Some Remarkable Reactions of the Biscarbyne Clusters [μ_3-(η^1-CR^1)-μ_3-(η^1-CR^2)-{(η^5-C$_5$H$_5$)Co}$_3$] with Electrophiles

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Trinuclear [(η^5-C$_5$H$_5$)Co]$_3$ biscarbyne clusters react with electrophiles such as iodine halides, Lewis and other acids, and oxygen to give products which have been derived by substitution at the apical and next-to-apical carbon atoms.

Carbyne–metal complexes have recently commanded increasing attention as models for carbyne intermediates in heterogeneous catalysis, particularly the Fischer–Tropsch and related reactions, and alkyne metathesis.[1,2] We have reported a facile and direct entry into [μ_3-(η^1-CR^1)-μ_3-(η^1-CR^2)-{(η^5-C$_5$H$_5$)Co}$_3$] biscarbyne cluster systems (1) by the reaction of (η^5-C$_5$H$_5$)Co(CO)$_2$ with alkynes, and some of their preliminary reactions.[3] These clusters offer the unique opportunity to study the chemistry of the apical carbon atom and its substituents without the interference of other ligands, such as CO in the related and extensively investigated alkylidynetricobalt nonacarbonyl system.[4] In particular, we noted that the apical protons in (1) were rapidly exchanged by deuteriated acids suggesting the occurrence of some type of electrophilic substitution proceeding *via* a cationic carbene–carbyne cluster. We now present further data on the unprecedented reactions of these clusters.

In order to test the presumed (formal) nucleophilic reactivity of the apical carbon atom we initially investigated halogens as potential electrophiles. Treatment of (1a)[3] with Br$_2$ or N-bromosuccinimide led to green insoluble precipitates, apparently the result of oxidative degradation. On the other hand, reaction with IBr gave a mixture (difficult to separate) of all five possible halogenated derivatives of (1) (R^1,R^2 = H, I, Br) as indicated by n.m.r. and mass spectral analyses. Cleaner results were obtained by treatment with I$_2$ in (CH$_2$Cl)$_2$ (50 °C, 14 h) under oxygen and in the presence of 15 vol % of water. The latter two conditions *are required* to ensure a maximum yield of (1b)† (70%) separated from (1c)† (11%) by chromatography on alumina. At 0 °C (1a) forms a precipitate with I$_2$ from which it may be regenerated in oxygenated
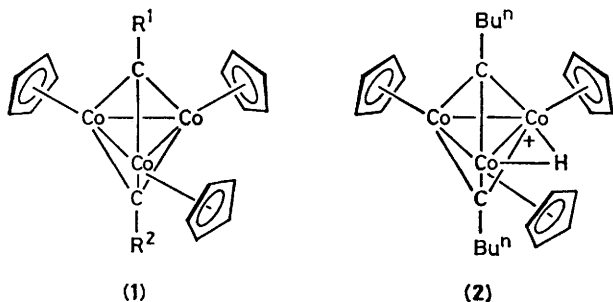
	R^1	R^2		R^1	R^2
a	H	H	e	Ph	Ph
b	I	H	f	MeO	H
c	I	I	g	Pr^{n}C:O	Bu^n
d	Bu^n	Bu^n	h	Pr^{n}CHOH	Bu^n

(1)   (2)

† This compound was fully characterized. (1b): black plates, decomp. >200 °C, *M* 523.8282 (calc. 523.8294); ^{1}H n.m.r. (C$_6$D$_6$) δ 4.376 (s, 15H) and 18.238 (s, 1H); i.r. (KBr) 1410m, 1343w, 1110m, 1000m, 862s, 830m, 802s, and 610s cm^{-1}. (1c): red-black plates, decomp. >200 °C, *M* 649.7245 (calc. 649.7263); ^{1}H n.m.r. (C$_6$D$_6$) δ 4.332 (s, 15H); i.r. (KBr) 1410m, 1345w, 1110m, 1008m, 835s, 810s, and 664s cm^{-1}. (1f): violet-brown crystals, decomp. >200 °C, *M* 427.9426 (calc. 427.9332); ^{1}H n.m.r. (CDCl$_3$) δ 4.516 (s, 15H), 4.859 (s, 3H), and 18.342 (s, 1H); i.r. (KBr) 2920m, 1225s, 1005w, 962w, 875m, 800s, and 625m cm^{-1}. (1g): violet crystals, m.p. 139—140 °C, *M* 524.0363 (calc. 524.0370); ^{1}H n.m.r. (C$_6$D$_6$) δ 1.270 (t, *J* 7.4 Hz, 3H), 1.318 (t, *J* 7.4 Hz, 3H), 1.883 (sex., *J* 7.4 Hz, 2H), 2.400 (sex., *J* 7.4 Hz, 2H), 2.556 (quin., *J* 6 Hz, 2H), 3.522 (t, *J* 7.3 Hz, 2H), 4.409 (s, 15H), and 5.000br. (t, *J* 8.0 Hz, 2H); i.r. (KBr) 2955m, 2930w, 2870w, 2850w, 1628s, 1347m, 1180m, 1005m, 837m, 820m, 803s, and 710m cm^{-1}. (1h): violet crystals, m.p. 128—129 °C, *M* 526.0531 (calc. 526.0526); ^{1}H n.m.r. (250 MHz, C$_6$D$_6$) δ 1.267 (t, *J* 7.3 Hz, 3H), 1.399 (t, *J* 7.4 Hz, 3H), 1.883 (sex., *J* 7.4 Hz, 2H), 2.15—2.90 (m, 6H), 2.881 (d, *J* 3.2 Hz, 1H), 4.391 (s, 15H), 4.996 (t, *J* 8.0 Hz, 2H), and 6.454 br. (d, *J* 9.7 Hz, 1H); i.r. (KBr) 3440w, 2955s, 2860m, 1007m, 840m, 825m, 802s, and 713m cm^{-1}.

solvents or through the action of $Na_2S_2O_3$. This initial product appears to be a charge-transfer complex. The yield of (1c) may be maximized (87%) using 2 mol. equiv. of I_2. Iodination of (1d) and (1e) could not be effected.

Compounds (1b, c) appeared good starting materials from which to generate (at least incipient) apical carbonium ions. Indeed, when (1b) in MeOH was exposed to $AgBF_4$ in CH_2Cl_2-C_6H_6 (60 °C, 6.5 h) a quantitative yield of the methoxy-carbyne (1f)† was isolated. This compound could also be the product of nucleophilic displacement of an Ag^+-co-ordinated iodide, or might alternatively be formed by a cluster addition–elimination process. Nucleophilic additions to cationic carbyne complexes are well known.[1] The halogenomethyl-idynetricobalt nonacarbonyls undergo halide displacement with thiolates by a suggested $S_{RN}1$ mechanism.[5,6]

It is remarkable that the trimetallic core of (1) survives the presence of the oxidizing species used in the above reactions. This is also shown by our finding that (1d) is not only incompletely consumed (80%) after refluxing (C_6H_{12}-EtOH, 1:1) in an air-flushed solution for 19 d, but also gives defined products, the ketone (1g) (40%)† and the alcohol (1h) (30%),† separated by reverse-phase high-performance liquid chromatography (MeCN).[7] The n.m.r. spectral assignments† of these complexes are greatly aided by the strongly deshielding effect of the trinuclear cobalt core observed previously.[3] Complex (1h) is very likely the product of a free radical oxidation, whereas (1g) might derive from (1h) by dehydrogenation.[8]

In order to pinpoint the site of electrophilic attack on (1), (1d) was treated with 1 mol. equiv. of CF_3SO_3H (CD_2Cl_2). The n.m.r. spectrum of the resulting deep green solution reveals the formation of a new complex in which the effective symmetry of (1d) is retained [δ (25 °C) 1.124 (t, J 7.3 Hz, 6H), 1.712 (sex., J 7.3 Hz, 4H), 1.986 (quin., J 7.6 Hz, 4H), 4.534 (t, J 7.8 Hz, 4H), and 5.019 (s, 15H)]. On cooling to -70 °C the (η^5-C_5H_5) signal splits into two peaks [δ 4.974 (10H) and 5.153 (5H)], but the butyl peak pattern stays unchanged. This suggests the presence of an edge-protonated structure (2) similar to that found in the protonation of the dirhodium carbene complex [(μ-CH_2){(η^5-C_5H_5)Rh(CO) }$_2$],[9] although a face-bridging hydride has been postulated in μ_3-(η^1-CR)-$FeCo_2(CO)_9H$,[10,11] and other structural alternatives are conceivable. The starting biscarbyne (1d) is regenerated quantitatively on addition of water. These findings indicate that the mechanism of H–D exchange on reaction of (1a) with

D^+ may involve a protonated apical carbon atom only as a reactive intermediate.[3]

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