Cobalt Carbonyls with Two Different Bridging Carbene Ligands: μ_2-(But-2-en-4-olide-4-ylidene)-μ_2-(2′,2′-disubstituted-ethene-1′-ylidene)dicobalt Hexacarbonyl (Co-Co) Compounds

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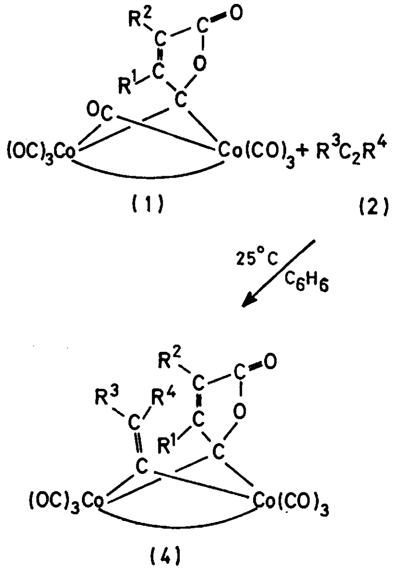
Summary (μ_2-2,3-R^1,R^2-But-2-en-4-olide-4-ylidene)(μ_2-1′,1′-R^3, R^4-ethene-2′-ylidene) dicobalt hexacarbonyl (*Co-Co*) compounds were prepared from the corresponding (μ_2-2,3-R^1,R^2-but-2-en-4-olide-4-ylidene)(μ_2-CO)Co$_2$(CO)$_6$ compounds and mono- or di-haloacetylenes and characterized by *X*-ray diffraction and spectra.

Transition metal complexes with bridging carbene ligands are rare. To the best of our knowledge no such compound with two different carbene bridges has been reported yet. The 'lactone' complexes (**1**) are known to react with acetylenes (**2**) (R^3 = H, R^4 = H, alkyl, aryl) to give two isomers of composition (**3**).[2,3] In an attempt to prepare derivatives of (**1**) with one unit of (**2**) we tried to utilize the unusual reactivity (low activity in carbonylation[4a] and cyclotrimerization,[4b] and thus in formation of new C,C bonds) of halogenoacetylenes towards cobalt carbonyls.



$\left.\begin{array}{l}\text{R}^1 = \text{H, R}^2 = \text{H,Pr}^\text{n},\\ \text{Bu}^\text{n}\text{,n-Pentyl,Ph}\end{array}\right\}\begin{array}{l}\text{R}^3 = \text{Cl, R}^4 = \text{Bu}^\text{n}\\ \text{R}^3 = \text{Br, R}^4 = \text{Br,Bu}^\text{n}\text{,Ph}\\ \text{R}^3 = \text{I, R}^4 = \text{I,Bu}^\text{n}\end{array}$

Scheme

[(C$_4$O$_2$R^{1}R^2)(R^{3}C$_2$R^4)$_2$]Co$_2$(CO)$_5$]
(**3**)

Compounds (**1**) react with halogenoacetylenes (**2**) to give the orange-red, diamagnetic complexes (**4**) in 60—90% yields (Scheme). The molecular formulae of compounds (**4**) are supported by satisfactory elemental (C,H,O,Co, halogen) analyses and (osmometric) molecular weight determinations. Mass spectra (20—70 eV) give $(M - 2\text{CO})^+$ as the highest observable ion, and the rest of the fragmentation is compatible with formula (**4**). The i.r. spectra show 5 to 6 terminal carbonyl absorptions [*e.g.* (**4**; R^1 = H, R^2 = Bu$^\text{n}$, R^3 = R^4 = Br) (n-hexane): 2114m, 2087s, 2068vs, 2058vs, 2050m,sh, and 2043w,sh cm^{-1}; $\nu(^{13}\text{CO})$: 2035vw, 2025vw, and 2017vw cm^{-1}] indicating a μ-L-μ-L′-Co$_2$(CO)$_6$ structure with different L and L′ bridges.[5] A band which may be attributed to activated olefinic ν(C–C) appeared at 1590—1550 cm^{-1}. ^{1}H N.m.r. spectra [*e.g.* (**4**; R^1 = R^2 = H, R^3 = Br, R^4 = Ph) in (CD$_3$)$_2$CO: δ 6·20 (1H, d, *J* 5 Hz, 2-H), 7·35 (5H, m, Ph), and 8·30 (1H, d, *J* 5 Hz, 3-H)] are similar to those of compounds (**1**)[6] in line position, separation, and H,H coupling.

Compounds (**4**) are generally microcrystalline solids but crystals suitable for *X*-ray diffraction could be grown from (**4**; R^1 = H, R^2 = n-pentyl, R^3 = R^4 = I). The structure (*R* = 12%) is shown in the Figure. The geometry shows the following main features: (i) the configuration of the Co atoms is pseudo-octahedral as in (**1**);[7] (ii) the Co$_2$(CO)$_6$ group is markedly asymmetric (in agreement with the i.r.

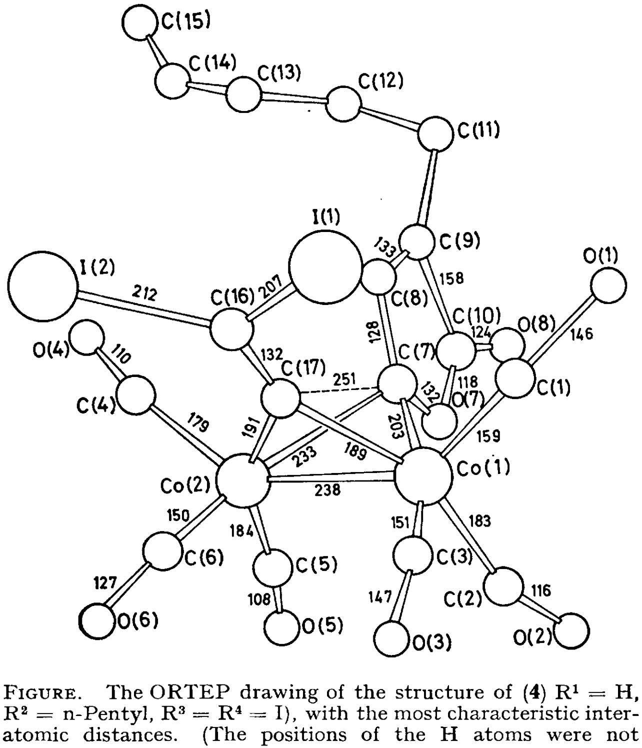


Figure. The ORTEP drawing of the structure of (**4**) R^1 = H, R^2 = n-Pentyl, R^3 = R^4 = I), with the most characteristic interatomic distances. (The positions of the H atoms were not localized.)

spectrum); (iii) the plane of the lactone ring is perpendicular to that of the CI_2 group; (iv) the double bond of the lactone ring is *cis* to the ethenylidene ligand, an arrangement similar to that of the ring and the μ_2-CO group in (**1**);[7] and (v) there is no bonding interaction between C-7 and C-17 [the most important difference from compounds (**3**)]. There is some disorder in the crystal involving the orientation of the CI_2 unit and the pentyl group.

It can reasonably be supposed on the basis of similarity of the spectra that the main structural features shown in the Figure are general for all the compounds (**4**).

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