR data for the 1,3,5-cyclotrimer of MBO (in $(CD_3)_2CO$): 7.45s (ring protons), 3.86s (OH), 1.48s (Me). For liquid 1,3,5-triisopropenyl benzene: 7.50s (ring protons), 5.37m (CH_2), 2.20q (Me).

[4] Nickel: different solvents, temperatures between 25 and 180 °C, reaction times 0.5–24 h. Cobalt: boiling dioxane (100–280 °C), reaction times 1–72 h. See Ref. [3b].

Table 1
Oligomerization reactions of selected alkynes in the presence of nickel- or cobalt-based catalysts (or precursors) and of clusters

Catalyst or precursor	Alkyne	Products	Ref.
$(PR_3)_2Ni(CO)_2$	$HC_2 \cdot CH_2(OH)$	1,2,4-Bz [a] (47%) 1,3,5-Bz (47%)	[3b]
	$HC_2 \cdot CH(OH)Ph$	1,3,5-Bz (16%)	[3b]
	$HC_2 \cdot C(=CH_2)Me$	1,2,4-Bz (10%)	[3b]
	$HC_2 \cdot C(=O)Me$	1,3,5-Bz (80%)	[3b]
	HC_2Ph	1,2,4-Bz (20%) [b] 1,3,5-Bz (1%)	[3b]
$(Cp)_2Ni$ [c]	HC_2Ph	1,2,4-Bz [d] 1,3,5-Bz other products [e]	[33]
$(PPh_3)_2NiX_2$ [f]	HC_2Ph	1,2,4-Bz (31%) 1,3,5-Bz (9%) linear polymer	[34]
$(Bu^n_3)_2NiX_2$ [f]	HC_2Ph	1,2,4-Bz (22%) 1,3,5-Bz (14%) linear polymer	[34]
$(Cy_3P)_2NiX_2$ [f]	HC_2Ph	1,2,4-Bz (40%) 1,3,5-Bz (9%) linear polymer	[34]
$(Ph_3P)NiX_2$ [f]	$HC_2 \cdot CMe_2(OH)$	1,3,5-Bz (80%) [g] 1,2,4-Bz (85%) [h]	[35]
$(Bu^n_3P)_2NiX_2$ [f]	$HC_2 \cdot CMe_2(OH)$	1,3,5-Bz (1–91%) [h]	[35b]
$(Bu^n_3P)_2NiBr_2$	$HC_2 \cdot CR(R')(OH)$ [i]	1,3,5-Bz other products [j]	[18]
	$C_2\{CMe_2(OH)\}$	other products [k]	[18b]
$(Ph_3P)_2Ni(NCS)_2$	$HC_2 \cdot C_6H_{10}(OH)$	other products [m]	[32]
$(Ph_3P)_2Ni(NCS)(IPA)$ [n]	$HC_2 \cdot C(=CH_2)Me$	1,2,4-Bz other products [o]	[32]
$Co(CO)_3NO$	$HC_2 \cdot CMe_2(OH)$	1,2,4-Bz (94%)	[3b]
$Co_2(CO)_6(RC_2R')$ [p]	$HC_2 \cdot CH_2(OMe)$	1,2,4-Bz (17%)	[3b]
$[Co_2(CO)_4]_2Hg$	$HC_2 \cdot CN$	1,2,4-Bz (38%)	[3b]
	$PhC_2 \cdot COOMe$	1,2,4-Bz (55%)	[3b]
	HC_2Ph	1,2,4-Bz (70%) [q]	[3b]
$(Cp)Co(CO)_2$ [r]	HC_2Ph	1,2,4-Bz [s] 1,3,5-Bz	[36]
	MeC_2Ph	1,2,4-Bz (87%) 1,3,5-Bz (3%)	[3b]
$Co_2(CO)_8$ [c]	HC_2Ph	1,2,4-Bz (45%) 1,3,5-Bz (4%)	[37]
$Co_2(CO)_6(C_2Ph_2)$ [c]	HC_2Ph	1,2,4-Bz (37%) 1,3,5-Bz (18%)	[37]
$Co_2(CO)_6(HC_2Ph)$ [c]	HC_2Ph	1,2,4-Bz (75%) 1,3,5-Bz (8%)	[37]
$Co_2(CO)_8$	$HC_2 \cdot CMe_2(OH)$	1,2,4-Bz other products [t]	this work
	$HC_2 \cdot C(Me)Ph(OH)$	polymer	this work
	$HC_2 \cdot C(=CH_2)Me$	1,3,5-Bz [u]	this work
	$HC_2 \cdot CMe_2 \cdot NHCO \cdot C_6H_9$		this work
	$HC_2 \cdot CH_2NEt_2$		this work
	$PhC_2 \cdot CC(=O)Me$	1,3,5-Bz	[14]
	PhC_2Me	1,2,4-Bz	this work
	HC_2Ph	1,2,4-Bz	this work
$Co_2(CO)_5(PPh_3)(PhC_2Me)$	PhC_2Me	1,2,4-Bz	this work

(continued)

Table 1 (*continued*)

Catalyst or precursor	Alkyne	Products	Ref.
$Co_2(CO)_5[(HC_2C\cdot CMe_2)_2NMe]$	HC_2Ph	1,2,4-Bz (50%) 1,3,5-Bz (50%)	[6]
$(CpMo)_2Ru(CO)_7(\mu_3\text{-}S)$	HC_2Ph	1,3,5-Bz other products [v]	[29]
$Os_3(CO)_{12}$	HC_2Ph	1,2,4-Bz [d] 1,3,5-Bz	[38]
$Ru_3(CO)_{12}/PPh_3$	$HC_2\cdot COOMe$	1,2,4-Bz other products	[39]

[a] 1,2,4-substituted benzene (in parentheses maximum yields).
[b] Melting point 100 °C.
[c] In neat phenylacetylene.
[d] Isomer ratio not given.
[e] Orange *trans*-polyphenylacetylene (15.7 units) and yellow oligomer (4.5 units).
[f] X = Cl, Br, I, NO_3, SCN.
[g] X = Br.
[h] X = I.
[i] R = Me, R′ = Me, Et. R = H, R′ = Pr^n, Ph. R-R′ = Cy.
[j] Dehydration products.
[k] Linear-cyclic partly dehydrated oligomers (5 units).
[m] Linear trimer, not dehydrated.
[n] IPA = isopropenylacetylene.
[o] Isomeric tetramers; polymer.
[p] Same alkyne as the substrate.
[q] Melting point 120 °C.
[r] Solvent supercritical water.
[s] Isomer ratio 1,2,4-/1,3,5-Bz = 6:1.
[t] Partly dehydrated oligomer (7 units).
[u] In the presence of strong excess of alkyne; catalyst complex **1c**.
[v] $(CpMo)_2Ru(CO)_2(\mu_3\text{-}S)(HC_2Ph)_3$, a precursor of 1,3,5-Bz.

in the presence of $(Ph_3P)_2NiX_2$ (X = Br) and 85% of the 1,2,4-cyclotrimer when X = I; (vi) the few data available for clusters seem to indicate again a tendency to form 1,2,4-cyclotrimers, with the notable exception of $(CpMo)_2Ru(CO)_7(\mu_3\text{-}S)$.

In this work we have observed that, for short reaction times, the propargyl amine and amide react slowly, whereas the propargyl alcohols are considerably reactive as already discussed. The yields of the MBO derivatives, with the same cobalt/ligand ratio, were strongly dependent upon reaction time, as already observed for $PhC_2\cdot C(=O)Me$ (FBO) [14]; interestingly MBO gives mainly the 1,2,4-cyclotrimer (in contrast with previous findings) and no dehydrated cyclotrimers. The formation of cyclotrimers of IPA was strongly dependent on the alkyne/cobalt ratio: worthy noting is that — contrasting with literature data — we found only the 1,3,5-cyclotrimer.

The alkynes with phenyl substituents give 1,2,4-cyclotrimers, according with literature data, with the notable exception of FBO which gives only the 1,3,5-product [14]; interestingly $HC_2\cdot C(=O)Me$ on nickel catalysts behaves in the same way.

As a conclusion we can observe that the products and their yields are strongly dependent on the type of catalyst, reaction conditions and alkyne substituents; apparently, the latter exert a considerable role: however, a satisfactory rationalization of the available data allowing predictions on which isomer of benzene could be obtained starting from a given alkyne is not possible at present. Indeed, even for closely related molecules (e.g. MBO, PBO, IPA or HC_2Ph, MeC_2Ph, $PhC_2\cdot C(=O)Me$) strongly different results were obtained. This may depend, for example, on electronic effects which can influence the formation (and isomerism) of the catalytic intermediates.

It is noteworthy that we could synthesize the organic products in considerable yields under relatively mild conditions and in shorter times with respect to the reactions in the literature [32]; also, in our conditions, the release of organic products occurs in very mild conditions, sometimes at room temperature.

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