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Preliminary communication

Reactions of polyenes, dienes and alkenes with methinyltricobalt enneacarbonyls

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Arenes coordinate to methinyltricobalt enneacarbonyls $YCCo_3(CO)_9$, through one cobalt atom[1,2] whereas cyclooctatetraene is linked symmetrically to the basal cobalt triangle[2,3]. This variation in coordination behaviour was thought to be a result of the different steric requirements of these ligands[3]. We have extended our studies to include a wide range of polyenes, dienes and alkenes and here report some representative reactions (Table 1).

TABLE 1

Organic molecules	Product(s) [a]
Trienes	$YCCo_3(CO)_6$triene(Y = Me, Ph, F), stereochemistry determined by size of triene and Y
Norbornadienes	$YCCo_3(CO)_7$norb; volatile, air-stable [b]
Cyclopentadiene	$YCCo_3(CO)_4Cp_2$; air-stable
Cyclooctadiene	Brown polymeric compounds resulting from carbonylation of the organic residue
Alkenes	
Acetylenes	$Co_2(CO)_6RCCR$, decomposition

[a] Characterised by analysis and mass spectra. [b] The Ph derivative was reported recently (ref. 5).

We conclude that (a) the nature and conformation of the products is determined by intramolecular steric interactions, the tendency of a ligand to undergo carbonylation and the type of apical substituent Y, (b) when Y = Cl, or Br, the major products are the known[4] acetylene compounds, $[Co_3(CO)_9C]_2C_2$, $[Co_3(CO)_9C_2]C_2[C_2Co_2(CO)_6]$ (c) the most stable derivatives are those where $Y = C_6H_5$. When the cobalt–ligand bond is relatively weak, as with alkenes, carbonylation results in the formation of insoluble polymeric compounds at ambient temperatures. Polymerization and carbonylation occur even with the most stable complexes at elevated temperatures (ca. 353 K).

Cyclopentadiene does not act as a diene but instead undergoes hydrogen abstraction to form cyclopentadienyl complexes in high yield. These derivatives $YCCo_3(CO)_4Cp_2$ provide the only examples where more than one organic molecule is coordinated to the cluster. A plausible structure consistent with the physical data (diamagnetic, ^1H(Cp) resonance τ5.32, three terminal ν(CO) 2045, 2002, 1985 cm^{-1} and one bridging ν(CO) 1799 cm^{-1}) is shown in Fig. 1.

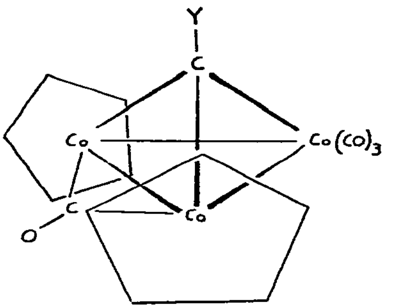

Fig. 1. Proposed structure of $YCCo_3(CO)_4Cp_2$.

An interesting type of non-rigid behaviour is exhibited by the norbornadiene complexes $YCCo_3(CO)_7$norb. From scale models it is clear that the diene must be coordinated to one cobalt atom but there are still two possible conformations, *cis* (to the apical group)–*cis* or *cis–trans* (Fig. 2). The temperature variation of the PMR spectrum for the methyl derivative is depicted in Fig. 3. Since the bridgehead and the two sets of olefin protons are related by a plane of symmetry in a *cis–cis* structure a 2/3/1/2 spectrum suggests that the frozen or instantaneous configuration is *cis–trans*. As the temperature increases the individual resonances collapse and the

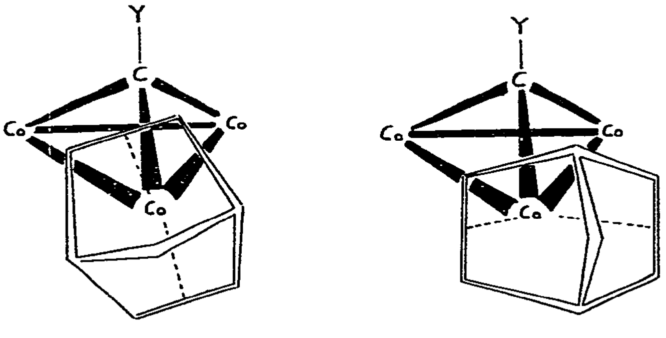

Fig. 2. Possible configurations for $YCCo_3(CO)_7$norb compounds (CO's omitted for clarity).

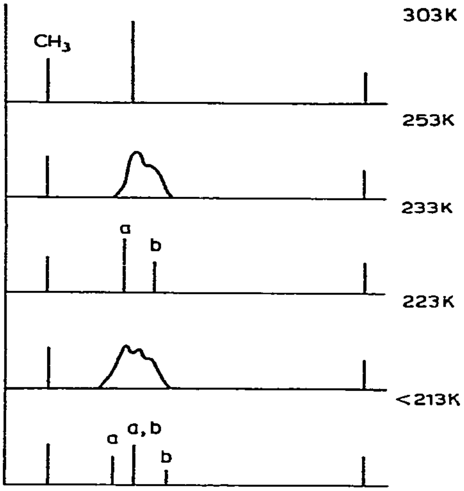

Fig. 3. Temperature variation in PMR spectrum of $CH_3CCo_3(CO)_7$norb; (a) olefin protons, (b) bridgehead protons.

usual time-averaged 4/2/2 spectrum is observed at 223 K. At room temperature the olefin and bridgehead protons also become equivalent (6/2 spectrum). The most likely rearrangement pathway would seem to be a cis—trans — cis—cis isomerisation. Products other than these norbornadiene complexes are formed at temperatures > 343 K; namely, $Co_4(CO)_{10}RCCR$ (R = Me or Ph), cyclopentadienyl compounds (see also ref. 5) and the norbornadiene dimer.

Models show that the coordinated organic ligands in these clusters are sterically hindered by the apical and carbonyl groups and studies are underway to determine whether steric factors influence the reactivity of these coordinated molecules.

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