Journal of Organometallic Chemistry, *479* (1994) 93–102

Reactions of di- and poly-nuclear complexes. 12 *. Synthesis and thermal decomposition reactions of tetranuclear clusters $[Co_4Cp_2(CO)_{5-n}L_n(RC_2R')]$ (L = PPh_2H; $n = 0$, 1 or 2) (R = R′ = CF_3, C_6F_5, C_6H_5 or Me; R = H, R′ = CF_3).

Philippe Quénec'h, René Rumin and François Y. Pétillon

URA CNRS 322, Laboratoire de Chimie, Electrochimie Moléculaires et Chimie Analytique, Faculté des Sciences, Université de Bretagne Occidentale, BP 452, 29275 Brest-Cédex (France)

(Received October 6, 1993)

Abstract

The dinuclear complexes $[(CO)_3\overline{Co(\mu\text{-}RC_2R')}Co(CO)_3]$ (R = R′ = CF_3, C_6F_5, C_6H_5 or Me; R = H, R′ = CF_3) react with $[CpCo(CO)_2]$ in refluxing octane to afford tetranuclear complexes $[Co_4Cp_2(CO)_4(\mu\text{-}CO)(\mu\text{-}RC_2R')]$ (**2**) in good yield; these tetracobalt clusters have been characterised by spectroscopic methods. Thermolysis of $[Co_4Cp_2(CO)_5(RC_2R')]$ (**2**) and of the related substituted complexes $[Co_4Cp_2(CO)_{4-n}(\mu\text{-}CO)(PPh_2H)_n(CF_3C_2CF_3)]$ results mainly in the loss of carbonyl and the formation of trinuclear clusters $[Co_3Cp_3(\mu_3\text{-}CO)(\mu_3\text{-}\eta^2\text{-}RC_2R')]$ (**3**) and $[Co_3Cp_2(CO)_2(\mu\text{-}PPh_2)(\mu_3\text{-}\eta_2\text{-}CF_3C_2CF_3)]$ (**7**), respectively. The conversion of clusters **3** and **7** into dialkylidyne complexes has been examined. The spectroscopic data for the new complexes are discussed and mechanisms proposed to account for their formation.

Key words: Cobalt; Tetranuclear clusters; Trinuclear clusters; Alkyne; Alkylidyne; Thermal decomposition

1. Introduction

The design of homonuclear and heteronuclear clusters can be viewed in several ways [2]. One that we have developed [3] involves the use of metal compounds as ligands added to other complexes. We have shown that the course of the reaction between two dissimilar dinuclear alkyne complexes is strongly dependent on the substituents in the alkyne: *closo* 'M_4C_2' octahedra are favoured with polar symmetrical acetylenes such as hexafluorobut-2-yne and dimethyl acetylenedicarboxylate, whereas μ_4-η^2-vinylidene tetranuclear clusters are generally formed when terminal acetylenes are used [3]. To check substituent effects, we have extended our study of these reactions to some additional symmetrical alkynes plus terminal alkynes. This work is described here, together with the thermal decomposition reactions of the tetranuclear complexes $[Co_4Cp_2\text{-}(CO)_{5-n}L_n(RC_2R')]$ (L = PPh_2H; $n = 0$, 1 or 2) (R = R′ = CF_3, C_6F_5, C_6H_5 or Me; R = H, R′ = CF_3) which are formed in the above reactions. We have shown that heating these tetracobalt compounds induces cluster contraction to give trinuclear species, and sometimes subsequent alkyne scission. Cleavage of an alkyne takes place mainly on trimetallic frameworks [4], although scission of alkynes coordinated to tetranuclear complexes has been reported [3,5]. The structural requirements for alkyne C–C bond cleavage in trimetallic complexes have been amply discussed [4d,f] but no firm conclusions have been drawn so far. We report here some results concerning the influence of metal atoms in tetranuclear clusters on alkyne scission.

2. Results and structural aspects

2.1. Synthesis and characterisation of $[Co_4Cp_2(CO)_4(\mu\text{-}CO)(RC_2R')]$

The reaction between $[(CO)_3\overline{Co(\mu\text{-}RC_2R')}Co(CO)_3]$ (**1**) (R = R′ = CF_3, C_6F_5, C_6H_5 or Me; R = H, R′ =

Correspondence to: Professor F.Y. Pétillon.

* For Part II, see ref. 1.

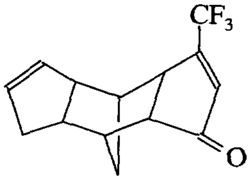
0022-328X/94/$7.00
SSDI 0022-328X(94)24428-L

CF_3) and [$CpCo(CO)_2$] in either refluxing octane or refluxing hexane provides a simple method for the synthesis of tetranuclear alkyne clusters [$Co_4Cp_2(CO)_5(RC_2R')$] (**2**) in high yield, together with small amounts of separable decomposition products [eqn. (1)].

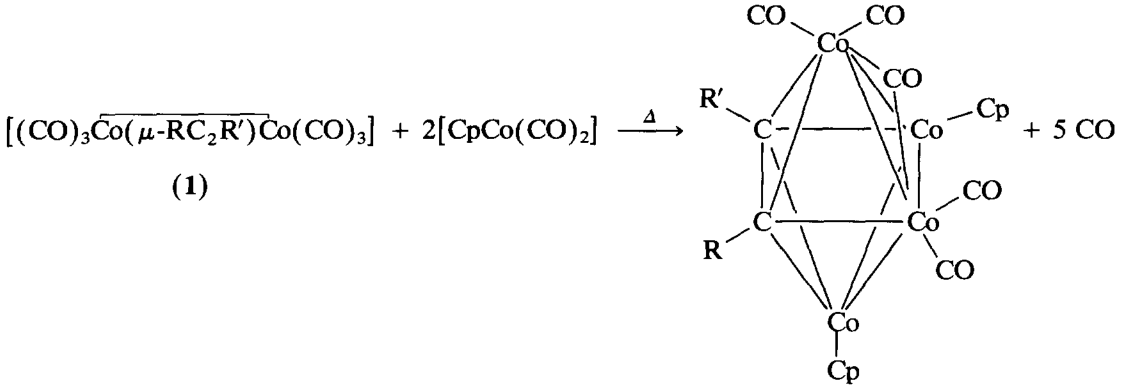
The tetrametallic alkyne clusters **2** are black-purple solids, soluble in hydrocarbon solvents, and not particularly air-sensitive. The mass, IR and NMR data of **26-e** (see Table 1, and Experimental details) show that they are isostructural with complex **2a** prepared previously by another route, whose structure was determined by X-ray diffraction [6]. Hence, we propose a structure for **26-e** which is related to **2a** [eqn. (1)].

The ^{19}F NMR spectrum of **2a** shows two resonances at low temperature, but above 278 K the two CF_3 signals coalesce as a consequence of rapid rotation about the axis which is perpendicular to the C–C bond. Such a rotation is hindered in **2b** and **2c** as the two resonances of the C_6F_5 (^{19}F NMR) and C_6H_5 (^1H NMR) groups bound to the carbon atoms of the alkyne do not collapse even at 393 K. This is merely a consequence of the crowding of these substituents on the alkyne. The ^1H NMR spectrum of **2d** at room temperature shows a four-line pattern attributable to two nonequivalent cyclopentadienyl and methyl groups. No temperature-dependence was observed up to 393 K, which rules out rotation of the alkyne in **2d**. This cannot be explained as a result of the steric effects of the methyl groups, but indicates that the high electron-donating ability of CH_3 strengthens the cobalt–alkyne bonds in **2d** and so prevents the rotation of the alkyne. In the trifluoropropyne complex **2e**, there are two possible isomers corresponding to the two possible positions for the bridging CF_3C_2H. Throughout the temperature range 173–298 K the ^{19}F NMR spectrum consisted of only one singlet. This may be interpreted either (i) as being due to the existence of a preferred isomer in solution or (ii) as a consequence of the rapid rotation of the alkyne about an axis perpendicular to the C–C bond: the conversion of one isomer to another might occur below 173 K due to the lack of crowding of the CF_3 and H groups compared to that of two CF_3, C_6F_5 and C_6H_5 groups in **2a**, **2b** and **2c**, respectively.

Reactions (1) also resulted in two other trimetallic products, when the substituents on the alkyne in **1** were C_6F_5 or C_6H_5. These products were formulated as [$Co_3Cp_3(CO)(RC_2R')$] (**3**) and [$Co_3Cp_3(CR)(CR')$] (**4**). They were formed by thermal decomposition of **2** (see below). When reaction (1) was performed with [$(CO)_3\overline{Co(\mu\text{-}CF_3C_2H)Co}(CO)_3$], an organic compound **5** (yield, 15%) was also obtained, together with the organometallic complexes **2e** and **3e**. The nature of **5** was established via its mass spectrum, which exhibits a parent peak at m/z 254 with an initial loss of carbonyl readily observable as a peak at m/z 226. The polycyclic structure shown for **5** is based on the composition and supported by IR, ^1H and ^{19}F NMR data, and by analogy with the structure of organic compounds obtained by cycloaddition reactions of alkynes and alkenes promoted by [$CpCo(CO)_2$] [7].



(**5**)



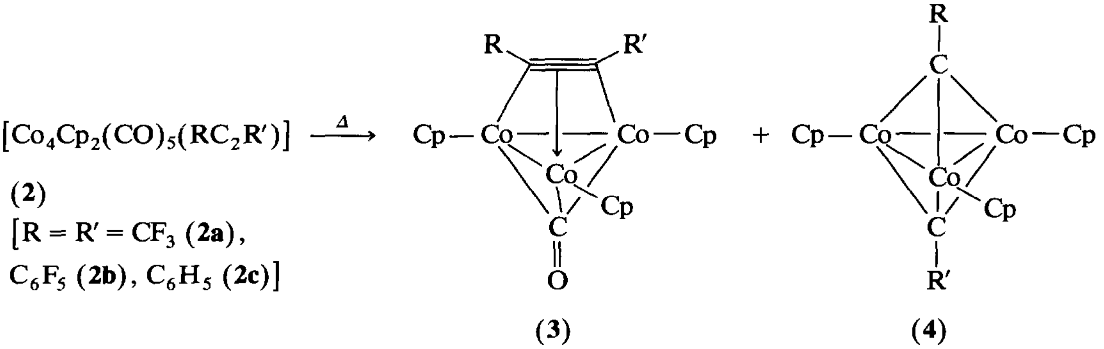
(**2**)

[R = R' = CF_3 (**2a**), C_6F_5 (**2b**), C_6H_5 (**2c**), Me(**2d**);
R = H, R' = CF_3 (**2e**)]

TABLE 1. Spectroscopic data

Complex	IR (cm^{-1}) ν(CO) [a]	NMR (δ) [b]		
		^{1}H [b]	^{19}F [b]	^{13}C{^{1}H} [b,c]
2a[6]	2052; 2024; 1995; 1975; 1840	4.79 (s, 5H, Cp); 5.33 (s, 5H, Cp)	−45.57 (s, 6F)	126.0 [b] (q, CF_3, $J_{C-F}\cong 275$ [d]); 126.4 (q, CF_3, J_{C-F} = 275); 145.1 (m, CCF_3) 187.8, 190.8, 200.7, 209.3, 224.6 (CO)
2b	2044; 2016; 1982; 1971; 1840	4.85 (s, 5H, Cp); 5.10 (s, 5H, Cp)	−125.81 (m, 1F); −129.9 (m, 1F); −131.54 (m, 1F); −132.39 (m, 1F); −157.20 (m, 2F); −161.83 (m, 2F); −162.65 (m, 2F)	127–146 [c] (m, CC_6F_5, C_6F_5); 187.1, 191.0, 202.5, 210.2, 224.5 (CO)
2c	2030; 1999; 1970; 1956; 1830	4.95 (s, 5H, Cp); 4.73 (s, 5H, Cp); 6.92 (m, 5H, Ph); 7.23 (m, 3H, Ph); 7.50 (m, 2H, Ph)		83.7, 86.7 (C_5H_5); 125.6–129.4 (Ph); 153.6 (Ph); 155.6 (Ph); 168.3 (C-Ph); 170.8 (C-Ph); 187.8, 191.8, 201.7, 210.6, 226.3 (CO)
2d	2030; 2003; 1975; 1960; 1830	2.67 (s, 3H, Me); 3.07 (s, 3H, Me); 4.78 (s, 5H, Cp); 4.95 (s, 5H, Cp)		
2e	2050; 2018; 1994; 1975; 1850	4.72 (s, 5H, Cp); 5.18 (s, 5H, Cp); 8.45 (s, 1H, ≡C–H)	−49.29 (s, 3F)	126.7 [b] (q, CF_3, J_{C-F} = 272); 141.9 (s, CH); 153.8 (q, CCF_3, J_{C-F} = 38); 188.2, 190.4, 200.9, 209.9, 225.6 (CO)
3b	1690	4.68 (s, 15H, Cp)	−134.35 (d, 4F, J_{F-F} = 20); −158.24 (t, 2F, J_{F-F} = 20); −163.48 (m, 4F)	
4a		4.66 (s, 15H, Cp)	−47.16 (s, 6F)	
4b		4.37 (s, 15H, Cp)	−131.61 (d, 4F, J_{F-F} = 20); −159.23 (t, 2F, J_{F-F} = 20); −163.42 (m, 4F)	86.3 [b] (s, C_5H_5); 136.1–140.1 (m, C_6F_5); 300.6 (s, CC_6F_5)
5	1710	1.25–3.25 (m, 10H); 5.65 (m, 2H); 7.85 (s, 1H)	−65.16 (s, 3F)	
7	2004; 1955	4.62 (s, 5H, Cp); 5.15 (s, 5H, Cp); 7.60 (m, 2H, Ph); 7.35 (m, 4H, Ph); 7.15 (m, 4H, Ph)	−49.75 (q, 3F, J_{F-F} = 10); −54.47 (dq, 3F, J_{F-F} = 10, J_{F-P} = 2)	124.9–145.7 [b] (m, C_6H_5); 126.6 (q, CF_3, J_{C-F} = 276); 126.9 (q, CF_3, J_{C-F} = 276); 142.6 (q, CCF_3, J_{C-F} = 37); 165.5 (q, CCF_3, J_{C-F} = 40); 202.0, 218.0 (CO)

[a] In CH_2Cl_2. Chemical shifts in ppm. [b] In $CDCl_3$. [c] In THF-d_8. [d] J in Hz.



(2)

$R = R' = CF_3$ (**3a**) [2%]
$R = R' = C_6F_5$ (**3b**) [17%]

$R = R' = CF_3$ (**4a**) [2.5%]
$R = R' = C_6F_5$ (**4b**) [24%]
$R = R' = C_6H_5$ (**4c**) [60%]

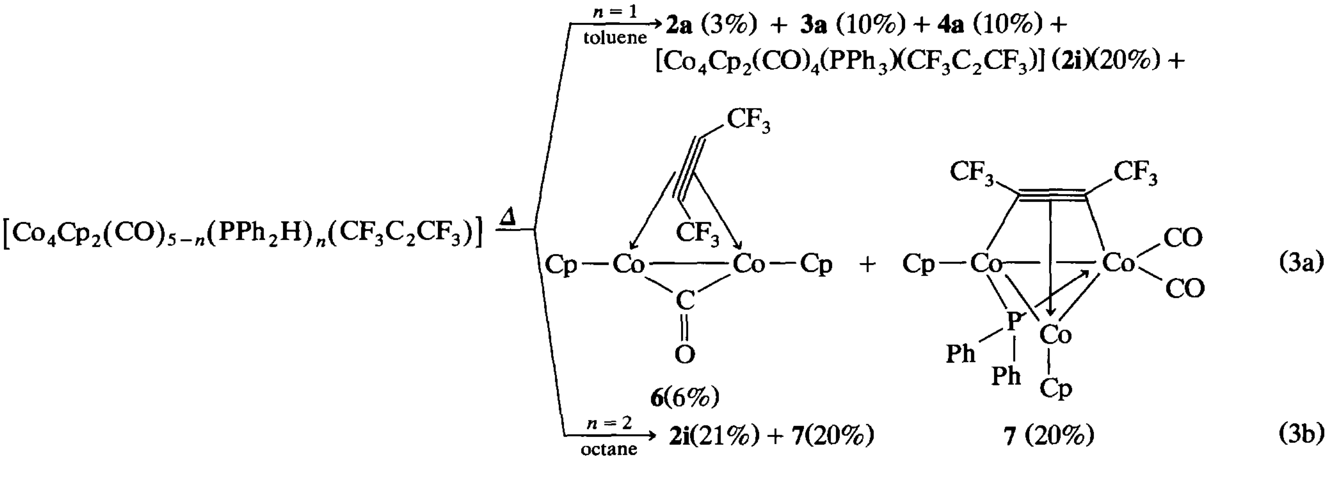
2.2. Thermal decomposition reactions of $[Co_4Cp_2(CO)_5(RC_2R')]$ *and* $[Co_4Cp_2(CO)_{5-n}(PPh_2H)_n(CF_3C_2CF_3)]$ *(n = 1 or 2)*

The thermal decomposition of **2a–c** in refluxing octane has been studied. The progress of the reaction was monitored by ^1H or ^{19}F NMR spectroscopies, which showed that **2b** and **2c** had disappeared after *ca.* 4 h and 20 h, respectively, whereas **2a** was recovered in yields up to 90% after 8 h. The reaction resulted in several products which were separated by column chromatography. Some products were neither isolated nor characterised, due to their instability or their low yield (less than 0.5%). Thermolysis of **2c** and chromatography of the products yielded only one complex, **4c**, formulated as $[Co_3Cp_3(CC_6H_5)_2]$, whereas thermolysis of **2a** and **2b** gave **3** and **4** [eqn. (2)].

Complexes **3** and **4** have been fully characterised by mass and spectroscopic data. The structure of **4** seems similar to that of known μ_3-alkylidyne complexes [4,8]. Compounds **3a** and **4c** have been reported previously [4i,7a], and the configurations shown in eqn. (2) for the other complexes have been established by comparison of their spectral data with those of **3a** and **4c**.

Thermolyses of mono- and di-substituted clusters $[Co_4Cp_2(CO)_{5-n}(PPh_2H)_n(CF_3C_2CF_3)]$ (**2f**, $n = 1$; **2g**, $n = 2$) [9] in refluxing toluene (**2f**) and refluxing octane (**2g**) were also investigated. With **2f**, numerous products were separated from the reaction mixture by chromatography. Six were obtained in sufficient amounts for characterisation, and these are shown in eqn. (3a). Most of the products were already known, but one, **7**, is new. Decomposition of **2g** appeared to give a cleaner reaction and only two products were isolated [eqn. (3b)].

Complex **7** was the major product of these thermal decomposition reactions and is formulated as $[Co_3Cp_2(CO)_2(PPh_2)(CF_3C_2CF_3)]$ from mass and spectral data (see Table 1 and Experimental details). Complex **7** exhibits a parent ion at m/z 710 in its mass spectrum and fragment ions corresponding to the suc-



cessive loss of two CO molecules. The IR spectrum indicates that the two carbonyls are terminal. In the NMR spectra, there are resonances for two CF_3, and two C_5H_5 groups, consistent with the structure depicted in eqn. (3). The application of simple cluster electron-counting rules [10] implies a *nido*-square-pyramidal geometry for **7**, as expected for a formally 48-electron species with five vertices and seven skeletal electron pairs. This suggests that the diphenylphosphine is edge-bridging.

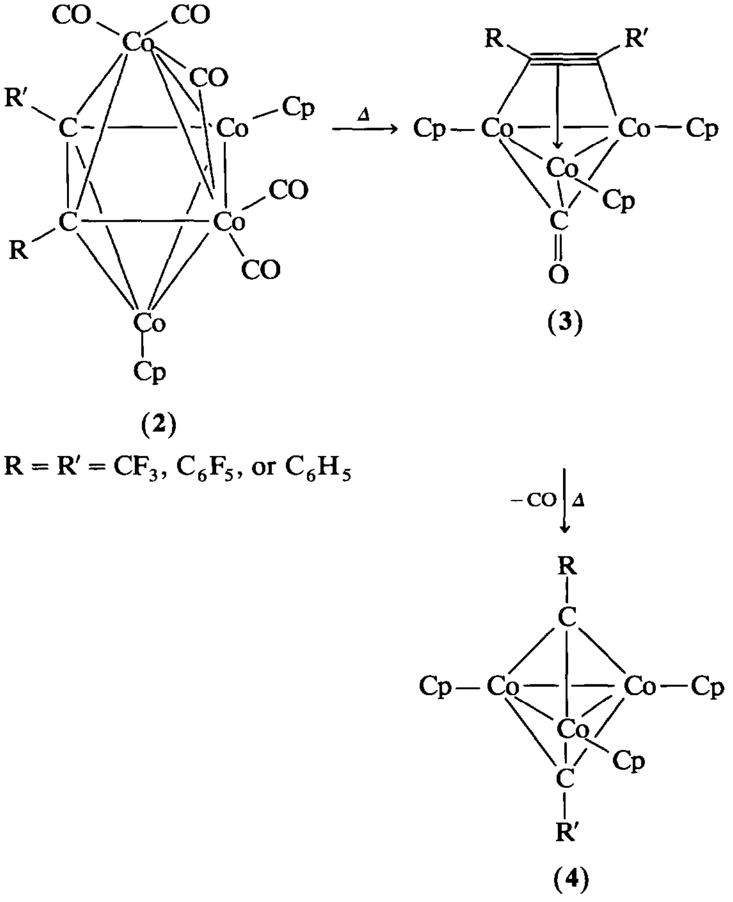
3. Discussion

3.1. *Patterns of syntheses of* closo-*octahedral clusters*

The formation of *closo* 'Co_4C_2' octahedra **2** is interesting when compared to other reactions we have investigated involving $[(CO)_3\overline{Co(\mu\text{-}RC_2R')Co}(CO)_3]$ (**1**) and metal compounds [3]. When the metal compound is a dimetal species (e.g., $[Cp(CO)\overline{Fe(\mu\text{-}CO)_2Fe}(CO)Cp]$ the structure of the clusters depends on the substituents in the alkyne in **1**. Formation of a *closo* octahedron is favoured when polar symmetrical alkynes are used. With terminal alkynes, the reaction goes mainly to μ_4-η^2-vinylidene tetranuclear clusters and no evidence for tetranuclear clusters is obtained when non-polar alkynes are involved [3]. In contrast, when monometal compounds are reactants, as we have now shown with $[CpCo(CO)_2]$, the reactions give exclusively *closo*-octahedral clusters. We conclude for reactions of dimetal species, *closo*-heteronuclear '$M_2M'_2C_2$' octahedra are formed when there are only electron-withdrawing substituents on the symmetrical alkynes, and that for monometal species *closo*-homonuclear 'M_4C_2' octahedra are obtained whatever the electronic or steric effects of the substituents in the alkyne. This difference in behaviour may be due (i) to the different electronegativities of the metals that are involved in the clusters and (ii) to the nuclearity of the metallic complex which acts as a ligand towards **1**. The influence of the electronic factors in these reactions is difficult to assess, but they could override the steric factors when the two are in competition.

3.2. *Thermolysis of* closo-*octahedra; alkyne scission on cluster framework*

The thermal decomposition reactions of the complexes $[Co_4Cp_2(CO)_5(RC_2R')]$ (**2a–c**) give two trinu-



(**2**)

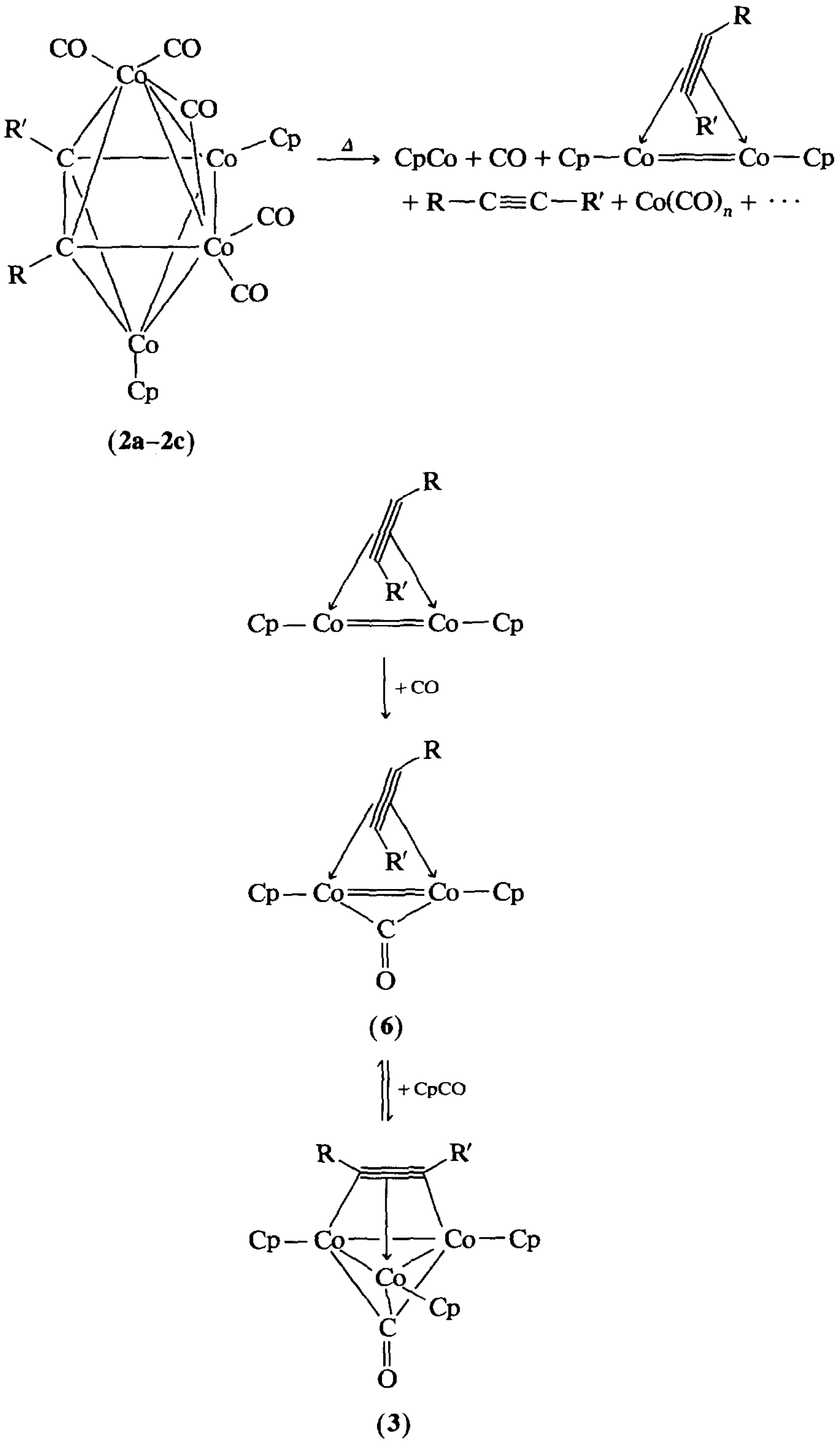
$R = R' = CF_3, C_6F_5$, or C_6H_5

(**3**)

(**4**)

Scheme 1.

clear clusters **3** and **4**, but **4** appears to be derived from **3**. A probable reaction sequence linking **2** and **4** is shown in Scheme 1. Thermal decomposition of the complexes **2** is favoured when alkynes with bulky substituents are used. Complex **2a** ($R = R' = CF_3$), which like complex **2b** ($R = R' = C_6F_5$) has electron-withdrawing substituents in the alkyne, is undoubtedly the most stable of complexes **2**. This shows that steric



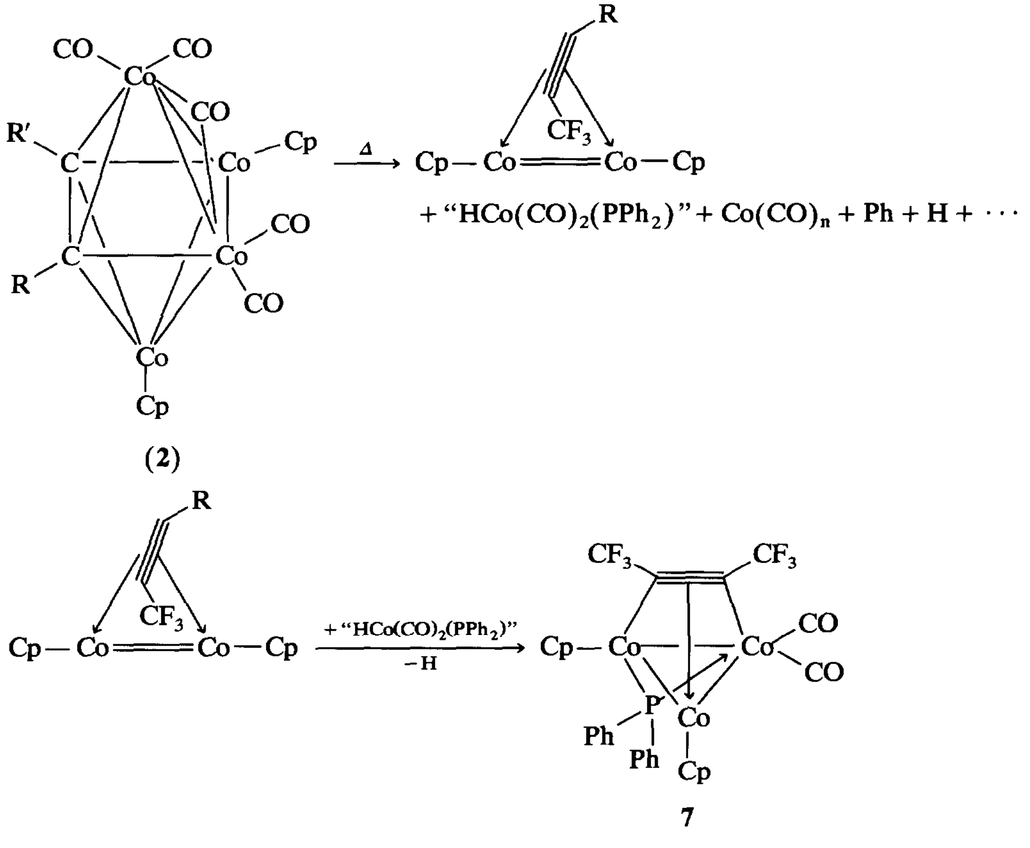
Scheme 2.

factors in the thermal decomposition reactions override the electronic factors.

As far as the mechanism of μ_3-carbonyl cluster formation (**2** → **3**) is concerned, a question remains as to how the trinuclear 'Cp_3Co_3' core assembles from the tetranuclear '$Co_4Cp_2(CO)_5$' unit. One possible reaction sequence (Scheme 2) is that which requires the formation of the bridging carbonyl complex [$CpCo(\mu$-$CO)(\mu$-$RC_2R')CoCp$] (**6**) as an intermediate. Complex **6** is readily formed by reaction of [$\{CpCo(CO)\}_2(\mu$-$CO)$] with CO [11]. The main argument in favour of this is the detection of **6** from the thermolysis of the related complex [$Co_4Cp_2(CO)_4(PPh_2H)(CF_3C_2CF_3)$]; heating **2f** at 90°C in toluene gave **6** in high yield (70%). A mechanism involving concomitant partial cluster contraction and ligand exchange cannot be ruled out but appears less likely, since only products with a 'Cp_3Co_3' core are formed here.

Two parallel reaction sequences are formed in the thermal decomposition of the monosubstituted cluster [$Co_4Cp_2(CO)_4(PPh_2H)(CF_3C_2CF_3)$ (**2f**). The first is similar to that observed for the thermolyses of complexes **2a–c**, and gives rise to **3a** and then to **4a**. The second sequence leading to **7** would involve both [$CpCo(\mu$-$CF_3C_2CF_3)CoCp$] and '$HCo(CO)_2(PPh_2)$' as possible intermediates (Scheme 3). This implies considerable fragmentation of **2f** as shown in Scheme 3. One of the main products of the thermal decomposition of **2f** contains PPh_3 (**2i**) which is quite unexpected. One possible way to obtain **2i** would be the replacement of PPh_2H with PPh_3, which is formed by the reaction of PPh_2 with Ph, which are fragments of the partial decomposition of **2f** (Scheme 3). Heating **2f** in THF with an excess of PPh_3 does not confirm such a sequence, however, since **2i** was obtained in this reaction in the same yield as in the thermal decomposition of **2f** without triphenylphosphine. Hence it appears that **2i** results from **2f** by replacing Ph by H in PPh_2H.

Thermal decarbonylation of complexes **3a–c** results in alkyne cleavage to form the bis(carbyne) clusters **4a–c**. The structural requirements for alkyne-bond cleavage in trinuclear complexes has been discussed before [4d,f]. On the basis of experimental and theoretical arguments, and a study of the pyrolysis of rhodium and iridium complexes [$Cp_3M_3(CO)(C_2R_2)$], Shapley and Hoffmann [4f] have postulated that carbonyl ligands in related systems reduce the barrier to alkyne cleavage. However, Vollhardt *et al.* [4d] demonstrated subsequently that an additional ligand in the cyclopentadienyl alkyne clusters of the cobalt triad is not a



Scheme 3.

requirement for bis(carbyne) cluster generation. Our results accord with this. Although no evidence for an unsaturated species was found in our experiments, we assume that the more likely reaction sequence for the thermal conversion of **3a–c** to **4a–c** is that which requires the formation of intermediate '**8**' (Scheme 4).

Thermal decompositions of the *closo*-homotetranuclear 'Co_4C_2' octahedra observed in our studies contrast sharply with the behaviour of the *closo*-heteronuclear octahedra '$Co_2Fe_2C_2$' that we reported recently [3]. Thermolyses of mixed clusters give rise to bis(carbyne) 'Co_2Fe_2' complexes, demonstrating that cleavage of C≡C bonds in octahedral clusters involves strongly π-acid substituents at the hinge metal atoms, as occurs with the FeCp groups in the heteronuclear complexes $[Co_2Fe_2Cp_2(CO)_5(RC_2R')]$ [3] which exhibit a better π-back-bonding capacity than the $Co(CO)_2$ groups in $[Co_4Cp_2(CO)_5(RC_2R')]$ (**2a–c**). Hence, alkyne scission involving homotetranuclear 'Co_4C_2' clusters cannot occur without previous fragmentation of the metal framework.

4. Experimental details

4.1. General procedures

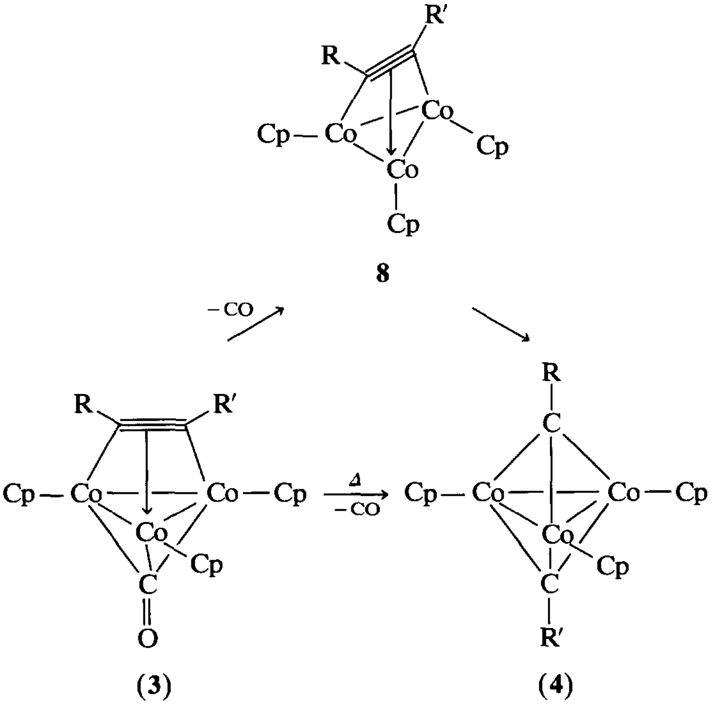
Reactions were performed under dinitrogen using standard Schlenk techniques, the solvents being deoxygenated and dried by standard methods. Literature methods were used for the preparation of $[(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3]$ [12]. All other reagents were commercial and were used as obtained.

IR spectra were obtained with a Perkin-Elmer 1430 spectrophotometer in dichloromethane solutions in the ν(CO) region. Mass spectra were measured on a GC/MS Hewlett-Packard 5995C instrument fitted with a Direct Introduction Probe. NMR spectra were recorded on either JEOL FX100 or Bruker AC300 spectrometers, relative to tetramethylsilane as an internal reference (^1H, ^{13}C) or to external $CFCl_3$ (^{19}F). Chemical analyses were performed by the Centre de Microanalyses du CNRS de Vernaison.

4.2. Preparation of $[Co_4Cp_2(CO)_5(RC_2R')]$ (2b–d)

In a typical procedure, *ca.* 0.8 g of $[(CO)_3Co(\mu\text{-}RC_2R')Co(CO)_3]$ was dissolved in octane (50 ml) and 2 equiv. of $[CpCo(CO)_2]$ in octane were added. The reaction mixture was heated under reflux for *ca.* 4 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed on either silica gel (R = R' = C_6F_5 or Me) or deactivated alumina (R = R' = C_6H_5). The products were eluted with mixtures of hexane/dichloromethane and thus separated from thermally decomposed products.

Complex **2b** (R = R' = C_6F_5): eluted with hexane/CH_2Cl_2 (9:1) (violet solution) (yield, 45%) and separated from **4b** (yield, 16%) eluted with hexane/CH_2Cl_2 (3.5:0.5) (red solution) and from **3b** (yield, 3%) eluted with CH_2Cl_2 (brown solution). Analysis: Calc. for



Scheme 4.

$C_{29}H_{10}Co_4F_{10}O_5$: C, 40.3; Co, 27.3; F, 21.9%. Found: C, 40.2; Co, 27.0; F, 21.5%.

Complex **2c** ($R = R' = C_6H_5$): eluted with hexane/CH_2Cl_2 (8:2) (black solution) (yield, 68%) and separated from **4c** (yield, 12%) with hexane/CH_2Cl_2 (9:1) (red solution). Mass spectrum *m/z*: 684 (M^+). Other peaks $M^+ - x$CO ($x = 1$–5).

Complex **2d** ($R = R' = Me$): eluted with hexane/CH_2Cl_2(7.5:2.5) (purple solution) (yield, 40%). Mass spectrum *m/z*: 560 (M^+). Other peaks $M^+ - x$CO ($x = 1$–5).

4.3. Preparation of $[Co_4Cp_2(CO)_5(CF_3C_2H)]$ (2e)

Complexes $[CpCo(CO)_2]$ (1 g, 5.5×10^{-3} mol) and $[(CO)_3\overline{Co(\mu\text{-}CF_3C_2H)Co}(CO)_3]$ (1 g, 2.8×10^{-3} mol) were dissolved in hexane (50 ml). The reaction mixture was heated under reflux for 21 h. The solvent was removed under vacuum and the residue chromatographed on deactivated alumina. Hexane eluted a purple band which gave 0.47 g (30%) of **2e**. A second band was eluted with hexane/CH_2Cl_2 (9:1). Removal of the solvent under reduced pressure gave a white powder which was sublimed to yield white crystals of **5** (yield, 15%). Further elution with hexane/CH_2Cl_2 (8:2) gave a brown band yielding **3e** (0.02 g, 2%).

Complex **2e** ($R = CF_3$, $R' = H$). Mass spectrum *m/z*: 600 (M^+). Other peaks $M^+ - x$CO ($x = 1$–5); 363 ($M^+ - 5CO - CoF_2$).

Complex **5**: Mass spectrum *m/z*: 254 (M^+); 226 ($M^+ -$ CO).

4.4. Preparation of $[Co_4Cp_2(CO)_{5-n}(PPh_2H)_n(CF_3C_2CF_3)]$ (2f, n = 1; 2g, n = 2)

These complexes were obtained according to a method described previously [9].

4.5. Thermal decomposition of $[Co_4Cp_2(CO)_5(RC_2R')]$ (2a–c)

(i) An octane (20 ml) solution of complex **2a** (0.4 g, 6×10^{-4} mol) was heated under reflux for 8 h, after which the solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2/hexane (1:9) and chromatographed on silica gel. Gradient elution with CH_2Cl_2/hexane (1:9 to 3:7) afforded three major bands. The first red band was identified as $[Co_3Cp_3(CCF_3)_2]$ (**4a**) (0.008 g, 2.5%). The second purple band was collected and the solvent was removed *in vacuo*. Recrystallisation from hexane/CH_2Cl_2 (9:1) afforded dark crystals of the starting material **2a** (0.36 g, 90%). The third band was also collected and the solvent removed *in vacuo*. This was identified as **3a** (0.006 g, 2%) from its IR and NMR spectra. Complex **4a**: Mass spectrum *m/z*: 534 (M^+).

(ii) In a similar manner to (i) above, thermolysis of **2b** (0.1 g, 1.2×10^{-4} mol) was conducted in refluxing octane for 4 h. The solvent was then removed *in vacuo*. Chromatography as in (i) afforded $[Co_3Cp_3(CC_6F_5)_2]$ (**4b**) (0.02 g, 24%) and $[Co_3Cp_3(CO)(C_6F_5C_2C_6F_5)]$ (**3b**) (0.015 g, 17%). Complex **3b**: Mass spectrum *m/z*: 758 (M^+); 730 ($M^+ -$ CO). Complex **4b**: Mass spectrum *m/z*: 730 (M^+).

(iii) The same general procedure was employed for the thermolysis of **2c** (0.1 g, 1.5×10^{-4} mol) which was heated under reflux in octane for 20 h, after which the IR spectrum showed no starting material. The solvent was removed from the resulting dark brown solution *in vacuo*. The residue was dissolved in CH_2Cl_2/hexane (1:9) and chromatographed. Elution with the same solvent mixture gave a red band of $[Co_3Cp_3(CC_6H_5)_2]$ (**4c**) (0.05 g, 60%).

4.6. Thermal decomposition of $[Co_4Cp_2(CO)_{5-n}(PPh_2H)_n(CF_3C_2CF_3)]$ (2f, n = 1; 2g, n = 2)

(i) A toluene (20 ml) solution of **2f** (0.2 g, 2.4×10^{-4} mol) was heated under reflux for 8 h, after which the solvent was removed *in vacuo*. The residue was dissolved in the minimum volume of CH_2Cl_2/hexane (1:9) and chromatographed on silica gel. Elution with the same solvent mixture afforded three major bands, which were identified as **4a** (0.013 g, 10%), $[Co_2Cp_2(CO)(CF_3C_2CF_3)]$ (**6**) (0.006 g, 6%) and **2a** (0.005 g, 3%), respectively. A 1.5:8.5 mixture of CH_2Cl_2/hexane eluted a brown band which gave 0.035 g (20%) of dark brown $[Co_3Cp_3(CO)_2(PPh_2)(CF_3C_2CF_3)]$ (**7**). Further elution with CH_2Cl_2/hexane (3:7) gave a dark green band yielding **2i** (0.043 g, 20%) which was identified by its IR and NMR spectra [9]. Finally, CH_2Cl_2 eluted a brown band which, upon removal of solvent, gave 0.013 g (10%) of **3a**.

Complex **6**: Mass spectrum *m/z*: 438 (M^+); 410 ($M^+ -$ CO). IR (CH_2Cl_2) ν(CO) (cm^{-1}): 1832 (s). ^1H NMR ($CDCl_3$) δ: 4.98 (s, 10H, Cp) ppm. ^{19}F NMR ($CDCl_3$) δ: -50.31 (s, 6F) ppm. $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 88.1 (s, C_5H_5); 126.7 (q, CF_3, $J_{C-F} = 269$ Hz) ppm.

Complex **7**: Mass spectrum *m/z*: 710 (M^+); 682 ($M^+ -$ CO); 654 ($M^+ - 2CO$); 557 ($M^+ - 2CO - CoF_2$); 460 ($M^+ - 2CO - 2CoF_2$); 415 ($M^+ - 2CO - C_2(CF_3)_2 - Ph$).

(ii) In a similar manner to (i) above, thermolysis of **2g** (0.4 g, 4.1×10^{-4} mol) was conducted in refluxing octane for 2 h. After this the solvent was removed *in vacuo*. Chromatography as in (i) afforded **2i** (0.07 g, 20%) and **7** (0.06 g, 20%).

References

1 R. Rumin, F. Robin-Le Guen, J. Talarmin and F.Y. Pétillon, Part 11, *Organometallics, 13* (1994) 1155.

2 R.D. Adams, in D.F. Shriver, H.D. Kaesz and R.D. Adams (eds.), *The Chemistry of Metal Cluster Complexes*, VCH, New York, 1990, Chap. 3.

3 R. Rumin, F. Robin, F.Y. Pétillon, K.W. Muir and I. Stevenson, *Organometallics, 10* (1991) 2274, and references cited therein.

4 (a) E. Cabrera, J.C. Daran and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, (1988) 607; (b) E.J. Wucherer and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl., 26* (1987) 355; (c) W. Bernhardt and H. Vahrenkamp, *Organometallics, 5* (1986) 2388; (d) B. Eaton, J.M. O'Connor and K.C.P. Vollhardt, *Organometallics, 5* (1986) 394; (e) Y. Chi and J.R. Shapley, *Organometallics, 4* (1985) 1900; (f) A.D. Clauss, J.R. Shapley, C.N. Wilker and R. Hoffmann, *Organometallics, 3* (1984) 619; (g) N.T. Allison, J.R. Fritch, K.P.C. Vollhardt and E.C. Walborsky, *J. Am. Chem. Soc., 105* (1983) 1384; (h) J.R. Fritch and K.P.C. Vollhardt, *Angew. Chem. Int. Ed. Engl., 19* (1980) 559; (i) J.R. Fritch, K.C.P. Vollhardt, M.R. Thompson and V.W. Day, *J. Am. Chem. Soc., 101* (1979) 2768; (j) R.B. King and C. Darmon, *Inorg. Chem., 15* (1976) 879.

5 (a) A.D. Shaposhnikova, M.V. Drab, G.L. Kamalov, A.A. Pasynskii, I.L. Eremenko, S.E. Nefedov, Y.T. Struchkov and A.I. Yanovsky, *J. Organomet. Chem., 429* (1992) 109; (b) J.R. Shapley, C.H. McAteer, M.R. Churchill and L.V. Biondi, *Organometallics, 3* (1984) 1595; (c) J.T. Park, J.R. Shapley, C. Bueno, J.W. Ziller and M.R. Churchill, *Organometallics, 7* (1988) 2307.

6 R. Rumin, Lj. Manojlović-Muir, K.W. Muir and F.Y. Pétillon, *Organometallics, 7* (1988) 375.

7 (a) M.B. Freeman, L.W. Hall and L.G. Sneddon, *Inorg. Chem. 19* (1980) 1132; (b) K.P.C. Vollhardt, *Angew. Chem. Int. Ed. Engl., 23* (1984) 539; (c) M.B. Gomes de Lima, J.E. Guerchais, F.J. Le Floch-Pérennou, P. L'Haridon, F.Y. Pétillon and J. Talarmin, *Organometallics, 6* (1987) 1930; (d) D.W. Macomber, A.G. Verma and R.D. Rogers, *Organometallics, 7* (1988) 1241.

8 See for example: (a) D. Nuel and R. Mathieu, *Organometallics, 7* (1988) 16; (b) M.K. Alami, F. Dahan, J.J. Bonnet and R. Mathieu, *Organometallics, 7* (1988) 1391; (c) J. Suades, F. Dahan and R. Mathieu, *Organometallics, 8* (1989) 842; (d) G. Fachinetti, S. Pucci, P.F. Zanazzi and U. Methong, *Angew. Chem., Int. Ed. Engl., 18* (1979) 619.

9 F.Y. Pétillon, R. Rumin and J. Talarmin, *J. Organomet. Chem., 346* (1988) 111.

10 K. Wade, *Adv. Inorg. Chem. Radiochem., 18* (1976) 1.

11 U. Kölle and B. Fuss, *Chem. Ber., 119* (1986) 116.

12 R.S. Dickson and P.J. Fraser, *Adv. Organomet. Chem., 12* (1974) 323.