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# Reactions of di- and poly-nuclear complexes

## V *. The reactions of $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ with phosphine and isocyanide ligands. Synthesis, spectroscopic characterization, and electrochemical studies of the mono- and di-substituted derivatives

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## Abstract

The reactions of the tetracobalt cluster $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ (**1**) with various monodentate and bidentate phosphines were examined under both thermal and electrochemical activation. With monophosphites ($P(OMe)_3$), monophosphines ($PMe_3$, $PPh_2H$, $PPh_3$), or isocyanides (t-BuNC) the mono- and di-substituted clusters $[Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)L_n(CF_3C_2CF_3)]$ ($n = 1$ or 2) were isolated in high yields from the thermal reactions as mixtures of isomers, and were characterised spectroscopically. With diphosphines $[PPh_2(CH_2)_nPPh_2$, $n = 1$ dppm, $n = 2$ dppe] disubstituted clusters were formed. The reactions of **1** with some of the bulky phosphorus donor ligands such as $PPh_3$ are regioselective. In the case of $PMe_3$ thermally-induced substitution of **1** led to partial fragmentation into the tricobalt cluster $[CpCo_3(CO)_2(\mu\text{-}CO)(PMe_3)_2(CF_3C_2CF_3)]$. The catalytic activity of the tetracobalt clusters in the homogeneous linear isomerisation of monoenes was examined.

## Introduction

Transition metal cluster complexes have attracted much attention as homogeneous catalysts and as models for catalysis at metal surfaces [1]. The major problem encountered in the use of clusters in catalysis is their thermal and photochemical instability [2]. A solution to this problem is to design clusters with flexible

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* For part IV see ref. 3.

supporting bridges capable of maintaining the integrity of a cluster framework and yet allowing facile metal–metal bond cleavage and reformation.

In previous work, we observed that the readily available dinuclear iron(II) complex, $[Cp(CO)Fe\{\mu\text{-}C(CF_3)=C(CF_3)(SMe)\}_2Fe(CO)Cp]$ reacts with cobalt octacarbonyl to afford the tetracobalt cluster $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ (**1**) by a ligand transfer process [3]. We have now investigated the reactions of **1** with phosphines, phosphites, and isocyanide under thermal, photochemical, and electrochemical conditions in order to study the CO substitution reactions. The substitution chemistry of organometallic complexes, either mono- or polynuclear, has been extensively investigated in the past few years [4–21]. The enhanced lability of paramagnetic species relative to that of the closed-shell parent is widely recognized [5]. Electron-transfer chain catalyzed (ETC) mechanisms [6–21] can operate provided (i) the parent- and the substituted radical anions (or cations) are sufficiently long lived to undergo substitution and electron transfer, respectively, and (ii) the substituted product is harder to reduce (or to oxidize) than the parent, a condition which provides the driving force for the homogeneous electron transfer [6–21]. Several ETC-catalyzed substitutions under reducing (chemical or electrochemical) conditions have been reported [6,8–21]. When the second condition is not met, i.e. when the homogeneous electron transfer is not spontaneous, an electrode-induced substitution may well take place [6d,22–24].

We have also examined the behaviour of the tetracobalt clusters in the homogeneous catalytic isomerisation of 1-hexene, and have compared the activity and the selectivity of **1** with those of its substituted derivatives toward the same substrate under identical conditions.

## Results and structural aspects

### *1. Synthetic aspects*

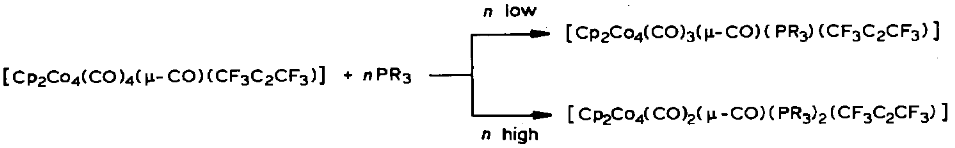
*Reactions of $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ (1) with unidentate phosphines or phosphites and isocyanides*

Reaction of 2 equiv. of $P(OMe)_3$ to a refluxing thf solution of **1** led to the isolation of a mixture of monosubstituted isomers **2a** and **2b** $[Cp_2Co_4(CO)_3(\mu\text{-}CO)\{P(OMe)_3\}(CF_3C_2CF_3)]$ which were separated from unreacted starting materials by column chromatography. At higher concentrations of phosphite ligand (1/10 ratio) the disubstituted isomeric compounds **3a** and **3b** $[Cp_2Co_4(CO)_2(\mu\text{-}CO)\{P(OMe)_3\}_2(CF_3C_2CF_3)]$ were formed together with **2a** and **2b**. Photochemical activation (thf solution, $\lambda > 300$ nm) of a mixture of **1** and an excess of trimethylphosphite (1/10 ratio) gave only the monosubstituted derivatives **2a** and **2b**.

Similarly the replacement of CO with phosphines ($PMe_3$, $PPh_2H$ and $PPh_3$) occurred quite readily in refluxing thf ($PPh_2H$ and $PPh_3$) or in dichloromethane at room temperature ($PMe_3$) to give good yields. A mixture of monosubstituted isomers $[Cp_2Co_4(CO)_3(\mu\text{-}CO)(PR_3)(CF_3C_2CF_3)]$ (**4a**, and **4b**, $R = PMe_3$; **7a**, and **7b**, $R = PPh_2H$) were formed when **1** reacted with low concentrations (1/1 ratio) of $PMe_3$ or $PPh_2H$. When an excess of $PPh_2H$ was used (1/5 ratio), a disubstituted complex **8** $[Cp_2Co_4(CO)_2(\mu\text{-}CO)(PPh_2H)_2(CF_3C_2CF_3)]$ was isolated. At higher concentrations of trimethylphosphine a disubstituted complex **5** $[Cp_2Co_4(CO)_2(\mu\text{-}CO)(PMe_3)_2(CF_3C_2CF_3)]$ was obtained together with a trinuclear cobalt compound

**6** $[CpCo_3(CO)_2(\mu\text{-}CO)(PMe_3)(CF_3C_2CF_3)]$. Only a monosubstituted isomeric compound was isolated when **1** was treated with a large excess of $PPh_3$, and no product arising from further substitution of CO by $PPh_3$ beyond $[Cp_2Co_4(CO)_3(\mu\text{-}CO)(PPh_3)(CF_3C_2CF_3)]$ (**9**) was formed even after prolonged reaction times.

Treatment of **1** with 1 equiv. of t-butylisocyanide in dichloromethane at room temperature generated the monosubstituted derivative $[Cp_2Co_4(CO)_3(\mu\text{-}CO)(t\text{-}BuNC)(CF_3C_2CF_3)]$ (**10**) within 5 min. Thermal activation of a thf solution of **1** and t-BuNC in 1/2 molar ratio afforded a mixture of disubstituted isomeric complexes **11a** and **11b** $[Cp_2Co_4(CO)_2(\mu\text{-}CO)(t\text{-}BuNC)_2(CF_3C_2CF_3)]$.



$$[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)] + nPR_3 \begin{cases} \xrightarrow{n\ \text{low}} [Cp_2Co_4(CO)_3(\mu\text{-}CO)(PR_3)(CF_3C_2CF_3)] \\ \xrightarrow[n\ \text{high}]{} [Cp_2Co_4(CO)_2(\mu\text{-}CO)(PR_3)_2(CF_3C_2CF_3)] \end{cases} \quad (1)$$

(1)

*Reactions of 1 with bidentate phosphines*

Addition of a large excess of $PPh_2(CH_2)_nPPh_2$ ($n = 1$, dppm; $n = 2$, dppe) to a refluxing thf solution of **1** yielded the substituted derivatives $[Cp_2Co_4(CO)_2(\mu\text{-}CO)(L_2)(CF_3C_2CF_3)]$ (**12**, L = 1/2 dppm; **13**, L = 1/2 dppe).

Complexes **12** and **13** were separated from the excess of diphosphine ligands by column chromatography.

$$\begin{aligned} &\underset{(\mathbf{1})}{[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]} + \underset{(L = \text{dppm, dppe})}{L\ (\text{in excess})} \quad \rightarrow \\ &\qquad\qquad [Cp_2Co_4(CO)_2(\mu\text{-}CO)(L_2)(CF_3C_2CF_3)] \quad (2) \end{aligned}$$

*2. Spectroscopic characterisation and hypothesized structure of the phosphine, phosphite or isocyanide-substituted cobalt clusters*

The compounds mentioned above were mainly characterised by microanalysis and by mass, IR and NMR spectroscopy (Experimental section and Table 1). Spectroscopic data in solution for these substituted species indicate that the geometry of the parent complex has been retained.

*Monosubstituted complexes*

The CO stretching region in the infrared spectra of the monosubstituted derivatives **9** and **10** is characterised by a pattern of four bands between 1700 and 2100 $cm^{-1}$ consistent with two Co(CO)L (L = $PPh_3$, t-BuNC) and $Co(CO)_2$ fragments bridged by one CO. For monosubstituted compounds **2**, **4** and **7**, the complex patterns of $\nu$(CO) bands suggests the presence of isomers in solution (hexane) as well as in the solid state (KBr pellets); this was confirmed by NMR spectroscopy, which revealed that in each case two isomers had been formed which could not be separated by column chromatography. The ratios of the two isomers of types **a** and **b** in $[Cp_2Co_4(CO)_3(\mu\text{-}CO)L(CF_3C_2CF_3)]$ (L = phosphine or phosphite) were determined by integration of the respective signals in the $^{31}P$, $^{19}F$ or $^{1}H$ NMR spectra. Compound **9** displays an IR pattern very similar to that for monosubstituted complexes of type **a**, suggesting strongly that the phosphorus coordination site is the

*(Continued on p. 116)*

Table 1

Spectroscopic data

| L | Compound [a] | | IR [b] $\nu$ (cm$^{-1}$) | | $^1$H NMR [c] |
|---|---|---|---|---|---|
| | | | $\nu$(CO) | $\nu$(CN) | |
| P(OMe)$_3$ | “Co$_4$”L | **2a** | 2032s, 1965m, 1945s, 1818m,br | | 5.24(s,5H), 4.77(s,5H), 3.66(d,$^3J$(P–H)) 11.3,9H) |
| | | **2b** | 2044s, 1994m, 1975s, 1836m,br | | 5.24(s,5H), 4.72(s,5H), 3.66(d,$^3J$(P–H) 11.3,9H) |
| | “Co$_4$”L$_2$ | **3a** | 1962m, 1935s, 1787m | | 5.13(s,5H), 4.63(s,5H), 3.67(d,$^3J$(P–H) 11.3,9H), 3.57(d,$^3J$(P–H) 11.3,9H) |
| | | **3b** | 1994s, 1950w, 1800mw | | 5.11(s,5H), 4.67(s,5H), 3.59(d,$^3J$(P–H) 11.3,18H) |
| PMe$_3$ | “Co$_4$”L | **4a** | 2011(s), 1958(vs), 1934(m), 1813(m) | | 5.23(s,5H), 4.74(s,5H), 1.40(d,$^2J$(P–H) 9,9H) |
| | | **4b** | 2027m, 1984m, 1962m, 1820m | | 5.19(s,5H), 4.68(s,5H), 1.35(d,$^2J$(P–H) 9, 9H) |
| | “Co$_4$”L$_2$ | **5** | 1945vs, 1917vs, 1793s | | 5.12(s,5H), 4.65(s,5H), 1.33(d,$^2J$(P–H) 9,9H), 1.31(d,$^2J$(P–H) 9,9H) |
| | “Co$_3$”L$_2$ | **6** | 2022s, 1971s, 1818m | | 4.68(s,5H), 1.40(d,$^2J$(P–H) 9,18H) |
| PPh$_2$H | “Co$_4$”L | **7a** | 2012m, 1964m, 1930m, 1819mw | | 7.40(m,10H), 5.34(d,$J$(P–H) 337,1H), 4.79(s,5H), 4.75(s,5H) |
| | | **7b** | 2032s, 1981m, 1954m, 1836mw | | 7.40(m,10H), 5.80(d,$J$(P–H) 348,1H), 4.79(s,5H), 4.75(s,5H) |
| | “Co$_4$”L$_2$ | **8** | 1955s, 1925s, 1785m [d] | | 7.40(m,20H), 5.77(d,$J$(P–H) 345,1H),<br>5.32(d,$J$(P–H) 340,1H),<br>4.76(s,5H), 4.72(s,5H) |
| PPh$_3$ | “Co$_4$”L | **9** | 2020s, 1974s, 1926s, 1809s [d] | | 7.50(m,15H), 4.85(s,5H), 4.80(s,5H) |
| t-BuNC | “Co$_4$”L | **10** | 2024s, 1996vs, 1968s, 1835s | 2160m | 5.15(s,5H), 4.63(s,5H), 1.32(s,9H) |
| | “Co$_4$”L$_2$ | **11a** | 1994mw, 1953s, 1805m | 2136m | 5.13(s,5H), 4.58(s,5H), 1.40(m,18H) |
| | | **11b** | 2005m, 1981s, 1815m | 2146m | 5.13(s,5H), 4.52(s,5H), 1.54(m,18H) |
| dppm | “Co$_4$”LL | **12** | 1962s, 1930s, 1768m | | 7.40(m,10H), 5.20(s,5H), 4.91(s,5H), 3.58(m,2H) |
| dppe | “Co$_4$”LL | **13** | 1968s, 1930s, 1756m | | 7.50(m,10H), 5.08(s,5H), 4.92(s,5H), 2.15(d,$J$(P–H) ~ 13,2H) |
| CO | “Co$_4$” [e] | **1** | 2055s, 2030s, 2000m, 1975s, 1849s | | 5.33(s,5H), 4.79(s,5H) |

| L | Compound [a] | | $^{19}$F NMR [c] | $^{13}$C NMR [c] (RT) | $^{31}$P NMR [d,h] |
|---|---|---|---|---|---|
| P(OMe)$_3$ | "Co$_4$"L | **2a** | 44.58(q,$J$(F–F) 7.3,3F),<br>43.97(q,$J$(F–F) 7.3,3F) | 127.1(d.q.,$J$(F–C) 277,$J$(P–C) 21,$CF_3$),<br>85.91(s,$C_5H_5$), 83.05(s,$C_5H_5$), 52.6(d,$J$(P–C) 4.6,<br>P(O$CH_3$)$_3$) | +137.5(s) [g] |
| | | **2b** | 45.21(m,3F), 44.58(m,3F) | 127(q,$J$(F–C) 276,$CF_3$), 85.9(s),$C_5H_5$),<br>83.85(s,$C_5H_5$); 52.3(d,$J$(P–C) 4.6,P(O$CH_3$)$_3$) | +143.2(s) |
| | "Co$_4$"L$_2$ | **3a** | 43.36(q,$J$(F–F) 7,3F),<br>42.20(d.q.,$J$(P–F) 2.2, $J$(F–F) 7,3F) | | +156.6(s), +136.9(s) |
| | | **3b** | 44.0(m,6F) | | +147.3(s), +142.2(s) |
| PMe$_3$ | "Co$_4$"L | **4a** | [44.07m; 42.85m] | | +9.56(s) |
| | | **4b** | | | +8.45(s) |
| | "Co$_4$"L$_2$ | **5** | 43.14(q,$J$(F–F) 7.3,3F), 41.32(m,3F) | | |
| | "Co$_3$"L$_2$ | **6** | 50.04(t,$J$ ~ 10,3F), 49.67(t,$J$ ~ 10,3F) | 84.3(s,$C_5H_5$), 18.1(d,$J$(P–C) 28,P($CH_3$)$_3$) [f] | −2.15(d), +12.7(d)<br>($J$(P–P) 42) |
| PPh$_2$H | "Co$_4$"L | **7a** | 44.50(q,$J$(F–F) 7.3,3F), 43.49(m,3F) | | [+14.2(s); +10.2(s)] |
| | | **7b** | 44.15(q,$J$(F–F) 7.3,3F), 42.35(m,3F) | | |
| | "Co$_4$"L$_2$ | **8** | 42.95(q,$J$(F–F) 7.4,3F), 39.97(m,3F) | 137.1–128.2(P($C_6H_5$)$_2$H), 85.91(s,$C_5H_5$),<br>82.90(s,$C_5H_5$) [i] | +13.3(s), +14.8(s) |
| PPh$_3$ | "Co$_4$"L | **9** | 44.60(q,$J$(F–F) 7.3,3F), 43.72(m,3F) | | |
| t-BuNC | "Co$_4$"L | **10** | 45.08(q,$J$(F–F) 6.7,3F),<br>44.53(q,$J$(F–F) 6.7,3F) | 85.81(s,$C_5H_5$), 82.94(s,$C_5H_5$), 30.16(s,But) | |
| | "Co$_4$"L$_2$ | **11a** | [44.40(q,$J$(F–F) 7.5),43.89(m)] | | |
| | | **11b** | | | |
| dppm | "Co$_4$"LL | **12** | 40.36(q,$J$(F–F) 7.3,3F), 39.03(m,3F) | | +40.45,<br>+30.5(AB,$J_{AB}$ 76) |
| dppe | "Co$_4$"LL | **13** | 42.04(q,$J$(F–F) 8.5,3F),<br>40.11(m,$J$(F–F) 8.0,<br>$J$(P–F) 1.5,3F) | | +35.4(s) |
| CO | "Co$_4$" [e] | **1** | 45.57(s) | 1.451(m,=$C$-CF$_3$), 126.36(q,$J$(C–F) 275,$CF_3$),<br>126.0(q,$J$(C–F) 275,$CF_3$),<br>86.46(s,$C_5H_5$), 83.22(s,$C_5H_5$) | |

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[a] L = monophosphine; LL = biphosphine; "Co$_4$" = $Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)(CF_3C_2CF_3)$, $n$ = 1 or 2; "Co$_3$" = $CpCo_3(CO)_3(CF_3C_2CF_3)$. [b] Hexane. [c] $\delta$ in ppm; $J$ in Hz; CDCl$_3$. [d] $\delta$ in ppm; $J$ in Hz; CH$_2$Cl$_2$. [e] $n$ = 0; ref. 3. [f] CD$_2$Cl$_2$. [g] Toluene-$d_8$. [h] At ~ −80 °C. [i] At −60 °C, CD$_2$Cl$_2$ ($\delta$(CO)): 236.7(s), 213.9(s), 203.7(s).

same in these two derivatives. The infrared spectra in the carbonyl region of the monosubstituted compounds of types **a** and **b** resembles that of the parent cluster **1**. The consistent trend within this family of homologues emphasizes that the stretching bands associated with both terminal and bridging ligands are systematically shifted to low frequency by ca. 20 $cm^{-1}$ for type **a** and ca. 40 $cm^{-1}$ for type **b** by phosphine substitution (Table 1). This observation is consistent with a greater degree of $\pi$ back-bonding in the cobalt–carbon linkages owing to the presence of the phosphines, which are stronger $\sigma$-donor but weaker $\pi$-acceptor ligands than the displaced carbon monoxide [25].

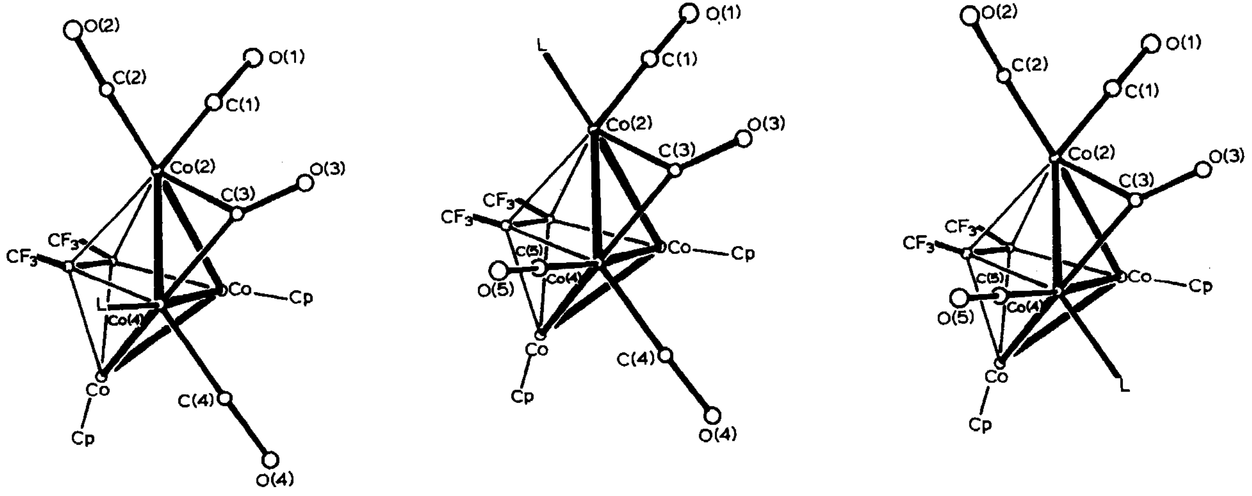
Inspection of the variable temperature $^{13}C$ NMR spectra of the parent cluster **1** [3] and substituted complexes provides no useful information on dynamics of these species. At room temperature the resonances assigned to $^{13}CO$ atoms are very broad. When the solution is cooled the increased quadrupolar relaxation of the $^{59}Co$ nuclei causes a sharpening of the resonances but does not allow the observation of the complete P–C coupling pattern. Furthermore there is no evidence for intramolecular CO exchange in the case of **1**, and such a feature seems to be maintained for the substituted products. Since the bridging carbonyl in cluster **1** is retained in the substituted derivatives there are four potential coordination sites for phosphorus or isocyanide, and thus four possible monosubstituted isomers. Of these, only one is observed for **9**, indicating that the CO substitution by $PPh_3$ in the "butterfly" cluster **1** is regioselective. With less bulky ligands, such as $PMe_3$, $P(OMe)_3$ and $PPh_2H$, two isomers are formed. The observation that the ratio of the type **a** and type **b** isomers for the derivative with the less bulky phosphine $PMe_3$ are very different (Table 2) suggests that the electronic factors play a part in determining the ligand coordination site, so that the four sites of the $Co_4$ unit seem to have non-equivalent acceptor requirements. The X-ray structure of the parent cluster **1** (Fig. 1) suggests that one (C(5)O(5)) of the carbonyl ligands is more labile and one (C(1)O(1)) is less labile than the others. Thus the data indicate that cluster **1** undergoes preferential displacement of the C(5)O(5) ligand by phosphines. However the fact that only one pair of isomers is obtained with the less bulky ligands suggests that steric contraints also may play a role in this context. Accordingly, since the C(1)O(1) ligand in the parent cluster is not very labile, three possible structures can be suggested for the monosubstituted complexes (see Scheme 1).

Table 2

Effect of ligand size and basicity on the **b**/**a** ratio for the equilibrium **b** $\rightleftharpoons$ **a** in the case of $[Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)L_n(CF_3C_2CF_3)]$

| L | Cone angle [a] (°) | Basicity [a] ($cm^{-1}$) | *n* | **b**/**a** |
|---|---|---|---|---|
| $PPh_3$ | 145 | 2068.9 | 1 | >100 |
| $PPh_2H$ | 128 | 2073.3 | 1 | 1.3 |
| | | | 2 | >100 |
| $P(OMe)_3$ | 107 | 2079.5 | 1 | 1.7 |
| | | | 2 | 2.0 |
| $PMe_3$ | 118 | 2064.1 | 1 | 1.5 |
| | | | 2 | >100 |

[a] Ref. 26.



(I)

(II)

(III)

Scheme 1. The possible isomers of the monosubstituted compounds (L = $PR_3$, $P(OMe)_3$ or t-BuNC).

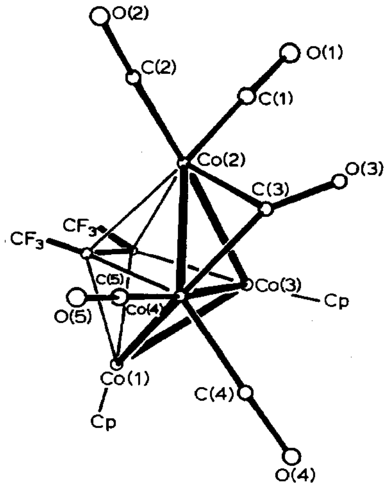


Fig. 1. A perspective view of the molecule of the parent cluster with selected bond lengths (Å) [27]: Co(2)–C(1) 1.699(21), Co(2)–C(2) 1.734(20), Co(2)–C(3) 1.954(18), Co(4)–C(4) 1.728(20), Co(4)–C(5) 1.789(21), Co(4)–C(3) 1.826(18).

Structures I and II seem to be more likely from the following observations:

(i) The X-ray data [27] show that the C(5)O(5) ligand is the most labile carbonyl in the parent cluster;

(ii) CNDO calculations [28] indicate that in acetylene carbonyl tetrametallic complexes, the hinge metal atoms carry higher positive electronic charge than their wing counterparts. Thus replacement of a carbonyl by a more basic phosphine ligand is favoured for CO in a hinge position if the process is mainly controlled by ground-state electronic factors:

(iii) Structure III would involve steric strain arising from interaction of the two adjacent cyclopentadienyl ligands.

At this stage, we cannot conclusively identify the separate isomers of types **a** and **b**.

*Disubstituted tetracobalt complexes*

The disubstituted derivatives **3** and **11** were both obtained as mixtures of two structurally different species that could not be separated by column chromatography, but the presence of two isomers **a** and **b** was established by NMR study. In contrast with the other disubstituted complexes no isomerism was observed. Comparison of the infrared spectra of the disubstituted products **3a**, **5**, **8**, **12** and **13** in the carbonyl region indicates that they are isostructural (Fig. 2). The shift (ca. 70 $cm^{-1}$) of the bridging carbonyl band from 1849 $cm^{-1}$ in the parent **1** was particularly diagnostic of disubstitution in the tetracobalt cluster [25]. The most important difference in the IR spectra between the mono- and di-substituted derivatives is the lowering (ca. 20 $cm^{-1}$) of all the values of $\nu(CO)$ on going from $[Cp_2Co_4(CO)_3(\mu\text{-}CO)L(CF_3C_2CF_3)]$ to $[Cp_2Co_4(CO)_2(\mu\text{-}CO)L_2(CF_3C_2CF_3)]$ (L = unidentate or 1/2 bidentate phosphine). For the disubstituted isocyanide complexes the $\nu(CO)$ bands are at higher frequency than those for the diphosphine disubstituted products, which is consistent with the good $\pi$-acceptor power of the iso-

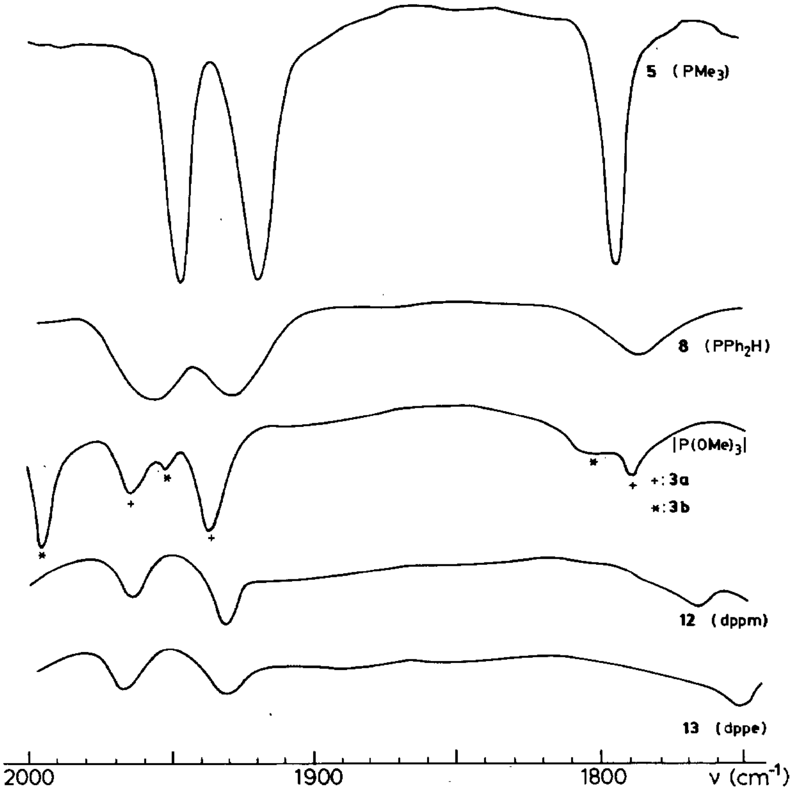
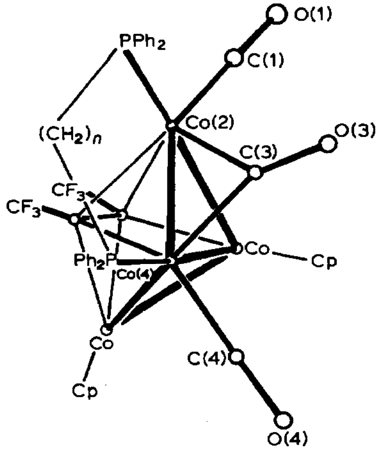


Fig. 2. Infrared spectra of disubstituted complexes in the carbonyl region.

cyanide ligands. The diphosphine ligand configuration in complexes **12** and **13** is suggested by the $^{31}P$ NMR data. It is noteworthy that a phosphorus atom involved in a five-membered chelate ring experiences anomalously large nuclear deshielding upon coordination compared to those observed for four- or six-membered rings [29]. This deshielding has been expressed in terms of a ring-effect parameter $\Delta R$ [30]; the ring-effect parameter $\Delta R$ values for **12** (ca. 60 ppm) and **13** (ca. 47 ppm) are consistent with the presence of a five-membered Co–P–C–P–Co ring in **12** and a six-membered Co–P–C–C–P–Co ring in **13** [31]. We thus concluded that disubstitution of **1** by dppm and dppe must have occurred across the carbonyl-bridged Co(2)–Co(4) bond to yield the structure shown in Fig. 3. The bridging position of the dppm and dppe ligands is also supported by the results of the electrochemical experiments (see section 3). An alternative possibility for **12** and **13** would be a structure in which the diphosphine has replaced the C(2)O(2) and the C(4)O(4) ligands in the parent cluster, but the steric constraint which would result from the close proximity of the phenyl moieties and the cyclopentadienyl ligands makes this less likely. Further support for the asymmetric structure (IV) of the diphosphine complexes comes from the $^{1}H$ NMR spectrum (Table 1), in which the non-equivalent $CH_2$ moiety of the dppm ligand gives rise to an ABXX′ pattern.

The structural similarity of both diphosphine products and complexes **3a**, **5** and **8** suggests that the monophosphine derivatives have the geometry V, with the phosphines also bonded to two different metal centres. The $^{31}P$ NMR spectrum of **8**

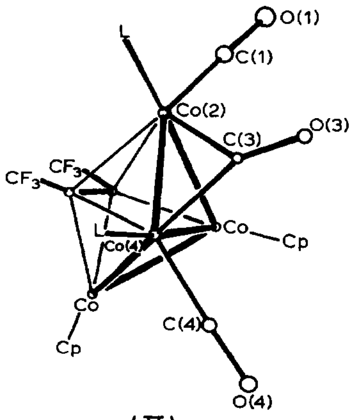


(IV)

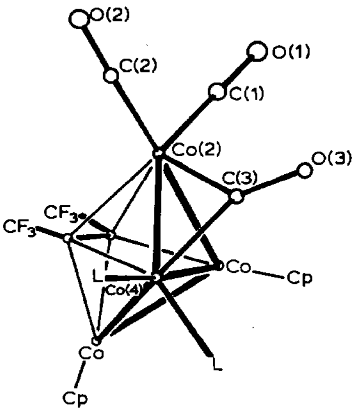
Fig. 3. Suggested structure for dppm and dppe substituted complexes.

is consistent with such a structure; the absence of symmetry in this complex gives rise to two resonances located at +13.3 and +14.8 ppm at −80 °C. At room temperature only a broad resonance is observed; but on cooling the signal splits into two singlets. An increase in the quadrupolar relaxation of the $^{59}$Co nuclei on cooling seems to be responsible for this splitting, and a possible rapid interconversion of isomers at room temperature is thus unlikely.

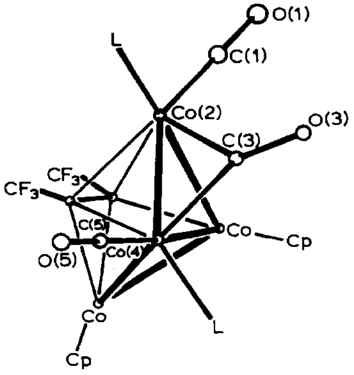
The most important difference in the IR spectra of the disubstituted complexes of types **a** and **b** is the shift to higher frequencies of the stretching bands of the terminal carbonyl ligands on going from **a** to **b**, with the notable feature that one of the $\nu$(CO) resonances is twice more shifted than the other one. This observation suggests that the geometry (VI), characterised by two phosphine or isocyanide ligands located on the same cobalt atom, could be discarded for complexes of type **b**. Substitution of two CO ligands in **1** by P(OMe)$_3$ or t-BuNC should give rise to



(V)



(VI)



(VII)

(L = P(OMe)$_3$ or t-BuNC)

identical shift values for both $\nu$(CO) bands. Thus it seems likely that the structures of **3b** and **11b** are as shown in VII. Steric effects also make arrangement VI improbable.

At room temperature the $^{19}$F NMR spectra of the disubstituted compounds consist of a quartet and a multiplet or two multiplets (Table 1). These patterns are consistent with IV (**12**, **13**), V (**3a**, **5**, **8**) or VII (**3b**, **11b**), and reveal the presence of non-equivalent CF$_3$ groups as expected for asymmetric molecular structures. The F–F coupling constant values (~ 7 Hz) are in good agreement with a *trans*-CF$_3$ configuration. Moreover the appearance in some spectra of multiplets is indicative of P–F coupling.

### *A disubstituted tricobalt cluster*

Thermal reaction of cluster **1** with a large amount of PMe$_3$ led to a trimeric species **6** along with the disubstituted tetracobalt complex **5**. Compound **6** was formulated as [CpCo$_3$(CO)$_3$(PMe$_3$)$_2$(CF$_3$C$_2$CF$_3$)] on the basis of its analysis and mass spectra. It displays IR and NMR spectral properties (vide infra) consistent with this formulation and with previously reported data for the iron complex

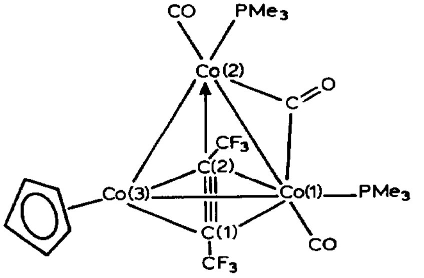


Fig. 4. Suggested structure for **6**.

$[Fe_3(CO)_9(\mu\text{-}C_2Ph_2)]$ [32]. The CO stretching region in the infrared spectrum is characterised by a three-band pattern between 1700 and 2100 $cm^{-1}$ consistent with formulation of two Co(CO) moieties bridged by one CO. The $^{31}P$ NMR spectrum at room temperature, shows two resonances which split on cooling (Table 1); the coupling constant $J(P\text{–}P) \sim 44$ Hz is consistent with two phosphine ligands located on two different cobalt atoms [33]. The room temperature $^{19}F$ NMR spectrum shows an $A_3B_3$ pattern with a coupling constant $J(F\text{–}F) \sim 10$ Hz consistent with a *trans*-$CF_3$ configuration. On the basis of the spectroscopic data we suggest for **6** the structure illustrated in Fig. 4. In this geometry the hexafluorobut-2-yne fragment lies above the plane of the Co triangle in such a way that one acetylene carbon, C(2), is coordinated to all three cobalt atoms, whereas the other, C(1), is bonded to two cobalt atoms only. As Dahl and coworkers did for the closely related iron cluster $[Fe_3(CO)_9(\mu\text{-}C_2Ph_2)]$ [32], we can regard the bonding of the alkyne with three cobalt atoms as an olefinic coordinating group through two normally $\pi$-electrons in a $\sigma$-type $sp^2$ orbital on C(2) directed toward an orbital of Co(2) with the two olefinic $\pi$-electrons then distributed over Co(1) and Co(3).

The structures of mono- or di-substituted compounds could not be determined by X-ray diffraction because no suitable crystals could be obtained.

## *3. Electrochemistry of* $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ *(1)*

### *Electrochemistry in the absence of ligands*

The cyclic voltammogram (CV) of the tetracobalt cluster **1** in a $thf/Bu_4NPF_6$ electrolyte shows two well-defined reduction peaks of equal heights, at $E_{1/2} = -1.13$ V and $E_{1/2} = -2.03$ V (Fig. 5). A third (composite) wave ($E_{p,red} = -2.72$ V) is irreversible, as is the multi-electron (more than 4 electrons by coulometry) oxidation process ($E_{p,ox} = 0.51$ V), thus indicating chemical reactions following both of these electron-transfer events. The usual electrochemical criteria [34], $\Delta E_p = E_{p,a} - E_{p,c}$,

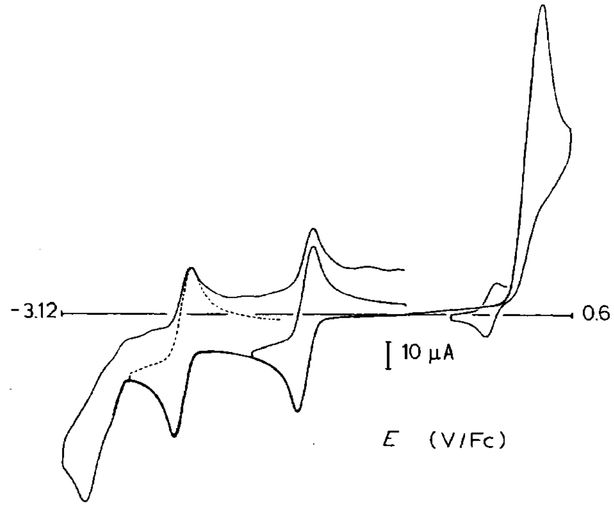


Fig. 5. Cyclic voltammetry of a ca. 1 m*M* solution of cluster **1** in thf/0.2 *M* $Bu_4NPF_6$. (Scan rate 0.2 V $s^{-1}$; vitreous carbon electrode).

Table 3

Reduction potentials of $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ (**1**), and its substituted derivatives $[Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)L_n(CF_3C_2CF_3)]$ [a]

| Compound | Ligand | $x$ | $E_{1/2,\mathrm{red1}}$ (V/Fc) | $\Delta E_p$ (mV) | $i_{p,a}/i_{p,c}$ | $E_{1/2,\mathrm{red2}}$ (V/Fc) | $\Delta E_p$ (mV) | $i_{p,a}/i_{p,c}$ |
|---|---|---|---|---|---|---|---|---|
| **1** | – | – | −1.13 | 80 | 0.9<br>1.0 [b] | −2.03 | 80 | 1.0<br>0.8 [b] |
| **1** [c] | – | – | −1.11 | 60 | 0.9 | −1.81 | 70 | 0.9 |
| **1** [d] | – | – | −1.20 | 70 | 0.9 | −1.90 | 80 | 0.6 |
| **2** | P(OMe)3 | 1 | −1.42 | 80 | 0.9 [e] | −2.22 | 90 | 0.6 [e] |
| **2** [c] | P(OMe)3 | 1 | −1.34 | 60 | | −2.01 | 90 | |
| **3** | P(OMe)3 | 2 | −1.66 | 90 | | −2.46 | | |
| **12** | dppm | 2 | −1.65 | 70 | 0.9 [e] | −2.58 | 90 [e] | |
| **14** | ddpe | 1 | −1.43 | 75 [e] | | | | |
| **13** | dppe | 2 | −1.70 | 80 | 0.8 [e] | −2.65($E_p$) [e] | | |
| **10** | t-BuNC | 1 | −1.44 | 70 | | −2.24 | 90 | |
| **11** | t-BuNC | 2 | −1.73 | 75 | | −2.48($E_p$) | | |
| **16** | t-BuNC | 3 | −2.0 | 70 | | | | |
| **15** [c] | MeCN | 1 | −1.39 | 70 | | | | |

[a] The redox potentials are obtained in a $thf/Bu_4NPF_6$ electrolyte, at a scan rate of 200 mV/s unless otherwise stated. For the bidentate ligands, dppm and dppe, $x = 1$ means the coordination of only one phosphorus, and $x = 2$ corresponds to the binding of both ends of the diphosphine. [b] In thf, 40 °C, 50 mV/s. [c] In $CH_3CN/0.1\ M\ Bu_4NPF_6$. [d] In $CH_2Cl_2/0.2\ M\ Bu_4NPF_6$. [e] In thf, 40 °C, 200 mV/s.

$i_{p,a}/i_{p,c}$ (Table 3), and $i_{p,c}/v^{1/2}$ ($E_{p,a}$ and $E_{p,c}$: anodic and cathodic peak potentials; $i_{p,a}$ and $i_{p,c}$: anodic and cathodic peak currents; $v$: scan rate) demonstrate that the first two reduction systems are associated with reversible, diffusion-controlled one-electron processes (eq. 3). Controlled-potential electrolyses (CPE) performed at the potential of the first reduction peak (−1.2 V) were complete after 1 F/mol of **1** was passed (Table 4). The CV of the catholyte is essentially identical with the curve before electrolysis except for the first system, which is now an oxidation wave ($E_{1/2} = -1.13$ V), and for the presence of a new electrochemically quasi-reversible oxidation ($E_{1/2} = -0.7$ V, $\Delta E_p = 90\text{–}100$ mV). The latter probably arises from the slow decomposition of the radical anion, as suggested by the increase of the oxidation current at −0.7 V when a solution of $\mathbf{1}^{\cdot -}$ is allowed to stand in the

Table 4

Results of controlled-potential electrolyses of **1** at −1.2 V in the absence and in the presence of ligands

| Ligand | equiv. | Temp (° C) | $n_{\mathrm{app}}$ (F mol) [a] | Product [b] | Current efficiency [c] |
|---|---|---|---|---|---|
| none | | r.t. | 1.1 | $\mathbf{1}^{\cdot -}$ | – |
| P(OMe)3 | 10 | r.t. | 0.7 | **2** (23), $\mathbf{1}^{\cdot -}$ (35) | 0.3 |
| P(OMe)3 | 10 | 40 | 0.3 | **2** (88) | 2.7 |
| dppm | 10.2 | 40 | 0.44 | **12** (70) | 1.5 |
| dppe | 10.8 | 40 | 0.44 | **13** (64) | 1.4 |

[a] Relative to **1**. [b] In parenthesis is shown the yield calculated from CV assuming identical diffusion coefficients ($D$) for the parent and the substituted clusters. [c] Defined as the number of moles of substituted cluster formed per Faraday of charge passed.

cell. No peak attributable to $Co(CO)_4^-$ ($E_{p,ox} = -0.37$ V; $E_{p/2} = -0.44$ V) is detected.

$$\text{products} \xleftarrow{+ne} \mathbf{1}^{2-} \underset{-2.03}{\overset{+e}{\rightleftharpoons}} \mathbf{1}^{\cdot -} \underset{-1.13}{\overset{+e}{\rightleftharpoons}} \mathbf{1} \xrightarrow{-ne} \text{products} \tag{3}$$

Although the CV in Fig. 5 indicates that $\mathbf{1}^{\cdot -}$ can be reversibly reduced (eq. 3), CPE conducted in a thf electrolyte at the potential of the second reduction step (−2.1 V) does not lead to the dianion. The cell current decays linearly with the charge until ca. 1 F/mol of **1** has passed, but remains almost constant afterwards. The same trend was observed in the non-coordinating solvent $CH_2Cl_2$, as well as at −10 °C in a thf medium. The steady current indicates that $\mathbf{1}^{\cdot -}$ is regenerated in a reaction which is slow on the cyclic voltammetry time scale. This is confirmed by the CV of the solution resulting from an electrolysis in thf at −2.1 V (2 F/mol) since $\mathbf{1}^{\cdot -}$ is the major product. This reaction, which may involve impurities in the medium, was not investigated further.

*Electrochemistry in the presence of ligands*

We have investigated the electrochemistry of **1** in the presence of some of the ligands which had been shown to replace CO in thermal processes.

*$P(OMe)_3$.* The presence of $P(OMe)_3$ in excess (about 10 equiv.) has essentially no effect on the CV of **1** (Fig. 6a). However, reactions which are not detected on the CV time scale (seconds) may take place during electrolyses [9a,35], and CPE of **1** at −1.2 V led to the formation of a substituted derivative **2** (Table 3), the nature of which was ascertained by comparison with an authentic sample of the monosubstituted complex [36*]. The electrolyses are complete after 0.7 F/mol of **1** has passed (Table 4). The plot of $i_{cell}$ against $Q$ ($i_{cell}$ = cell current, $Q$ = charge passed) displays the convex curvature previously observed in the case of ETC-catalyzed substitution reactions [18c]. However, in the present case, the substitution is not quantitative and is characterized by low current efficiencies. Similar amounts of **2** and $\mathbf{1}^{\cdot -}$ are recovered at the end of the electrolysis, as well as a new product, ($E_{p,ox}$ ca. −0.26 V), probably arising from the degradation of $\mathbf{1}^{\cdot -}$ in the presence of $P(OMe)_3$, or from the decay of $\mathbf{2}^{\cdot -}$. The addition of the phosphorus ligand to an electrogenerated solution of $\mathbf{1}^{\cdot -}$ yielded the same compound as that observed after CPE ($E_{p,ox}$ ca. −0.26 V), with essentially no $\mathbf{2}^{\cdot -}$ present. The species responsible for the −0.26 V oxidation process must retain the ligand since a similar peak, although at a slightly different potential, is observed when t-BuNC is added to $\mathbf{1}^{\cdot -}$ [37*].

As shown by the insignificant change in the CV of **1** caused by $P(OMe)_3$, as well as by the appearence of $\mathbf{1}^{\cdot -}$ in the presence of an excess of phosphite, the substitution reaction, eq. 5, must include a slow step. The overall substitution reaction (eq. 8) comprises the various steps represented by eqs. 4–7.

$$\mathbf{1}^{\cdot -} + P(OMe)_3 \rightarrow \mathbf{2}^{\cdot -} + CO \tag{5}$$

$$\mathbf{1} + 1e \rightleftharpoons \mathbf{1}^{\cdot -} \tag{4}$$

$$\mathbf{1} + \mathbf{2}^{\cdot -} \rightarrow \mathbf{1}^{\cdot -} + \mathbf{2} \tag{6}$$

$$\mathbf{2}^{\cdot -} - 1e \rightleftharpoons \mathbf{2} \tag{7}$$

$$\mathbf{1} + P(OMe)_3 \rightarrow \mathbf{2} + CO \tag{8}$$

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* Reference number with asterisk indicates a note in the list of references.

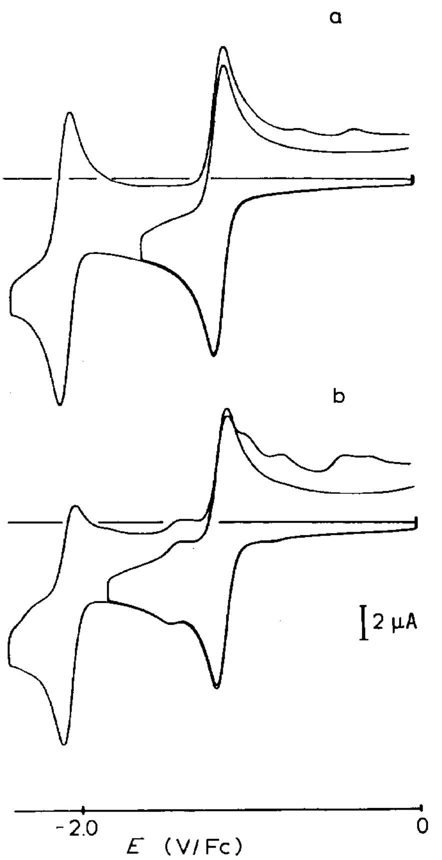


Fig. 6. Cyclic voltammetry of cluster **1** (ca. 0.35 m*M*) in thf/0.2 *M* $Bu_4NPF_6$ in the presence of $P(OMe)_3$ (12 equivalents). (a) room temperature; (b) 40 °C. (scan rate 0.2 V $s^{-1}$; vitreous carbon electrode).

We investigated the electrochemical behaviour of **1** at 40 °C in the presence of $P(OMe)_3$. As can be seen from Fig. 6b, substituted product(s) are detected. CPE of **1** (at −1.2 V) at 40 °C are complete after ca. 0.3 F/mol of **1** has passed (Table 4). The monosubstituted derivative **2** was formed in good yield (calculated from CV, see footnote 27 in ref. 38 and legend of Table 4), with a small amount of the by-product (oxidation peak at −0.26 V). No $\mathbf{1}^{\cdot -}$ was recovered under these conditions.

Controlled-potential electrolyses of **2** at its first reduction peak (−1.5 V) should lead to the substitution of a second CO. However, only a small amount of the disubstituted cluster **3** is formed, and the species oxidized at −0.26 V is again a major product. The first substitution of $P(OMe)_3$ for CO results in an increase in the electronic charge in **2** relative to that for **1**, illustrated by the negative shift (−0.29 V) of the reduction potential. The increased Co → CO $\pi$ back-bonding in **2** (and $\mathbf{2}^{\cdot -}$) relative to that in **1** (and $\mathbf{1}^{\cdot -}$) makes the CO group less labile in the former, and this hampers a further substitution (eq. 9):

$$\mathbf{2}^{\cdot -} + P(OMe)_3 \rightarrow \mathbf{3}^{\cdot -} + CO \qquad (9)$$

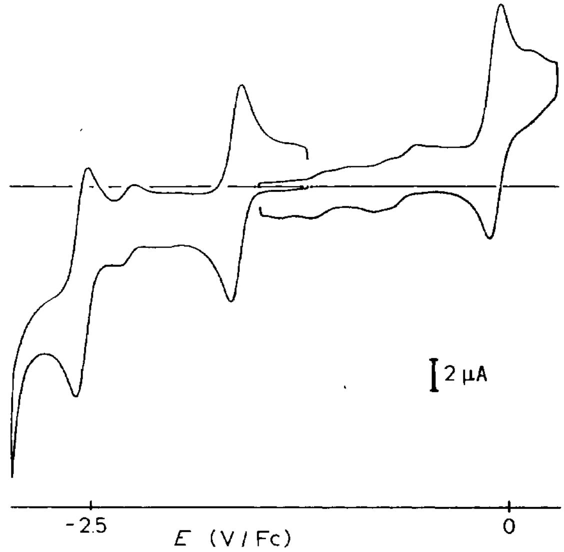


Fig. 7. Cyclic voltammetry of the solution resulting from the controlled-potential reduction of cluster **1** (ca. 0.5 m*M*) at −1.2 V in the presence of 20 equivalents dppm (*T* 40 °C; *n* ~ 0.4 F/mol of **1**). (scan rate 0.2 V $s^{-1}$; vitreous carbon electrode).

Deactivation of $\mathbf{2}^{\cdot -}$ is thus expected to be an important pathway (eq. 10):

$$\mathbf{2}^{\cdot -} \rightarrow \text{product} \xrightarrow[-0.26\ \text{V}]{-ne} \ldots \qquad (10)$$

*dppm.* No other peaks than those of **1** are observed when the CV of the cluster is carried out at room temperature in the presence of the bidentate ligand. Electrolyses were not performed at this temperature.

CPE at −1.2 V (40 °C, ddpm present) lead to a substituted derivative of **1**, e.g. **12** (Table 3); small redox processes due to minor unidentified products are also observed (Fig. 7). The shape of the curve $i_{\text{cell}} = f(Q)$ or $i_{\text{cell}} = f(t)$ as well as the amount of charge consumed (Table 4) again indicates that an ETC process takes place.

The potential of the first reduction of **12**, $E_{1/2} = -1.65$ V, is almost identical with that for the bis-substituted cluster **3**, indicating that both ends of the bidentate ligand are bound to cobalt centres. The nature of **12** was confirmed by a comparison with the CV of the product formed in the thermal reaction. In the case of triiron carbonyl clusters, the replacement of two CO by either two $P(OMe)_3$ or one diphosphine (dppe) also leads to substituted clusters which are reduced at the same potential [17a–c].

In contrast to the oxidation processes of **1** and **2**, the oxidation of **12** is reversible ($E_{1/2} = -0.08$ V) (Fig. 7), which is probably indicative of a bridging position of the dppm ligand [39*]. The assignment of the observed redox processes is shown in eq. 11:

$$\mathbf{12}^{2-} \underset{-2.58}{\rightleftharpoons} \mathbf{12}^{\cdot -} \underset{-1.65}{\rightleftharpoons} \mathbf{12} \underset{-0.08}{\rightleftharpoons} \mathbf{12}^{\cdot +} \qquad (11)$$

*dppe.* When a 4 m*M* solution of **1** and dppe (10 equiv.) is kept for about 1 h in the cell at 40 °C, substituted products (ca. 15–20%) are formed; the reversible reduction processes observed at −1.43 and −1.70 V (Table 3) suggest the stepwise substitution of two carbonyl groups.

CPE carried out at −1.2 V (40 °C, 10 equiv. dppe) is complete after ca. 0.4 F/mol of **1** is passed. For a 4 m*M* solution of **1**, i.e. under conditions similar to those mentioned above, the CPE requires 15–20 min to go to completion: the thermal substitution contributes only slightly to the overall process. The CV of the catholyte demonstrates that the bis-substituted cluster is the major product ($E_{1/2}$ = −1.70 V) **13**, whereas the reversible system at −1.43 V assigned to **14** is essentially absent.

As observed for the dppm analogue, the oxidation of the dppe derivative is a reversible process ($E_{1/2}$ = −0.07 V), and this again suggests that the bidentate ligand is bound to two distinct Co centres [39*].

*$CH_3CN$.* Cyclic voltammetry in neat acetonitrile at 40 °C demonstrates that a substitution takes place. The reversible reduction potential of the new derivative is quite comparable with those for the other monosubstituted complexes (Table 3), and is assigned to a $CH_3CN$ species. CPE of **1** in $CH_3CN$ gives a small amount of the substituted derivative **15** along with $\mathbf{1}^{\cdot -}$ and decomposition products.

*t-Butyl isocyanide.* Addition of an excess t-BuNC to a solution of **1** in an thf/0.2 *M* $Bu_4NPF_6$ electrolyte results in an instant change in the CV of the cluster. The redox couples associated with **1** are replaced by new reversible reduction couples (Table 3), which we tentatively assign to the mono-, bis-, and tris-substituted clusters, although the last named were not formed in the thermal substitution processes.

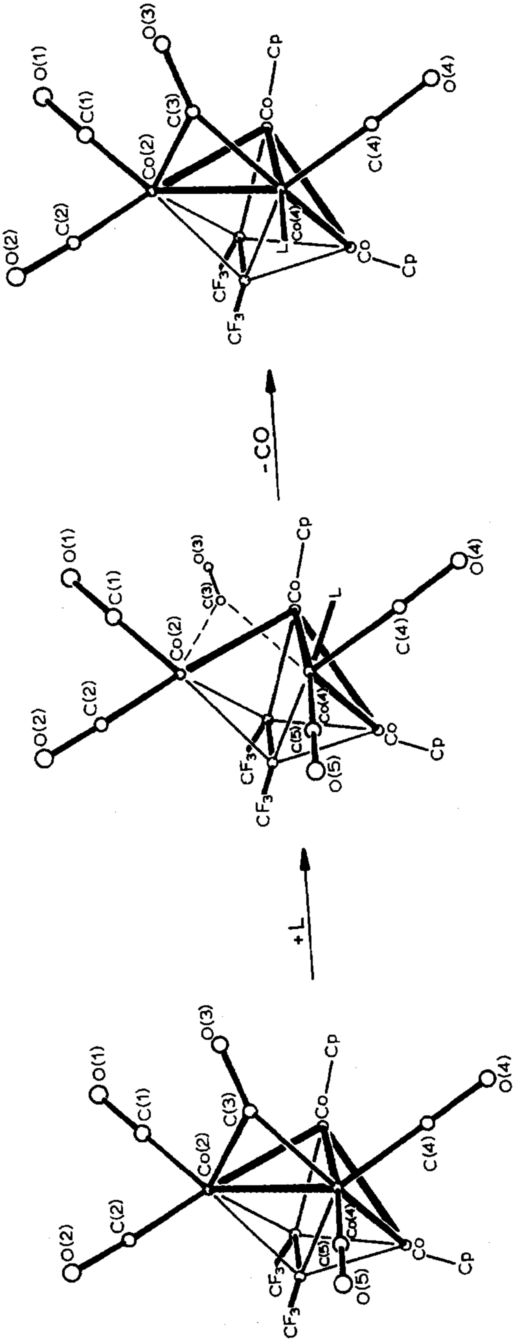
### 4. *Tetracobalt clusters catalyzed isomerization of 1-hexene*

It was found that cluster **1** readily catalyzes the isomerization of 1-hexene to give a mixture of *cis*- and *trans*-2-hexene in 40 and 55% yields, respectively, and small amounts of *trans*-3-hexene (5%). When the reaction was carried out in neat 1-hexene ($3.2 \times 10^{-3}$ mol) with $1.9 \times 10^{-6}$ mol of cluster **1** at 130 °C, approximatively 30% of the 1-hexene was isomerized to *cis*- and *trans*-2-hexene after 1h, giving a turnover for the catalysis of approximatively 500 mol of hexene/mol of cobalt cluster per hour. Spectral (IR and $^1$H NMR) analyses of the solid obtained following evaporation of the olefin mixture showed that the bulk of the cluster **1** remained unchanged. In isomerization of 1-hexene there is an increase in selectivity but a decrease in turnover when mono- or di-substituted clusters are used as catalysts. For instance, the monophosphite cluster **2** and the diphosphine-substituted compound **8** catalyze the isomerization of 1-hexene to give a mixture of *trans*- and *cis*-2-hexene in 74 and 18% yield, respectively, and *trans*-3-hexene (8%). However the turnover for the catalysis decreases from 500 mol of 1-hexene/mol of cobalt cluster per hour with **1** to 60 and 120 with **2** and **8**, respectively. Spectroscopic data show that phosphines maintain the metal clusters intact under the conditions used as for the unsubstituted cluster **1**. The effects of phosphines in altering the product distributions in catalytic processes are well-documented [42].

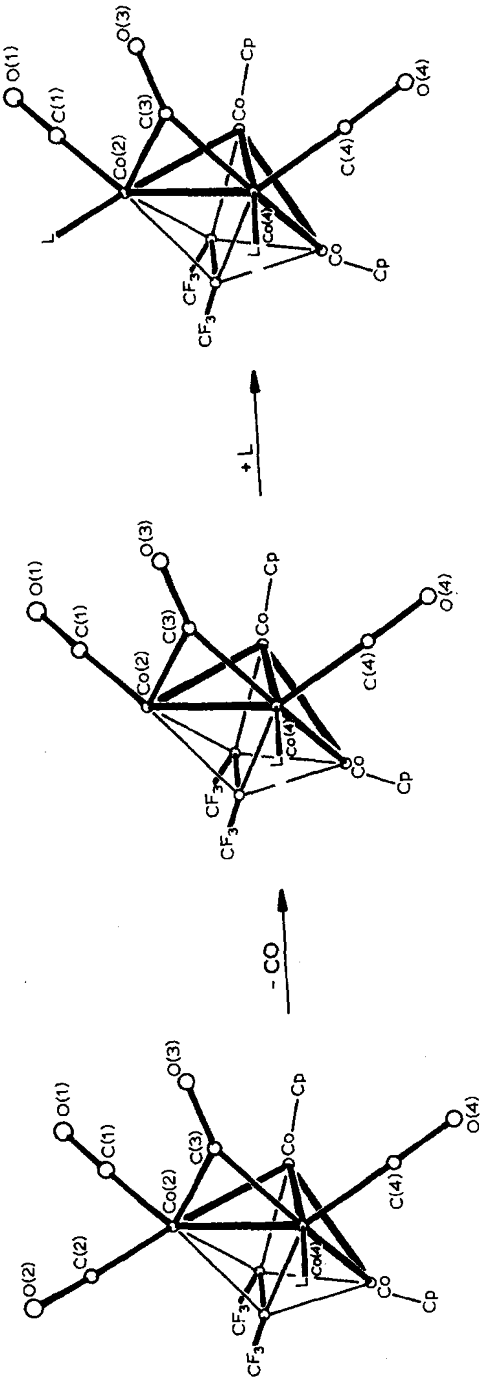
## Discussion

The thermal substitution reactions described above proceed cleanly and give no side product in detectable amount (except for $PMe_3$), even when the reactions are carried out under forcing conditions. Two isomeric substitution products (**a** and **b**)

*(Continued on p. 130)*



Scheme 2



Scheme 3

were detected in most cases; the **a** and **b** isomers must be close in energy since they have identical redox potentials; their ratio depends on the size of the ligand as illustrated by the data listed in Table 2. With a bulky ligand such as $PPh_3$, only the singly-substituted isomer of type **a** is formed; probably, there is less steric hindrance at this substitution site. For smaller ligands, the basicity factor dominates, and in general the **b** isomer becomes more abundant as the basicity of the ligand increases. Steric hindrance should be responsible for the non-observance of disubstituted compounds for $PPh_3$. For the other nucleophiles, basicity becomes the controlling factor; the two stronger bases $PMe_3$ and $PPh_2H$ give only isomers of type **a**, whereas a mixture of **a** and **b** isomers is obtained for $P(OMe)_3$.

The $^1H$, $^{13}C$ and $^{19}F$ NMR spectra of the mono- and disubstituted tetracobalt complexes show that the alkyne molecule is not involved in any rearrangement across the $Co_4$ framework, which contrasts with the rotation of the alkyne moiety in trimetallic clusters such as $[Os_3(CO)_{10}(RC_2R)]$ [43]. This supports the assumption that alkyne mobility is observed only in species possessing a *nido*-polyhedral structure [44]. Therefore, exclusive substitution of CO occurs, in good yield, in the reactions carried out under either thermal or electrochemical activation. A possible mechanism for the thermally-induced substitution of $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ would involve attack by the nucleophile (phosphine or isocyanide) on the intact cluster. In this type of compound the LUMO is generally a metal-centred orbital [45]. The essentially metallic character of the LUMO of **1** is indicated by the electrochemical results: although the reversible reduction processes of **1** are shifted to more negative potentials on substitution of donor ligands for CO, (Table 3), the redox potentials of the resulting clusters are more sensitive to the number of substituted CO than to the nature of the incoming ligands. Thus similar reduction potentials are obtained for the mono-substituted derivatives, **2**, **10**, and **15** despite the different donor/acceptor abilities of $P(OMe)_3$, t-BuNC and MeCN [7b,46]. The electronic effects of the ligands therefore appears to be "levelled" when they are bound to the $Co_4$ core, and we interpret this as an indication that the LUMO is mainly a metal orbital. Provided these orbitals do not differ too much in energy, the reaction of the HOMO of the incoming nucleophile with the LUMO of the $Co_4$ cluster could lead to the binding of L with concomitant cleavage of the carbonyl-bridged Co–Co bond [47*,48] (Scheme 2).

Such a mechanism takes account of the ability of cluster **1** to act as an intact entity in substitution and catalytic reactions through the generation of vacant coordination sites by metal–metal bond scission [49]. Coordinative unsaturation resulting from dissociative CO loss could be involved in the second substitution, but the reaction of the HOMO of the nucleophile with the LUMO of the mono-substituted clusters again seems more likely (Scheme 3). The infrared spectra of these clusters, e.g. $[Cp_2Co_4(CO)_3(\mu\text{-}CO)L(CF_3C_2CF_3)]$, show a shift of the $\nu(CO)$ to lower frequencies (Table 1), suggesting a strengthening of the M–C bonds, as expected from the increase of the electronic density on the cluster (cf. the negative shift of the reversible potentials on substitution, Table 3). This is indicative of the fact that the labilization of CO toward dissociation in $[Cp_2Co_4(CO)(\mu\text{-}CO)L(CF_3C_2CF_3)]$ results from a transition-state stabilization by the presence of the ligand rather than from a labilization arising from ground-state effects [50]. Nevertheless, in the absence of a kinetic study, the point at which the disposition of the phosphine or isocyanide is determined cannot be established with certainty.

One of the main characteristics of the substitution process for **1** under electrochemical activation is its poor efficiency. Although several observations indicate that an ETC-catalyzed mechanism is taking place, the value of the number of electron transferred as well as the current efficiency show that the process is essentially not catalytic at room temperature (see Table 4, $P(OMe)_3$). However, increasing the temperature to 40 ° C results in faster reactions and a lowered charge consumption.

As the increased electron density in the radical anion with respect to the neutral parent results in an enhanced metal→CO back donation [14c], it is generally thought that the substitution of the radical anion proceeds via the cleavage of a metal–metal bond [13,14] or of a metal-bridging ligand bond [15b]. In the case of bicapped triiron carbonyl clusters the rupture of a metal-capping ligand bond has been very elegantly demonstrated [17a–c].

Dissociative mechanisms for ETC-catalyzed substitution reactions have also been observed [12,17d,19,51]. In the present case, population of a metal–metal antibonding orbital, eventually leading to the cleavage of a Co–Co bond and to the exposure of a 17e metal centre, looks a reasonable possibility for the substitution.

Thermally induced substitution of **1** with trimethylphosphine leads to partial fragmentation into the tricobalt cluster **6**. The formation of **6** involves an unusual, but not unknown [52], loss of a cyclopentadienyl ligand from one metal by some unidentified mechanism.

## Experimental

All the experiments (including electrochemical procedures) were carried out under $N_2$ or Ar. Solvents were purified by standard methods and degassed before use.

### *Syntheses*

The complex $[Cp_2Co_4(CO)_4(\mu\text{-}CO)(CF_3C_2CF_3)]$ was prepared by published procedures [3,27]. Standard Schlenk techniques were used for preparations. Silica gel was used for chromatographic separation and purifications.

*Preparation of the mono- and di-phosphite adducts* $[Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)\{P(OMe)_3\}_n(CF_3C_2CF_3)]$ *(n = 1 or 2)*

A solution of 0.1 g ($1.5 \times 10^{-4}$ mol) of $[Cp_2Co_4(CO)_5(CF_3C_2CF_3)]$ (**1**) and 54 μl ($4.5 \times 10^{-4}$ mol) of $P(OMe)_3$ in thf was refluxed for 0.5 h under a nitrogen stream. The solvent was then evaporated off, the residue dissolved in a minimum of $CH_2Cl_2$, and the solution chromatographed on silica gel. Elution with hexane/$CH_2Cl_2$ (1/0.55) afforded a deep-violet band, which yielded about 78% (based on the amount of the cobalt cluster taken) of a mixture of the two isomers **2a** (63%) and **2b** (37%), which was purified by crystallisation from hexane/dichloromethane solution at −20 ° C.

Complexes **2a** and **2b** are deep-violet solids, soluble in common organic solvents. Anal. Found for **2**: C, 32.9; P, 4.0; Co, 30.9. $C_{21}H_{19}Co_4F_6O_7P$ calc: C, 33.0; P, 4.0; Co, 30.9%. The mass spectrum showed ions corresponding to $[M]^+$, $m/e$ 764, $[M - nCO]^+$, $m/e$ 736 ($n = 1$), 708 ($n = 2$), 680 ($n = 3$), 652 ($n = 4$), $[CO_4(C_5H_5)_2(CF_3C_2)\{P(OMe)_3\}]^+$, $m/e$ 583, $[Co_4(C_5H_5)_2(C_4F_6)]^+$, $m/e$ 528, $[Co_3(C_5H_5)_2(CF_3C_2CF)]^+$, $m/e$ 431, $[Co_2(C_5H_5)_2(C_4F_2)]^+$, $m/e$ 334.

When **1** (0.2 g, $3 \times 10^{-4}$ mol) was treated in a similar way with a large excess of trimethylphosphite (360 $\mu$l, $3 \times 10^{-3}$ mol) for 2.5 h, a mixture of the mono- and di-substituted complexes **2** (0.15 g, 44%) and **3** (0.09 g, 40%) was formed. Products **2** and **3** were separated by column chromatography, with 1/0.55 and 1/1 hexane/$CH_2Cl_2$ respectively as eluents. Complex **3** was obtained as a black solid mixture of two isomers **3a** (66%) and **3b** (34%) both of which are black solids. Anal. Found for **3**: C, 32.1; P, 6.8. $C_{23}H_{28}Co_4F_6O_9P_2$ calc: C, 32.1; P, 7.2%. The mass spectrum showed ions corresponding to $[M]^+$, $m/e$ 860, $[M-n\mathrm{CO}]^+$, $m/e$ 832 ($n = 1$), 804 ($n = 2$), 776 ($n = 3$), $[Co_4(C_5H_5)_2(CO)(C_4F_6)\{P(OMe)_3\}]^+$, $m/e$ 680, $[Co_4(C_5H_5)_2(C_4F_6)\{P(OMe)_3\}]^+$, $m/e$ 652, $[Co_4(C_5H_5)_2(CF_3C_2)\{P(OMe)_3\}]^+$, $m/e$ 583, $[Co_4(C_5H_5)_2(C_4F_6)]^+$, $m/e$ 528, $[Co_3(C_5H_5)_2(C_4F)\{P(OMe)_3\}]^+$, $m/e$ 498, $[Co_2(C_5H_5)_2(C_4F_2)]^+$, $m/e$ 334, $[Co_2(C_5H_5)_2(C_4F)]^+$, $m/e$ 315.

Complex **2** was also synthesised in quantitative yield by photolysis of **1** in the presence of 3 equiv. of $P(OMe)_3$ in hexane for 0.5 h under a nitrogen stream. In this reaction **2** was the only product isolated.

*Preparation of the mono- and di-phosphine complexes* $[Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)(PR_3)_n(CF_3C_2CF_3)]$ *($n = 1$ or 2; $R_3 = Me_3$, $Ph_2H$ or $Ph_3$) and the tricobalt cluster* $[CpCo_3(CO)_3(PMe_3)_2(CF_3C_2CF_3)]$

*$PMe_3$.* A mixture of **1** in $CH_2Cl_2$ was stirred at room temperature for 1 h (0.1 g, $1.5 \times 10^{-4}$ mol) and trimethylphosphine ($2 \times 10^{-4}$ mol) to give the monosubstituted derivatives **4** in 95% yield. Complexes **4** were purified by chromatography; elution with a solution of hexane/$CH_2Cl_2$ (4/1) gave a violet band which upon removal of solvent yielded a mixture of isomers **4a** (60%) and **4b** (40%). Complexes **4** crystallise with one hexane molecule. Anal. found for **4**: C, 40.8; P, 3.9; Co, 28.6. $C_{27}H_{33}Co_4F_6O_4P$ calc: C, 40.4; P, 3.9; Co, 29.3%.

When **1** (0.3 g, $4.5 \times 10^{-4}$ mol) was treated with an excess of trimethylphosphine ($13.5 \times 10^{-4}$ mol) in $CH_2Cl_2$ at room temperature three compounds were obtained, and were separated and purified by chromatography. Elution with hexane/$CH_2Cl_2$ (4/1) afforded a violet band which yielded 26% of **4**. Elution with hexane/$CH_2Cl_2$ (3/1) then gave the most abundant deep-red fraction from which **6** was isolated; it was purified by crystallisation from hexane/$CH_2Cl_2$ solution at −40 °C (0.14 g, 50%). Finally elution with hexane/$CH_2Cl_2$ (1.8/1) removed the deep-green band, and evaporation gave product **5**, which was purified by crystallisation from hexane/$CH_2Cl_2$ solution (0.09 g, 22%). **5** crystallises with two hexane molecules.

Anal. found for **5**: C, 44.3; P, 6.6; Co, 25.5. $C_{35}H_{56}Co_4F_6O_3P_2$ calc: C, 44.9; P, 6.6; Co, 25.2%.

Anal. found for **6**: C, 34.6; P, 9.7; Co, 27.3. $C_{18}H_{23}Co_3F_6O_3P_2$ calc: C, 33.8; P, 9.7; Co, 27.6%. The mass spectrum showed ions corresponding to $[M]^+$, $m/e$ 640, $[M-n\mathrm{CO}]^+$, $m/e$ 612 ($n = 1$), 584 ($n = 2$), 556 ($n = 3$), $[Co_3(C_5H_5)(CO)(PMe_3)(C_4F_6)]^+$, $m/e$ 508, $[Co_3(C_5H_5)(PMe_3)(C_4F_6)]^+$, $m/e$ 480, $[Co_3(C_5H_5)(CO)_3(PMe_3)_2]^+$, $m/e$ 478, $[Co_3(C_5H_5)(CO)_2(PMe_3)_2]^+$, $m/e$ 450, $[Co_2(C_5H_5)(CO)(PMe_3)(C_4F_6)]^+$, $m/e$ 449, $[Co_2(C_5H_5)(PMe_3)(C_4F_6)]^+$, $m/e$ 421, $[Co(C_5H_5)(C_4F_6)]^+$, $m/e$ 286, $[Co(C_5H_5)(C_4F_5)]^+$, $m/e$ 267, $[Co_3]^+$, $m/e$ 177.

*$PPh_2H$.* 0.2 g ($3 \times 10^{-4}$ mol) of **1** and 0.08 g ($4.3 \times 10^{-4}$ mol) of $PPh_2H$ were heated in thf at reflux for 0.5 h. The solvent was evaporated to dryness, the residue was redissolved in a minimum of $CH_2Cl_2$, and the solution chromatographed on silica gel. Hexane/$CH_2Cl_2$ (4/1) eluted a violet band which upon removal of

solvent gave 0.16 g (65%) of a mixture of isomers **7a** (56%) and **7b** (44%). A second deep-violet band was eluted with hexane/$CH_2Cl_2$ (1.5/1), and removal of the solvent under reduced pressure gave 0.05 g (17%) of **8**. Complexes **7** and **8** were washed with pentane and recrystallised from hexane/$CH_2Cl_2$ at $-20°$C.

When a large excess of $PPh_2H$ (0.28 g, $15 \times 10^{-4}$ mol) was used to react with **1** (0.2 g, $3 \times 10^{-4}$ mol), for 0.5 h, only the disubstituted complex **8** was obtained (80% yield).

Anal. found for **7**: C, 42.7; H, 2.7; P, 3.5. $C_{30}H_{21}Co_4F_6O_4P$ calc: C, 43.5; H, 2.6; P, 3.7%.

Anal. found for **8**: C, 50.8; H, 3.6; P, 6.0. $C_{41}H_{32}Co_4F_6O_3P_2$ calc: C, 50.1; H, 3.3; P, 6.3%.

*$PPh_3$*. When a mixture of **1** (0.15 g, $2.25 \times 10^{-4}$ mol) and triphenylphosphine (0.6 g, $22.6 \times 10^{-4}$ mol) in thf was refluxed for 1 h, only the monosubstituted derivative **9** was isolated (94%). It was purified by chromatography which removed the uncharged $PPh_3$.

Anal. found for **9**: C, 47.0; P, 3.6. $C_{36}H_{25}Co_4F_6O_4P$ calc: C, 47.9; P, 3.4%.

### *Preparation of mono- and di-isocyanide complexes $[Cp_2Co_4(CO)_{4-n}(\mu\text{-}CO)(t\text{-}BuNC)_n(CF_3C_2CF_3)]$ ($n = 1$ or 2)*

A mixture of **1** (0.1 g, $1.5 \times 10^{-4}$ mol) and, t-BuNC (17 μl in $CH_2Cl_2$ $1.5 \times 10^{-4}$ mol) was stirred for 5 min at room temperature and the solvent was then evaporated to dryness. Chromatography of the residue on a silica gel column with hexane/$CH_2Cl_2$ (4/1) as eluent afforded a deep-violet band that gave complex **10** in 80% yield.

Anal. found for **10**: C, 38.3; N, 1.7. $C_{23}H_{19}Co_4F_6NO_4$ calc: C, 38.2; N, 1.9%. The mass spectrum showed ions corresponding to $[M]^+$, *m/e* 723, $[M-n\text{CO}]^+$, *m/e* 695 ($n = 1$), 667 ($n = 2$), 639 ($n = 3$), 611 ($n = 4$), $[Co_4(C_5H_5)_2(CO)_4(C_4F_6)]^+$, *m/e* 640, $[Co_4(C_5H_5)_2(CO)_3(C_4F_6)]^+$, *m/e* 612 $[Co_4(C_5H_5)_2(CO)_2(C_4F_6)]^+$, *m/e* 584, $[Co_4(C_5H_5)_2(CO)(C_4F_6)]^+$, *m/e* 556, $[Co_4(C_5H_5)_2(C_4F_2)(t\text{-}BuNC)]^+$, *m/e* 535, $[Co_4(C_5H_5)_2(C_4F_6)]^+$, *m/e* 528 $[Co_3(C_5H_5)_2(C_4F_4)(t\text{-}BuNC)]^+$, *m/e* 514, $[Co_2(C_5H_5)_2(C_4F_2)(t\text{-}BuNC)]^+$, *m/e* 417, $[Co_2(C_5H_5)_2(C_4F_2)]^+$, *m/e* 334, $[Co(C_5H_5)_2(C_4F_2)]^+$, *m/e* 275.

When a mixture of 0.2 g ($3 \times 10^{-4}$ mol) of **1**, 68 μl ($6 \times 10^{-4}$ mol) of t-butyl isocyanide, in $CH_2Cl_2$ was stirred for 2 h at room temperature with the disubstituted complex (70% yield) was formed as a mixture of isomers **11a** (70%) and **11b** (30%). They were purified by chromatography with hexane/$CH_2Cl_2$ (1/1) as eluent.

Anal. found for **11**: C, 41.8; N, 3.5. $C_{27}H_{28}Co_4F_6N_2O_3$ calc: C, 41.7; N, 3.6%. The mass spectrum showed ions corresponding to $[M]^+$, *m/e* 778, $[M-n\text{CO}]^+$, *m/e* 750 ($n = 1$), 722 ($n = 2$), 694 ($n = 3$), $[Co_4(C_5H_5)_2(CO)_3(C_4F_6)(t\text{-}BuNC)]^+$, *m/e* 695, $[CO_4(C_5H_5)_2(CO)_2(C_4F_6)(t\text{-}BuNC)]^+$, *m/e* 667, $[Co_4(C_5H_5)_2(CO)(C_4F_6)(t\text{-}BuNC)]^+$, *m/e* 639, $[Co_4(C_5H_5)_2(C_4F_6)(t\text{-}BuNC)]^+$, *m/e* 611, $[Co_3(C_5H_5)_2(C_4F_4)(t\text{-}BuNC)_2]^+$, *m/e* 597, $[Co_4(C_5H_5)_2(C_4F_6)]^+$, *m/e* 528, $[Co_3(C_5H_5)_2(C_4F_4)(t\text{-}BuNC)]^+$, *m/e* 514, $[Co_2(C_5H_5)_2(C_4F_2)(t\text{-}BuNC)]^+$, *m/e* 417.

### *Synthesis of biphosphine complexes $[Cp_2Co_4(CO)_2(\mu\text{-}CO)(LL)(CF_3C_2CF_3)]$ (LL = dppm or dppe)*

A mixture of 0.1 g ($1.5 \times 10^{-4}$ mol) of **1** with a large excess of dppm (0.58 g, $15 \times 10^{-4}$ mol) in thf was refluxed for 1 h then evaporated to dryness. The residue was chromatographed on silica gel. Hexane/$CH_2Cl_2$ (4/1) eluted a slightly yellow band, which upon removal of solvent gave 0.33 of unreacted dppm. Further elution with hexane/$CH_2Cl_2$ (2.3/1) gave a deep-violet band yielding **12** (0.12 g, 84%).

Anal. found for **12**: C, 50.6; H, 3.6; P, 6.2. $C_{42}H_{32}Co_4F_6O_3P_2$ calc: C, 50.6; H, 3.3; P, 6.2%.

Similarly, reaction of 0.2 g ($3 \times 10^{-4}$ mol) of **1** with an excess of dppe (1.2 g, $30 \times 10^{-4}$ mol), gave 0.2 g (67% yield) of **13**.

Anal. found for **13**: C, 50.4; H, 3.5; P, 5.9. $C_{43}H_{34}Co_4F_6O_3P_2$ calc: C, 51.1; H, 3.4; P, 6.1%.

### *Isomerization experiments*

Each reaction was performed in sealed glass tubes (volume 3 ml) containing cluster **1** (1.2 mg, $1.9 \times 10^{-6}$ mol), **2** (2 mg, $2 \times 10^{-6}$ mol) or **8** (1.5 mg, $1.5 \times 10^{-6}$ mol), along with the 1-hexene (0.4 ml, $3.2 \times 10^{-3}$ mol) to be isomerized; the tubes were filled with nitrogen by standard vacuum techniques. The reactions were conducted at 130 °C for 1 h (**1**) or 5 h (**2** or **8**), and at this stage about 30% of 1-hexene had been isomerized. The isomerization solutions were examined by $^1H$ and $^{13}C$ NMR spectroscopy to reveal the extent of formation of isomerized hexene. The organic products in the solutions after the isomerization experiments were analysed by GLC (PPG/Chromosorb W).

### *Electrochemistry*

The apparatus, the set of electrodes and the purification of solvents and electrolytes used in the electrochemical experiments (cyclic voltammetry, controlled-potential electrolyses) were as described previously [53]. The experiments were carried out in a thermostated cell (Metrohm) either at room temperature or 40 °C (thermostat Haake, type F1). The potentials are quoted relative to the ferrocene–ferrocenium cation couple, ferrocene being added as an internal standard at the end of the CV experiments.

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