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 $[\mu^3 \eta^1 - CR^1][\mu^3 \eta^1 - CR^2][(\eta^5 - C_5H_5)Co]_3$  WITH  
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David E. Van Horn and K. Peter C. Vollhardt

December 1981

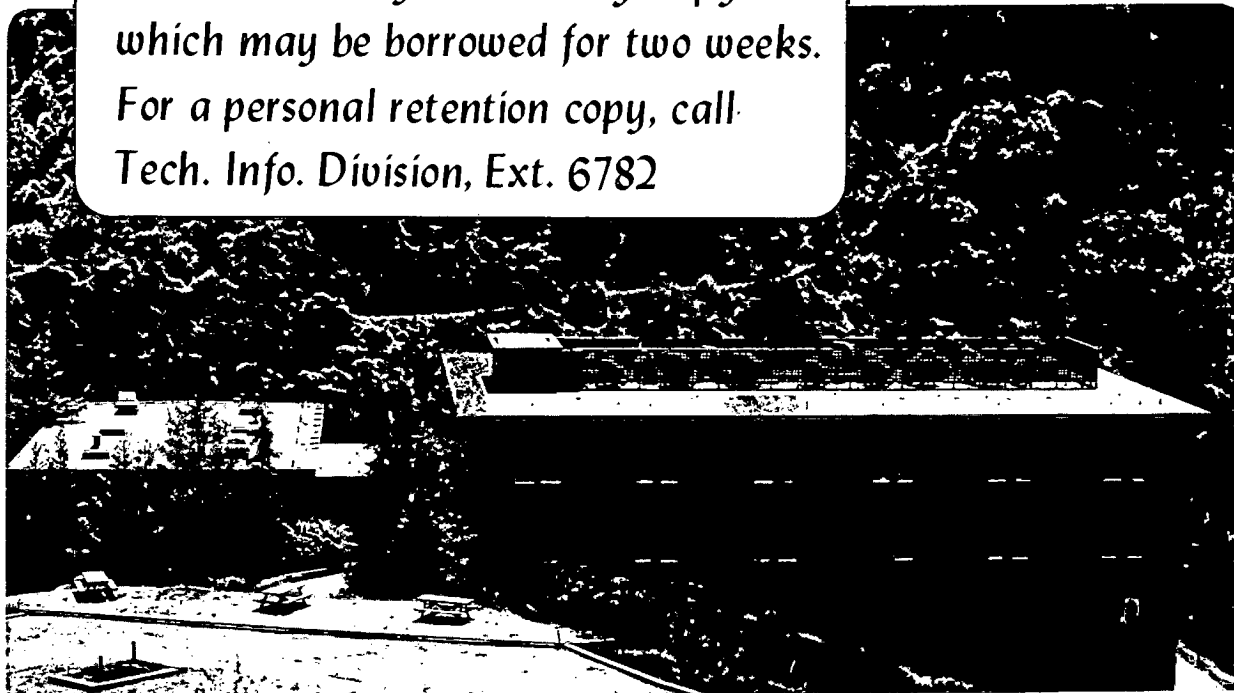
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Some Remarkable Reactions of the Biscarbyne Clusters

$[\mu^3 \eta^1 - CR^1][\mu^3 \eta^1 - CR^2][(\eta^5 - C_5H_5)Co]_3$  with Electrophiles

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Summary Trinuclear  $(\eta^5 - C_5H_5)Co)_3$  biscarbyne clusters react with electrophiles such as iodine halides, Lewis and other acids, and oxygen to give products derived from substitution at the apical and next to apical carbon atoms.

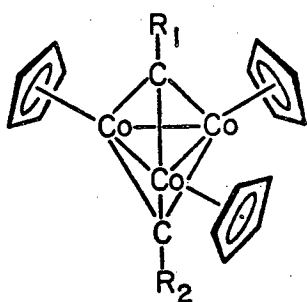
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Carbyne metal complexes have recently commanded increasing attention as models for carbyne intermediates in heterogeneous catalysis, particularly the Fischer-Tropsch and related reactions, and alkyne metathesis.<sup>1,2</sup> We have reported a facile and direct entry into  $[\mu^3 \eta^1 - CR^1][\mu^3 \eta^1 - CR^2][(\eta^5 - C_5H_5)Co]_3$  biscarbyne clusters (1) by the reaction of  $\eta^5 - C_5H_5Co(CO)_2$  with alkynes, and some of their preliminary reactions.<sup>3</sup> These systems offer the unique opportunity to study the chemistry of the apical carbon and its substituents without the

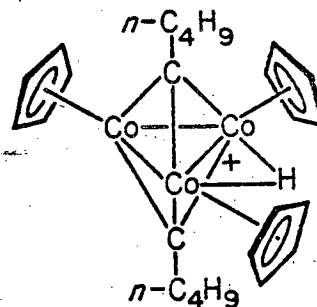
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interference of other ligands, such as CO in the related and extensively investigated alkylidynetricobalt nonacarbonyl system.<sup>4</sup> In particular, we noted that the apical protons in (1) were rapidly exchanged by deuterated acid, suggesting the occurrence of some type of electrophilic substitution proceeding through a cationic carbene-carbyne-cluster. We now present further data on the unprecedented reactions of these clusters which also bear on this observation.

In order to test the presumed (formal) nucleophilic reactivity of the apical carbon we initially investigated halogens as potential electrophiles. Treatment of (1a)<sup>3</sup> with Br<sub>2</sub> or N-bromosuccinimide led to green insoluble



1



2

- a; R<sub>1</sub> = R<sub>2</sub> = H  
 b; R<sub>1</sub> = I, R<sub>2</sub> = H  
 c; R<sub>1</sub> = R<sub>2</sub> = I  
 d; R<sub>1</sub> = R<sub>2</sub> = n-C<sub>4</sub>H<sub>9</sub>  
 e; R<sub>1</sub> = R<sub>2</sub> = C<sub>6</sub>H<sub>5</sub>  
 f; R<sub>1</sub> = CH<sub>3</sub>O, R<sub>2</sub> = H  
 g; R<sub>1</sub> = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>C(=O),  
     R<sub>2</sub> = n-C<sub>4</sub>H<sub>9</sub>  
 h; R<sub>1</sub> = CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CHOH,  
     R<sub>2</sub> = n-C<sub>4</sub>H<sub>9</sub>

precipitates, apparently the result of oxidative degradation. On the other hand, reaction with IBr gave a difficult to separate mixture of all (five) possible halogenated derivatives of 1 ( $R_1, R_2 = H, I, Br$ ) as indicated by NMR and mass spectral analysis. Cleaner results were obtained by treatment with  $I_2$  in  $(CH_2Cl)_2$  ( $50^\circ C$ , 14h) under oxygen and in the presence of 15 vol% water. The latter two conditions are required to ensure a maximum yield of (1b)<sup>†</sup> (70%) separated from (1c)<sup>†</sup> (11%) by chromatography on alumina. At  $0^\circ C$  (1a) forms a precipitate with  $I_2$  from which it may be regenerated in oxygenated 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 two equivalents 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  $CH_3OH$  was exposed to  $AgBF_4$  in  $CH_2Cl_2/C_6H_6$  ( $60^\circ C$ , 6.5h) a quantitative yield of the methoxy-carbyne (1f)<sup>†</sup> was isolated. This compound could also be the product of nucleophilic displacement of a  $Ag^+$ -coordinated iodide, or might alternatively be formed by a cluster addition-elimination

process. Nucleophilic additions to cationic carbyne complexes are well known.<sup>1</sup> The halomethylidynetricobalt nonacarbonyls undergo halide displacement with mercaptides by a suggested  $S_{RN}1$  mechanism.<sup>5,6</sup>

It is remarkable that the trimetallic core of (1) survives the presence of the oxidizing species used in the above reactions. Another manifestation of this extraordinary stability is our finding that (1d) is not only incompletely consumed (80%) after refluxing ( $C_6H_{12} - CH_3CH_2OH, 1:1$ ) in an air flushed solution for 19d(!), but also gives defined products, the ketone (1g) (40%)<sup>†</sup> and the alcohol (1h) (30%)<sup>†</sup>, separated by reverse phase high performance liquid chromatography ( $CH_3CN$ ).<sup>7</sup> The NMR spectral assignments<sup>†</sup> of these complexes are greatly aided by the strongly deshielding effect of the trinuclear cobalt core observed previously.<sup>3</sup> Complex (1h) is very likely the product of a free radical oxidation, whereas (1g) might derive from (1h) by dehydrogenation.<sup>8</sup>

In order to pinpoint the site of electrophilic attack on (1), (1d) was treated with 1 equivalent of  $CF_3SO_3H(CD_2Cl_2)$ . The NMR spectrum of the resulting deep green solution reveals

the formation of a new complex in which the effective symmetry of (ld) is retained [ $\delta$  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° the  $\eta^5$ -C<sub>5</sub>H<sub>5</sub>-signal splits in two [ $\delta$  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 ( $\mu$ -CH<sub>2</sub>) [( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Rh(CO)]<sub>2</sub>,<sup>9</sup> although a face bridging hydride has been postulated in [ $\mu^3\eta^1$ -CR] Fe Co<sub>2</sub>(CO)<sub>9</sub>H<sup>10,11</sup> and other structural alternatives are conceivable. Starting biscarbyne (ld) is regenerated quantitatively on addition of water. These findings indicate that the mechanism of H/D exchange on reaction of (la) with D<sup>+</sup> may involve a protonated apical carbon only as a reactive intermediate.<sup>3</sup>

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11.

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† This compound was fully characterized; (lb): black plates, dec.p. > 200°C, M 523.8282 (calcd. 523.8294); <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>6</sub>) δ 4.376 (s, 15H) and 18.238 (s, 1H); i.r. (KBr) 1410 m, 1343w, 1110m, 1000m, 862s, 830m, 802s, and 610s cm<sup>-1</sup>. (lc): red-black plates, dec.p. > 200°C, M 649.7245 (calcd. 649.7263); <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>6</sub>) δ 4.332 (s, 15H); i.r. (KBr) 1410 m, 1345 w, 1110 m, 1008m, 835s, 810s, and 664s cm<sup>-1</sup>. (lf): violet-brown crystals, dec.p. > 200°C, M 427.9426 (calcd. 427.9332); <sup>1</sup>H n.m.r. (CDCl<sub>3</sub>) 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<sup>-1</sup>. (lg): violet crystals, m.p. 139-140°C, M 524.0363 (calcd. 524.0370); <sup>1</sup>H n.m.r. (C<sub>6</sub>D<sub>6</sub>) δ 1.270 (t, J=7.4Hz, 3H), 1.318 (t, J=7.4Hz, 3H), 1.883 (sex, J=7.4Hz, 2H), 2.400 (sex, J=7.4Hz, 2H), 2.556 (quin, J=6Hz, 2H), 3.522 (t, J=7.3Hz, 2H), 4.409 (s, 15H), and 5.000 (bt, J=8.0Hz, 2H); i.r. (KBr) 2955m, 2930w, 2870w, 2850w, 1628s,

1347m, 1180m, 1005m, 837m, 820m, 803s, and 710 m cm<sup>-1</sup>.

(1h): violet crystals, m.p. 128-129°C, M 526.0531 (calcd.

526.0526); <sup>1</sup>H n.m.r. (250 MHz, C<sub>6</sub>D<sub>6</sub>) δ 1.267 (t, J=7.3Hz,

3H), 1.399 (t, J=7.4Hz, 3H), 1.883 (sex, J=7.4Hz, 2H), 2.15-

2.90 (m, 6H), 2.881 (d, J=3.2Hz, 1H), 4.391 (s, 15H), 4.996

(t, J=8.0Hz, 2H), and 6.454 (bd, J=9.7Hz, 1H); i.r. (KBr)

3440w, 2955s, 2860m, 1007m, 840m, 825m, 802s, and 713 m cm<sup>-1</sup>.

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