Letter

Double dehydration of a diynediol promoted by a single $Co_2(CO)_6$ unit; activation of an uncoordinated propargylic centre[†]

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The acid-catalysed elimination of two molecules of water from a diynediol requires only one of the alkyne functionalities to be coordinated to a dicobalt hexacarbonyl fragment; it is proposed that the reaction proceeds *via* an unprecedented type of intermediate in which a carbocationic centre is stabilised by a non-adjacent dicobalt hexacarbonyl moiety.

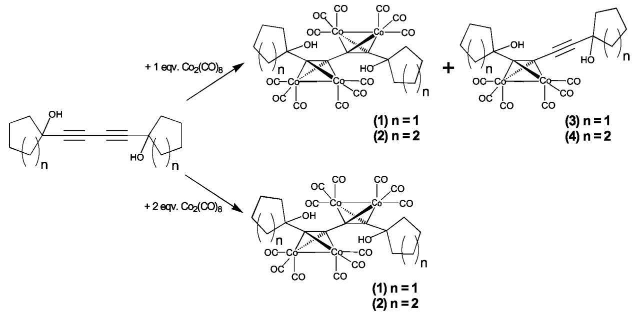
The ability of a metal fragment to stabilise an adjacent carbocation has long been recognised.[1] The $Co_2(CO)_6$ moiety has found particular use in the field of organic synthesis due to its ability to stabilise a propargyl cation.[1c] Thus, treatment of cobalt-complexed propargyl alcohols with HBF_4 leads to the formation of carbocations of general formula $[Co_2(CO)_6(\mu{:}\eta^2\text{-}RC{\equiv}CCR^1R^2)]^+$. Despite their relative stability, however, it is only very recently that the crystal structure of a $Co_2(CO)_6$ stabilised carbocation has been determined.[2] This structure provides confirmation of what had long been postulated, namely that the Co_2C_2 tetrahedron becomes skewed to allow the carbocationic centre to approach within bonding distance of one of the cobalt atoms. It is this close contact and the associated delocalisation of positive charge onto the metal centre which has been regarded as the key to the stability of such carbocationic complexes.

Previous studies of dicobalt hexacarbonyl-coordinated propargyl alcohols with alkyl groups on the propargyl centre have shown that acid-catalysed dehydration reactions are commonplace.[3] These dehydration reactions presumably involve the formation of intermediate carbocations by protonation of the OH group and subsequent loss as H_2O. The corresponding Nicholas type chemistry of diynediols has received scant attention,[4–6] and to our knowledge the dehydration of the related diynediols when coordinated to one or two $Co_2(CO)_6$ units has not been similarly studied.

We have now utilised cycloalkyl substituted diynediols to synthesise the series of complexes $[\{Co_2(CO)_6(\mu\text{-}\eta^2\text{-}XC{\equiv}C)\text{-}\}_2]$ ($X = C_5H_8OH$ **1**; $X = C_6H_{10}OH$ **2**) and $[Co_2(CO)_6(\mu\text{-}\eta^2\text{-}XC{\equiv}CC_2X)]$ ($X = C_5H_8OH$ **3**; $X = C_6H_{10}OH$ **4**) as model systems for dehydration studies of dicobalt hexacarbonyl-coordinated diynediols with alkyl substituents (Scheme 1).

The bis(dicobalt hexacarbonyl)-coordinated complexes **1** and **2** undergo facile high yield double-dehydration under mild conditions (low temperatures, catalytic quantities of HBF_4) to give **5** and **6** (Scheme 2).

This is analogous to the dehydration of the corresponding monoyne systems,[3] and presumably proceeds *via* intermediate carbocations in which the cationic centres are stabilised by the adjacent $[Co_2(CO)_6\text{-}\mu\text{-}\eta^2\text{-}(C{\equiv}C)]$ moieties The structure of **5** was confirmed by X-ray analysis (Fig. 1).[‡]



Scheme 1 Formation of **1**, **2**, **3** and **4**.

More remarkably, the coordination of only one dicobalt hexacarbonyl fragment to the diynediols under investigation is sufficient to promote dehydration of the cycloalkyl substituents on both the adjacent and the remote propargyl sites. Thus treatment of the mono-coordinated diynediols[§] $[Co_2(CO)_6\text{-}(\mu\text{-}\eta^2\text{-}XC{\equiv}C\text{–}C{\equiv}CX)]$ ($X = C_5H_8OH$ **3**; $X = C_6H_{10}OH$ **4**) with catalytic amounts of HBF_4 led in each case to the elimination of two molecules of water per complex and the formation in high yield of the corresponding complexes **7** and **8** containing two double bonds, one within each of the cycloalkyl substituents (Scheme 3).[¶] This suggests that the stabilising effect of a

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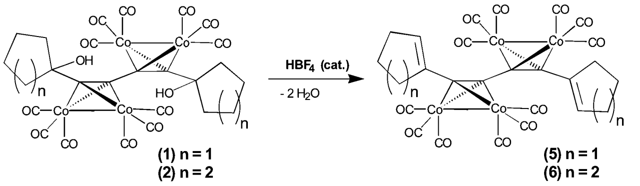
[†] Electronic supplementary information (ESI) available: full spectroscopic details of compounds **1**–**10**. See http://www.rsc.org/suppdata/nj/b2/b206295j/

[‡] Crystal data for **5**: $C_{26}H_{14}Co_4O_{12}$, $M = 754.09$, triclinic, space group $P\bar{1}$, $a = 11.1190(3)$ Å, $b = 13.7900(3)$ Å, $c = 18.7716(5)$ Å, $\alpha = 91.375(2)$, $\beta = 92.809(2)$, $\gamma = 97.593(2)°$, $V = 2848.25(12)$ Å^3, $T = 180(2)$ K, $Z = 4$, $\mu = 2.351$ mm^{-1}, $D_c = 1.759$ Mg m^{-3}, 32 497 reflections collected, 12 850 independent reflections ($R_{int} = 0.0691$), goodness-of-fit on F^2 1.019, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0442$, $wR2 = 0.0943$, largest diff. peak 0.530 and hole –0.606 e Å^{-3}, 757 parameters, 0 restraints. Compound **5** contains three crystallographically independent molecules within its asymmetric unit: two of these possess a strict crystallographic inversion centre. The bond lengths and angles of these molecules are similar and thus only one molecule is discussed.

[§] To a stirred suspension of the corresponding diyne (1 mmol) in 350 ml of diethyl ether was added one equivalent (1 mmol) of $Co_2(CO)_8$ in small portions under a flow of argon. After stirring for 6 hours the evolution of CO ceased. Silica-gel column chromatography (4:1 hexane:ethyl acetate) produced two bands. The first band proved to be the bis(dicobalt hexacarbonyl) coordinated complex whereas the second corresponded to the mono-coordinated complex.

[¶] To a solution of 1 mmol of the complexes (**1**–**4**) in 200 ml dichloromethane at –78 °C under argon were added five drops of 48% HBF_4 in ether. Warming to room temperature and further stirring for 2 hours with subsequent chromatography on silica gel (hexane) afforded a single band of the corresponding complexes (**5**–**8**) in high yield.



Scheme 2 Formation of **5** and **6**.

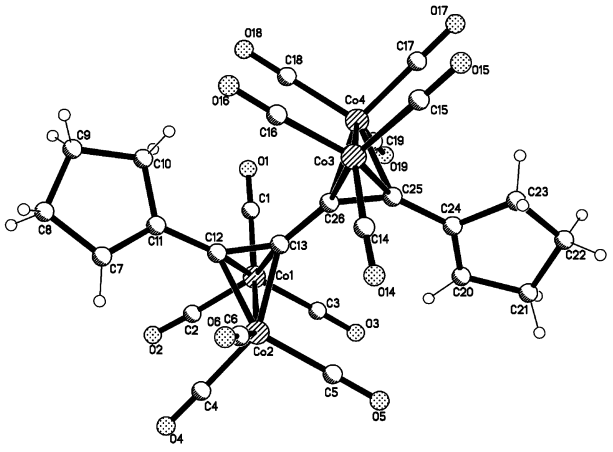


Fig. 1 Molecular structure and atom numbering scheme for $[\{Co_2(CO)_6\text{-}\mu\text{-}\eta^2\text{-}(C_5H_7)C{\equiv}C\text{-}\}_2]$ **5** with selected bond distances (Å) and angles (°). C7–C11 1.355(4), C24–C20 1.325(4), C11–C10 1.477(5), C24–C23 1.492(4), C20–C21 1.500(4), C21–C22 1.502(5), C22–C23 1.521(5), C10–C9 1.515(5), C9–C8 1.507(5), C8–C7 1.511(5), C11–C12 1.445(4), C13–C26 1.433(4), C25–C24 1.447(4), C7–C11–C12 126.1(3), C12–C11–C10 123.3(3), C7–C11–C10 110.6(3), C8–C7–C11 111.8(3), C11–C10–C9 104.1(3).

dicobalt hexacarbonyl fragment may be transmitted through an uncoordinated alkyne to a remote carbocationic centre. Although double-dehydration of uncoordinated diynediols is known, it requires very harsh conditions,[7] whereas in the current case the reaction takes place under very mild conditions (catalytic amounts of HBF_4, $< 0\,°C$).Although we were unable to obtain X-ray quality crystals of either **7** or **8**, definitive evidence as to their structures is provided by the crystal structure of $[Co_2(CO)_4dppm\{\mu\text{-}\eta^2\text{-}(C_5H_7)C{\equiv}C\text{–}C{\equiv}C(C_5H_7)\}]$ **9**, obtained by substitution of two molecules of CO in **7** by bis(diphenylphosphino)methane (dppm).|| This substituted product crystallised readily (Fig. 2). The analogous substitution of **8** by dppm led to the complex $[Co_2(CO)_4dppm\{\mu\text{-}\eta^2\text{-}(C_6H_9)C{\equiv}C\text{–}C{\equiv}C(C_6H_9)\}]$ **10**. The bond lengths and angles within the Co_2C_2 cores are unremarkable in both **5** and **9**.[6,8]

The short C(14)–C(13) bond length in **9** [1.435(6) Å], although typical of such enyne separations,[9] implies a degree of conjugation in the uncoordinated enyne unit which might aid charge delocalisation and promote the stability of the proposed intermediate carbocation from which **7** is derived. The two five-membered rings are not well resolved, hence the C–C single bond distances in these rings were restrained to a common target value during the least squares refinement; a similar constraint was applied to the 2 C=C distances (in all, 2 extra least squares parameters, final values 1.501(6) and 1.352(11)).**

In the double dehydration of **3** and **4** to give **7** and **8** only the carbocationic centre in the first proposed intermediate **A** is adjacent to a $Co_2(CO)_6$ moiety (Scheme 3). It could be argued that the first dehydration occurs at the $Co_2(CO)_6$ protected propargyl alcohol site and that the single $Co_2(CO)_6$ moiety then switches to the uncoordinated triple bond, with the second dehydration occurring in a stepwise manner. Although we cannot entirely exclude this possibility, the near quantitative yields in which **7** and **8** are obtained do not seem consistent with this, since the reactive $Co_2(CO)_6$ fragment might be expected to decompose rapidly in the acidic reaction media. It seems more likely that the dehydration of the cycloalkyl substituent at the carbon atom separated by the uncoordinated C≡C bond from the $[Co_2(CO)_6\text{-}\mu\text{-}\eta^2\text{–}C{\equiv}C]$ moiety is due to stabilisation of the second proposed intermediate carbocation **B** by the remote dicobalt hexacarbonyl fragment. The rigidity of the system enforced by the uncoordinated C≡C triple bond means that such stabilisation must be a through-bond rather than a through-space phenomenon.

In conclusion, we have demonstrated that the dehydration of both alkyl substituents at the propargyl sites of the diynediols studied here requires the coordination of only one $Co_2(CO)_6$ moiety. This implies that the carbocationic intermediates presumably involved in the acid-catalysed dehydration of diynediols under mild conditions can be stabilised by a non-adjacent $Co_2(CO)_6$ moiety. Such remote stabilisation of a carbocation is unprecedented.

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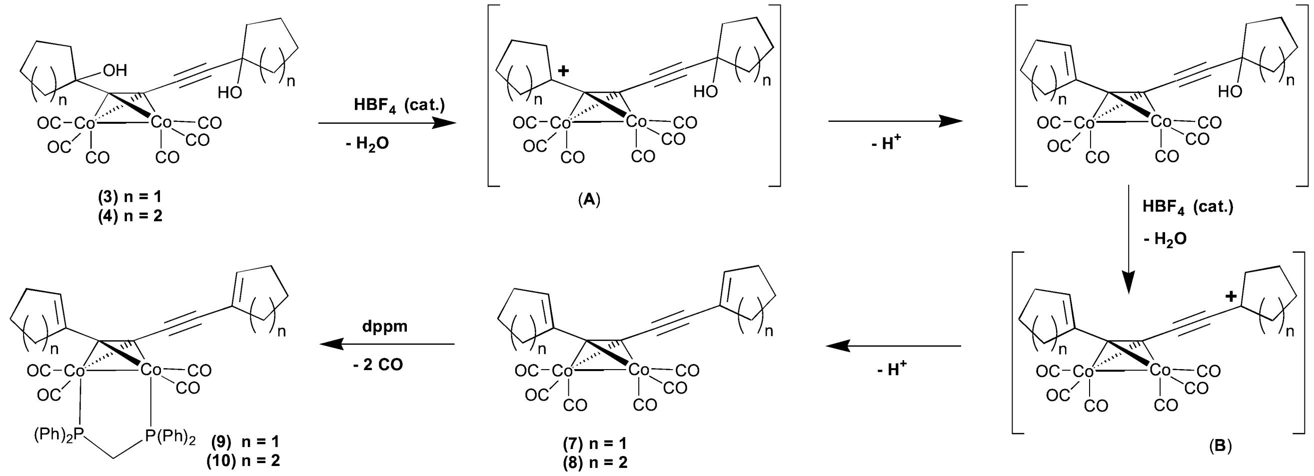
|| To a solution of the complexes (**7**–**8**) 0.5 mmol in toluene (50 ml) was added dppm (0.5 mmol) and the mixture was heated to 70 °C for one hour. Chromatography on silica gel (hexane:dichloromethane 4:1 v/v) afforded two fractions. The first and major one proved to be the mono(dicobalt tetracarbonyl) dppm-coordinated complexes (**9**–**10**), whereas the minor second fraction corresponded to the bis(dicobalt tetracarbonyl) dppm-coordinated complexes.

** Crystal data for **9**: $C_{43}H_{36}Co_2O_4P_2$, $M = 796.52$, triclinic, space group $P\bar{1}$, $a = 12.2764(4)$ Å, $b = 15.3093(6)$ Å, $c = 21.7463(8)$ Å, $\alpha = 104.381(2)$, $\beta = 90.547(2)$, $\gamma = 106.997(2)°$, $V = 3771.2(2)$ Å^3, $T = 180(2)$ K, $Z = 4$, $\mu = 1.006$ mm^{-1}, $D_c = 1.403$ Mg m^{-3}, 30 195 reflections collected, 13 151 independent reflections ($R_{int} = 0.0826$), goodness-of-fit on F^2 0.975, final R indices [$I > 2\sigma(I)$]: $R1 = 0.0495$, $wR2 = 0.1021$, Largest diff. peak 0.433 and hole −0.487 e Å^{-3}, 921 parameters, 20 restraints. Compound **9** contains two crystallographically independent molecules within its asymmetric unit: two of these possess a strict crystallographic inversion centre. The bond lengths and angles within all three molecules are similar and thus only one molecule is discussed. Data for **5** and **9** were collected using a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems cryostream. Cell refinement, data collection and data reduction were performed with the programs DENZO[10] and COLLECT[11] and multi-scan absorption corrections were applied to all intensity data with the program SORTAV.[12] Both structures were solved and refined with the programs SHELXS97 and SHELXL97[13] respectively. CCDC reference numbers 189063 (**5**) and 175553 (**9**). See http://www.rsc.org/suppdata/nj/b2/b206295j/ for crystallographic data in CIF or other electronic format.



Scheme 3 Proposed reaction pathway leading to formation of **7**, **8**, **9** and **10**.

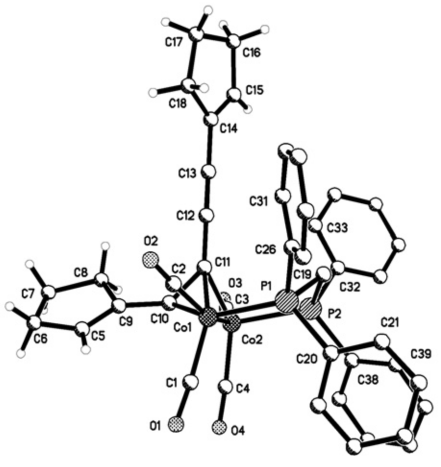


Fig. 2 Molecular structure and atom numbering scheme for [$Co_2(CO)_4$dppm{μ-η^2-(C_5H_7)C≡C–C≡C(C_5H_7)}] **9** with selected bond distances (Å) and angles (°). C9–C5 1.322(5), C14–C15 1.382(6), C9–C8 1.513(5), C14–C18 1.440(6), C8–C7 1.533(5), C7–C6 1.526(5), C6–C5 1.504(5), C15–C16 1.500(6), C16–C17 1.515(8), C17–C18 1.517(7), C14–C15 1.382(6), C14–C18 1.440(6), C14–C13 1.435(6), C9–C10 1.446(5), C5–C9–C10 126.9(3), C8–C9–C10 122.0(3), C13–C14–C18 122.6(5), C13–C14–C15 125.5(4), C6–C5–C9 113.4(4), C5–C9–C8 111.1(3), C14–C15–C16 109.7(5), C15–C14–C18 111.8(4), C11–C12–C13 178.2(4), C12–C13–C14 178.7(5).

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