C–H Bond Activation of Simple Alkenes with Cyclopentadienylcobalt Fragments: Preparation and Structure of Tri- and Tetra-cobalt μ-Cycloalkyne Cluster Complexes

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Twofold C–H bond activation of cycloalkenes resulting in the formation of tri- and tetra-nuclear cycloalkyne bridged cluster complexes takes place on reaction with reactive sources of (η^5-C_5H_5)Co fragments.

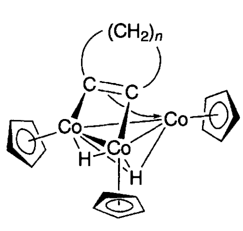
The activation of C–H bonds by metal complexes is generally thought to be the realm of the heavier transition elements. However, under certain conditions this reaction can also be facile and favourable with first row transition metals.† Using the organometallic fragments [(η-C_5R_5)CoL_n] (n = 0, 1) as building blocks, the enhanced C–H reactivity of certain metal-coordinated hydrocarbons can be utilised to synthesise novel oligonuclear complexes,[1] and quite unusual transformations of hydrocarbons can be achieved.[1,2]

Here we report the facile double C–H activation of simple, non-functionalised alkenes in the course of formation of tri- and tetra-nuclear cyclopentadienylcobalt cluster complexes.

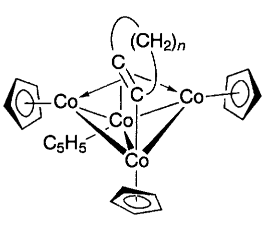
When the cycloalkenes C_nH_{2n-2} (n = 5–8) (neat or in hexane solution) are treated with the Jonas reagent[3] [(η^5-C_5H_5)Co(C_2H_4)$_2$] at 40–60 °C, a brown mixture is obtained. Using column chromatography (Al_2O_3–5% H_2O–hexane) the trinuclear cluster complexes **1a–d** are isolated in up to 40% yields. The same trinuclear products are obtained in similar yields when the reductive degradation of cobaltocene with potassium[4] is used to generate (η^5-C_5H_5)Co fragments at −5 °C in the presence of the cycloalkenes. In addition, minor amounts of the tetranuclear species **2a–c** are obtained, which can be separated from **1a–c** by repeated chromatography.

Characterisation of **1a–d** and **2a–c** is based on spectroscopic data,‡ and on single crystal X-ray structure determinations§ of **1c**, **d** and **2b**, **c**; the results from these analyses are in complete agreement. In both **1** and **2** a cycloalkyne is coordinated to a metal cluster as a bridging ligand. In complexes **1**, the two hydrogen atoms, which were abstracted from the cycloalkene, are retained as hydrido ligands. Their presence is revealed by two ^{1}H NMR resonances in the high field region (δ *ca.* −12, −29). The molecular structure of **1d** is depicted in Fig. 1 together with relevant bond parameters. The cobalt atoms form an isosceles triangle which is bridged by the cyclooctyne in the μ_3-η^1:η^1:η^2 fashion. The geometric parameters of the Co_3(μ_3-alkyne) unit [short σ-bonds Co(1/2)–C(1/8), longer bonds Co(3)–C(1/8), short distance C(1)–C(8) corresponding to a somewhat lengthened double bond] are in accord with literature values[5,6] for this type of alkyne coordination to a metal cluster. The two hydrides were located from difference electron density syntheses, one bridging the longer Co(1)–Co(2) edge and one bridging the Co_3-face of the metal cluster framework.

Complexes **1** are fluxional in solution. Several dynamic processes are observable by variable-temperature NMR spectroscopy, namely (*a*) alkyne rotation on top of the metal cluster (most likely in a 'windscreen wiper' fashion[7]); (*b*) migration of the μ_2-hydride around the CoCo edges; and (*c*) exchange between the two chemically different hydride sites (μ_2 and μ_3).



1a–d, n = 3–6



2a–c, n = 3–5

The high symmetry of the tetranuclear cluster complexes **2a–c** is reflected in their very simple NMR spectra. The molecular structure of **2c**, as determined in the crystal, is shown in Fig. 2. The molecule has a tetracobalt butterfly core which is bridged by the η^2:η^1:η^1:η^2-cycloheptyne ligand. The hinge Co(3)–Co(3A) bond of the Co_4 butterfly is somewhat longer than the other (wing) Co–Co bonds. The geometry of the Co_4C_2 unit [shorter (σ) bonds C(1)–Co(3), longer bonds C(1)–Co(1/2), long bond C(1)–C(1A)] is as expected[6] for an alkyne-bridged tetrametal butterfly cluster.

C–H bond activation in alkenes, particularly unsubstituted monoenes, is relatively rare, and has previously been achieved most effectively by pre-formed ruthenium and osmium clusters.[8] Some of the products, the cluster complexes [(μ-H)$_2${(CO)$_3$M}$_3$(μ_3-η^1:η^1:η^2-alkyne)] (M = Ru, Os),[9] are structurally closely related to **1**. The reactions described here are, however, more complicated, with C–H activation probably taking place at some intermediate state of cluster formation from mononuclear species. The ease of reaction is quite remarkable for first row transition metals.

Conventionally, **1** and **2** may be described as metal cluster complexes with μ_3-η^1:η^1:η^2- (μ-η^2-||-) and μ_4-η^2:η^1:η^1:η^2-alkyne ligands. Alternatively, they may be considered polyhedral *nido*-2,3-(RC)$_2${(η^5-C_5H_5)Co}$_3$ and *closo*-2,3-(RC)$_2${(η^5-C_5H_5)Co}$_4$ clusters. According to the Wade–Mingos rules,[10] 14 cluster bonding electrons (cbe) are needed in both cases, these being furnished by the (η^5-C_5H_5)Co (4 cbe each) and CR (3 cbe each) cage constituents, and, in the case of

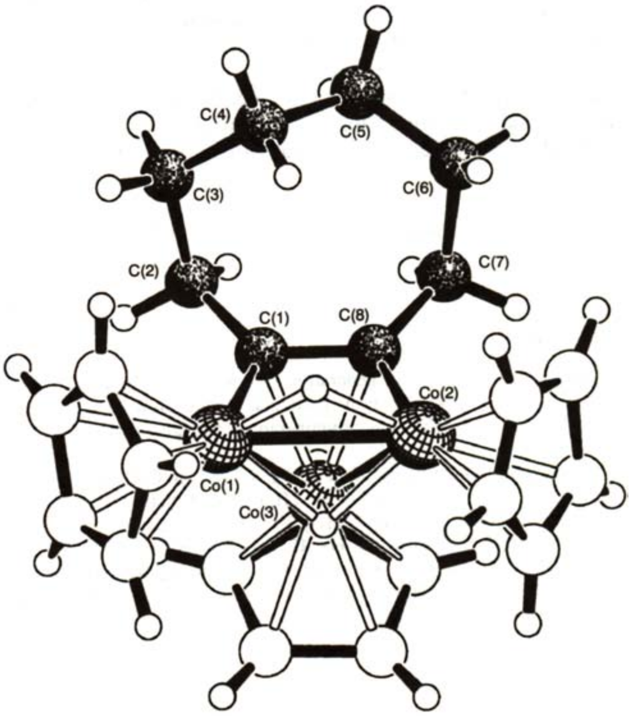


Fig. 1 The molecular structure of **1d** in the crystal. Only one set of the disordered atoms is shown. Selected bond lengths (Å): Co(1)–Co(2) 2.500(1), Co(1)–Co(3) 2.445(2), Co(2)–Co(3) 2.444(2), Co(1)–C(1) 1.914(3), Co(2)–C(8) 1.916(3), Co(3)–C(1) 1.966(3), Co(3)–C(8) 1.972(3), C(1)–C(8) 1.392(4).

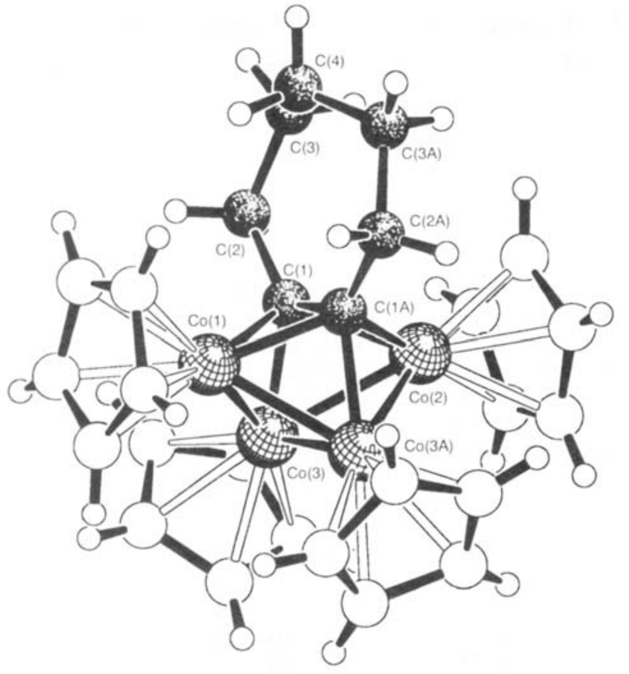


Fig. 2 The molecular structure of **2c** in the crystal. Only one set of the disordered atoms is shown. Selected bond lengths (Å): Co(1)–Co(3) 2.366(1), Co(2)–Co(3) 2.444(2), Co(3)–Co(3A) 2.417(2), Co(1)–C(1) 1.965(2), Co(2)–C(1) 1.961(2), Co(3)–C(1) 1.923(3), C(1)–C(1A) 1.499(5).

1, the two '*endo*' hydrogens (1 cbe each). A number of $(RC)_2\{(\eta^5\text{-}C_5H_5)Co\}_3$ clusters without hydrido ligands are also known; with 12 cbe, *closo* structures are attained. Here, the 1,2-C_2Co_3 cage isomers (classically described as $[\{(\eta^5\text{-}C_5H_5)Co\}_3(\mu\text{-}\eta^2\text{-}\perp\text{-alkyne})]$) are much less common than their 1,5-C_2Co_3 counterparts, the bis(μ_3-carbyne) cluster complexes $[1,5\text{-}(CR)_2\{(\eta^5\text{-}C_5H_5)Co\}_3]$.[11] Interestingly, such a complex, $[\{(\eta^5\text{-}C_5H_5)Co\}_3(\mu_3\text{-}CMe)_2]$, is one of the C–H activation products of coordinated ethene.[2c] In that system, a *nido* complex analogous to **1** and with a bridging ethyne ligand is not formed, at least not in isolable amounts.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. H. W. gratefully acknowledges the award of a Heisenberg Fellowship.

Received, 27th January 1995; Com. 5/00513B

Footnotes

† A prominent example is the generation of ferrocene from cyclopentadiene and iron, which, depending on the particular form of iron (bulk metal[12] or atoms[13]) may be brought about at temperatures as high as 300 or as low as −196 °C.

‡ *Selected NMR spectroscopic data* (at B_0 = 7.4 T, in C_6D_6) for **1a**: ^{1}H: δ −28.8 (s, br, 1H, Co_3H), −11.4 (s, br, 1H, Co_2H), 1.96 (m, 2H, CH_2), 2.45 (m, 4H, CH_2), 4.68 [s, 15H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 30.0 (CH_2), 42.9 (CH_2), 80.6 [$(\eta^5\text{-}C_5H_5)$], 165.7 (br, C). For **1b**: ^{1}H: δ −28.7 (s, br, 1H, Co_3H), −11.8 (s, br, 1H, Co_2H), 1.58 (m, 4H, CH_2), 2.56 (m, 4H, CH_2), 4.68 [s, 15H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 26.0 (CH_2), 44.7 (CH_2), 81.1 [$(\eta^5\text{-}C_5H_5)$], 160.2 (br, C). For **1c**: ^{1}H: δ −28.3 (s, br, 1H, Co_3H), −11.8 (s, br, 1H, Co_3H), 1.60 (m, 4H, CH_2), 1.80 (m, 2H, CH_2), 2.50 (m, 4H, CH_2), 4.68 [s, 15H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 29.0 (CH_2), 33.2 (CH_2), 47.0 (CH_2), 81.6 ([$\eta^5\text{-}C_5H_5$)], 165.5 (br, C). For **1d**: ^{1}H: δ −28.7 (s, br, 1H, Co_3H), −11.8 (s, br, 1H, Co_2H), 1.5–1.8 (m, 8H, CH_2), 2.3–2.5 (m, 4H, CH_2), 4.69 [s, 15H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 26.9 (CH_2), 31.8 (CH_2), 43.3 (CH_2), 81.1 [$(\eta^5\text{-}C_5H_5)$], 81.4 [$(\eta^5\text{-}C_5H_5)$], 166.5 (br, C). For **2a**: ^{1}H: δ 2.84, (quint., 2H, CH_2), 3.72 (t, 4H, CH_2), 4.36 [s, 10H, $(\eta^5\text{-}C_5H_5)$], 4.45 [s, 10H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 27.7 (CH_2), 54.8 (CH_2), 81.1 [$(\eta^5\text{-}C_5H_5$]), 82.3 [$(\eta^5\text{-}C_5H_5)$], quaternary carbons not observed. For **2b**: ^{1}H: δ 2.09 (m, 4H, CH_2), 3.32 (m, 4H, CH_2), 4.39 [s, 10H, $(\eta^5\text{-}C_5H_5)$], 4.44 [s, 10H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 27.7 (CH_2), 54.8 (CH_2), 81.1 [$(\eta^5\text{-}C_5H_5)$], 82.3 [$(\eta^5\text{-}C_5H_5)$], quaternary carbons not observed. For **2c**: ^{1}H: δ 1.93 (m, 6H, CH_2), 3.31 (m, 4H, CH_2), 4.36 [s, 10H, $(\eta^5\text{-}C_5H_5)$], 4.50 [s, 10H, $(\eta^5\text{-}C_5H_5)$]; $^{13}C\{^1H\}$: δ 30.1 (CH_2), 34.0 (CH_2), 59.5 (CH_2), 81.2 [$(\eta^5\text{-}C_5H_5)$], 82.8, [$(\eta^5\text{-}C_5H_5)$], 164.5 (C).

§ *Crystal data* for **1d**: $C_{23}H_{29}Co_3$, triclinic, a = 9.015(5), b = 9.114(5), c = 13.899(7) Å, α = 86.74(4), β = 79.23(4), γ = 64.65(4)°, V = 1013.5(9) Å^3, space group $P\bar{1}$, Z = 2, $2\theta \leqslant 54°$. Reflections measured: 4429; unique: 4429. The $(\eta^5\text{-}C_5H_5)$ ligand on Co(3) showed a twofold rotational disorder. C(4) and C(5) were also found disordered in two positions with final SOFs 0.8 and 0.2. The positions of the two hydrido ligands were taken from a difference Fourier synthesis and refined. $R1$ = 0.035 [on F, 3464 reflections with $F_o > 4\sigma(F_o)$], $wR2$ = 0.083 (on F^2, all reflections).

For **2c**: $C_{27}H_{30}Co_4$, orthorhombic, a = 9.423(7), b = 14.255(10), c = 17.046(10) Å, V = 2290(3) Å^3, space group $Pcmn$, Z = 4, $2\theta \leqslant 60°$. Reflections measured: 4192; unique: 3452. All $(\eta^5\text{-}C_5H_5)$ ligands were treated as rigid groups, those on Co(2) and Co(3) showed a twofold rotational disorder. $R1$ = 0.033 [on F, 2840 reflections with $F_o > 4\,\sigma(F_o)$], $wR2$ = 0.090 (on F^2, all reflections).

Data collection: STOE-Siemens four circle diffractometer, ω-scan, Mo-Kα radiation (graphite monochromator), ambient temperature (**1d**) or 220 K (**2c**), empirical absorption correction. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques, [SHELXS-86, SHELXL-93 (G. M. Sheldrick, Universität Göttingen, 1986; 1993)]. Unless stated otherwise all hydrogen atoms were inserted at calculated positions. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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