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Gas-phase reactions of cobalt(III) β-ketoenolates with Brønsted acid reagents†

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The gas-phase reactions of a variety of 3-substituted pentane-2,4-dionate cobalt(III) complexes of formula $[Co\{MeC(O)CR^1C(O)Me\}_2\{MeC(O)CR^2C(O)Me\}]$ ($R^1 = R^2 = H$ **a**; $R^1 = H$, $R^2 = Cl$ **b**, Br **c**, NO_2 **d**, SCN **e**, Me **f** or Et **g**; $R^2 = H$, $R^1 = Cl$ **h**, Br **i**, NO_2 **j**, SCN **k**, Me **l** or Et **m**) with various Brønsted acid systems, *e.g.* $[CH_5]^+$, $[t\text{-}C_4H_9]^+$, $[H_3]^+$, $[D_3]^+$, $[NH_4]^+$ and $[ND_4]^+$, were studied by chemical ionization (CIMS) and ion-trap mass spectrometry (ITMS). In all cases the following main reactions were observed: (*i*) ion-to-molecule charge transfer with formation of the corresponding molecular ions, $[Co\{MeC(O)CR^1C(O)Me\}_2\{MeC(O)CR^2C(O)Me\}]^{\cdot+}$; (*ii*) unprecedented $[H_2]^+$ (or $[D_2]^+$) transfer from the gaseous Brønsted acids to the neutral cobalt complexes with the formation of the ions $[M + 2H]^+$ or $[M + 2D]^+$, respectively, which give rise by fragmentation to the ions $[MeC(O)CRC(O)Me + 2H]^+$ or $[MeC(O)CRC(O)Me + 2D]^+$, which in many cases, are the most abundant species; (*iii*) H^+ (or D^+) transfer from the Brønsted acids to the neutral cobalt complexes with the formation of the ions $[M + H]^+$ or $[M + D]^+$, respectively. The ITMS study of the gas-phase reaction between the ion $[Co(acac)_2]^+$ (acac = pentane-2,4-dionate) and complexes **a**–**g** revealed two processes, the ion-to-molecule charge transfer which results in the formation of the radical cations $[Co(acac)_2\{MeC(O)CRC(O)Me\}]^{\cdot+}$, and a largely predominant process which leads to two bimetallic ions, $[Co_2(acac)_4]^+$ and $[Co_2(acac)_3]^+$, which, according to kinetic studies, arise from two parallel reactions. The results are discussed in terms of analogies and differences between the gas- and the solution-phase reactions of tris(β-ketoenolato)cobalt(III) complexes with Brønsted acids. The preparation of the complexes **e**, **g** and **k**–**m**, not previously reported, is described; furthermore, **f** has been obtained in higher yields through an alternative one-step synthesis. All new compounds have been characterized by elemental analysis, mass and ^1H NMR spectrometry.

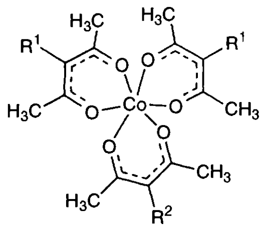
In 1992[2] some of us discovered that the reaction of cobalt(III) β-ketoenolates, [Co(β-dik)$_3$] **1** (β-dik = β-ketoenolate anion), with Brønsted acids, typically trifluoroacetic acid, may result in an intermolecular ligand-to-metal electron-transfer process with the formation of radical species which were detected and characterized by ESR spectroscopy.[1–3] Some aspects of the chemistry behind this reaction were understood through IR, UV/VIS, ESR, and ion-spray mass spectrometry studies.[3] In particular, we concluded that the role of the acid is that of causing the formation of cationic highly oxidizing cobalt(III) species, [Co(β-dik)$_2$]$^+$ **2**, by the gradual removal of β-ketoenolate ligands from the cobalt(III) co-ordination sphere [equation (1)]. Complexes **2** react in their turn with the starting

$$\underset{\mathbf{1}}{[Co(\beta\text{-dik})_3]} + H^+ \longrightarrow \underset{\mathbf{2}}{[Co(\beta\text{-dik})_2]^+} + \beta\text{-Hdik} \quad (1)$$

neutral complexes **1** undergoing an electron-transfer process which results in the formation of radical cations **3** and of paramagnetic cobalt(II) derivatives **4** [equation (2)].[3]

$$\underset{\mathbf{1}}{[Co(\beta\text{-dik})_3]} + \underset{\mathbf{2}}{[Co(\beta\text{-dik})_2]^+} \longrightarrow \underset{\mathbf{3}}{[Co(\beta\text{-dik})_3]^{\cdot+}} + \underset{\mathbf{4}}{[Co^{II}(\beta\text{-dik})_2]} \quad (2)$$

Owing to the increasing availability of tools and techniques for the study of gas-phase ion chemistry[4] we have been attracted to the idea of carrying out a study of the reaction of cobalt(III) β-ketoenolates with Brønsted acids in the gas phase with the aim of acquiring further experimental evidence in favour of the above reactivity. Thus, the ion–molecule reaction (1) was explored through the chemical ionization mass spectra of complexes **5** obtained in the presence of a variety of Brønsted acids. In addition, the reaction of the cation $[Co(acac)_2]^+$ (acac = pentane-2,4-dionate) with several neutral cobalt(III) β-ketoenolates was studied by ion-trap mass spectrometry (ITMS).



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a $R^1 = R^2 = H$
b $R^1 = H, R^2 = Cl$
c $R^1 = H, R^2 = Br$
d $R^1 = H, R^2 = NO_2$
e $R^1 = H, R^2 = SCN$
f $R^1 = H, R^2 = Me$
g $R^1 = H, R^2 = Et$

h $R^1 = Cl, R^2 = H$
i $R^1 = Br, R^2 = H$
j $R^1 = NO_2, R^2 = H$
k $R^1 = SCN, R^2 = H$
l $R^1 = Me, R^2 = H$
m $R^1 = Et, R^2 = H$

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† Radical Species from Transition-metal Complexes. Part 3.
Non-SI units employed: Torr ≈ 133 Pa, eV ≈ 1.60×10^{-19} J.

A number of analogies emerge from this study between the solution- and the gas-phase chemistry of the reaction of cobalt(III) β-ketoenolates with Brønsted acids which give some general validity to the reactivity pattern described by equations (1) and (2). Moreover, the study allowed us to observe the unprecedented $[H_2]^+$ (or $[D_2]^+$) transfer from gaseous Brønsted acid reagent ions to neutral molecules.

Results and Discussion

Synthesis of complexes 5

Complexes **5a**–**5d** and **5h**–**5j** were prepared according to published procedures (see Experimental section). The new complexes **5e** and **5k** were prepared by partial electrophilic functionalization of the intercarbonylic carbon atoms of **5a** with thiocyanogen following a procedure similar to that reported by Collman *et al.*[5] for the synthesis of the corresponding homoleptic derivative, *i.e.* tris(3-thiocyanatopentane-2,4-dionato)cobalt(III). They were isolated from the crude reaction mixture by column chromatography. As far as the complexes **5f**, **5g**, **5l** and **5m** are concerned, to our knowledge the literature reports only on the multistep synthesis of **5f** involving first the isolation of $[Co(acac)_2(CO_3)]^-$ and then its reaction with 3-methylpentane-2,4-dione.[6] Our efforts to obtain these four complexes by treating $[Co(CO_3)_3]^{3-}$ with a 2 : 1 or a 1 : 2 mixture of pentane-2,4-dione and the corresponding 3-alkylpentane-2,4-dione failed; invariably almost exclusive formation of tris(pentane-2,4-dionato)cobalt(III) occurred. Instead, **5f** and **5g** were obtained in 19 and 34% yields, respectively, by treating bis(pentane-2,4-dionato)cobalt(II) first with hydrogen peroxide and then with 3-methyl- or 3-ethyl-pentane-2,4-dione.[7] Alternatively, both complexes can be obtained in much higher yields (*ca.* 80%) through a one-step synthesis by heating a 1 : 2 mixture of $[Co\{MeC(O)CR(O)Me\}_3]$ (R = Me or Et) and pentane-2,4-dione in dichloromethane at 90 °C [equation (3)]. Interestingly, also **5l** and **5m** can be

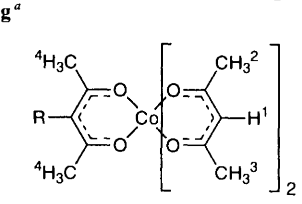
$$[Co\{MeC(O)CRC(O)Me\}_3] + 2\,Hacac \xrightarrow{heat} \underset{\mathbf{5f}\ \text{or}\ \mathbf{5g}}{[Co(acac)_2\{MeC(O)CRC(O)Me\}]} + 2\,MeC(O)CHRC(O)Me \quad (3)$$

prepared in good yields (higher than 70%) in this way, by adopting a 1 : 1 $[Co\{MeC(O)CRC(O)Me\}_3]$ (R = Me or Et) : pentane-2,4-dione molar ratio [equation (4)].

$$[Co\{MeC(O)CRC(O)Me\}_3] + Hacac \xrightarrow{heat} \underset{\mathbf{5l}\ \text{or}\ \mathbf{5m}}{[Co(acac)\{MeC(O)CRC(O)Me\}_2]} + MeC(O)CHRC(O)Me \quad (4)$$

All complexes were characterized by ^1H NMR (Tables 1 and 2) and mass spectrometry; the formulation of the new complexes was also based on elemental analyses. Complexes **5** are dissymmetric, each possessing only one C_2 symmetry axis. This makes the methyl groups of the ligand bearing the R^2 substituent chemically and magnetically equivalent and the four methyl groups of the R^1-substituted ligands give rise to two groups of two magnetically equivalent methyls and two well resolved NMR signals. Examination of the tabulated data allows one to conclude that the resonances due to the methyl protons of the substituted β-ketoenolate ring are shifted to lower fields in accordance with previous observations.[8,9]

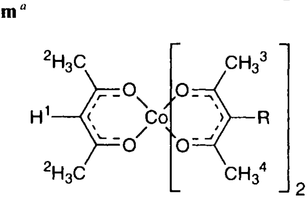
Table 1 Proton NMR data for complexes $[Co(acac)_2\{MeC(O)CR\text{-}C(O)Me\}]$ **5b**–**5g**[a]



Compound	R	H^1	H^2	H^3	H^4
5b	Cl	5.52	2.16	2.19	2.40
5c	Br	5.51	2.16	2.19	2.47
5d	NO_2	5.56	2.17	2.25	2.43
5e	SCN	5.55	2.17	2.23	2.60
5f[b]	Me	5.49	2.13	2.16	2.24
5g[c]	Et	5.50	2.13	2.16	2.26

[a] In $CDCl_3$; spectra recorded at 200 MHz; given as chemical shifts (δ). [b] 3-Methyl, δ 1.91.[6] [c] 3-Ethyl, δ 2.29 (q, J = 7.3 Hz, CH_2) and 1.0 (t, J = 7.3 Hz, CH_3).

Table 2 Proton NMR data for complexes $[Co(acac)\{MeC(O)CR\text{-}C(O)Me\}_2]$ **5h**–**5m**[a]



Compound	R	H^1	H^2	H^3	H^4
5h	Cl	5.53	2.19	2.39	2.42
5i	Br	5.53	2.19	2.46	2.50
5j	NO_2	5.61	2.26	2.42	2.51
5k	SCN	5.58	2.23	2.60	2.67
5l[b]	Me	5.49	2.13	2.15	2.23
5m[c]	Et	5.49	2.13	2.16	2.26

[a] In $CDCl_3$; spectra recorded at 200 MHz; given as chemical shifts (δ). [b] 3-Methyl, δ 1.91. [c] 3-Ethyl, δ 2.28 (q, J = 7.3, CH_2) and 1.0 (t, J = 7.3 Hz, CH_3).

The relative intensities of the most important metal-containing ions observed in the ITMS of the complexes $[Co(acac)_2\{MeC(O)CRC(O)Me\}]$ **5a**–**5g** are reported in Table 3. The spectrum of **5a** is very similar to that previously reported for this compound by McDonald and Shannon.[10] The most characteristic aspect of the fragmentation is the loss of the 3-substituted chelate ring. The driving force for this fragmentation should be the stability of the odd-electron neutral radical eliminated.[11] The spectra of the complexes $[Co(acac)\{MeC(O)CRC(O)Me\}_2]$ **5h**–**5m**, which were recorded only for analytical purposes, show in general a low-intensity signal due to the molecular ion and an intense peak attributable to the ion $[Co(acac)_2]^+$ (m/z 257). This suggests a very high stability for the latter ion, the formation of which from complexes **5h**–**5m**, however, is not obvious since it implies that R and H exchange, maybe through an intramolecular process.[10] Owing to the high chemical purity of the samples, as shown unambiguously by their ^1H NMR spectra as well as by the fact that their mass spectra do not change on varying the source temperature from 80 up to 140 °C, these observations cannot be simply due to the contamination of the complexes with others containing the $Co(acac)_2$ moiety. Therefore, we are currently studying these complexes further by various mass spectral techniques.

Reaction of complexes 5 with gaseous Brønsted acid reagent ions

It has been previously shown that complex $[Co(acac)_3]$ **5a** is able to react in solution with a variety of cationic species such as H^+, Li^+, Na^+, K^+ and $[NH_4]^+$ thus giving rise to an ion-spray mass spectrum which contains peaks attributable to ions resulting from condensation reactions.[3] In particular, it was

Table 3 Relative intensities of the metal-containing ions observed in the ion-trap mass spectra of complexes **5a**–**5g**

	Relative intensity (%)*						
Ion	**5a**	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
$[Co(acac)_2\{MeC(O)CRC(O)Me\}]^+$	15	25	3	3	5	5	2
$[Co(acac)\{MeC(O)CRC(O)Me\}]^+$	—	20	10	—	—	10	8
$[Co(acac)_2]^+$	100	100	100	100	100	80	100
$[Co\{MeC(O)CRC(O)Me\}]^+$	—	10	—	—	—	—	—
$[Co(acac)]^+$	100	50	90	100	90	100	90

* Evaluated on the basis of the base peak.

Table 4 Chemical ionization mass spectra of $[Co(acac)_3]$ **5a**

		Relative intensity in the presence of Brønsted acid precursor (%)*		
Ion	*m/z*	CH_4	i-C_4H_{10}	H_2
$[acac + 2H]^+$	101	100	75	95
$[Co(acac)]^+$	158	—	—	45
$[Co(acac)_2]^+$	257	25	15	100
$[Co(acac)_2 + H]^+$	258	55	100	50
$[Co(acac)_3]^+$	356	—	—	50
$[Co(acac)_3 + H]^+$	357	5	30	45
$[Co(acac)_3 + 2H]^+$	358	—	15	—
$[Co_2(acac)_3]^+$	415	6	15	15
$[Co_2(acac)_4]^+$	514	—	10	60

* Evaluated on the basis of the base peak. The direct-inlet probe was kept at 85 °C, when operating in the presence of methane (0.12 Torr), and at 100 °C, when operating in the presence of isobutane (0.16 Torr) or dihydrogen (0.30 Torr), respectively.

shown that the ion $[Co(acac)_3 + H]^+$ easily loses the neutral protonated ligand Hacac, giving rise to the ion $[Co(acac)_2]^+$ [equation (1)]. With the aim of studying further the role played by different proton donors, **5a** was examined by chemical ionization (CI) mass spectrometry. The results obtained by using various Brønsted acids derived from CH_4, i-C_4H_{10} or H_2 are reported in Table 4.

Particularly intriguing is the presence of a very intense peak at *m/z* 101 attributable to an ion of formula $[acac + 2H]^+$ which results apparently from a double protonation of the acetylacetonate anion. Interestingly, by using D_2 as reactant gas, the ion $[acac + 2D]^+$ (*m/z* 103) is observed thus suggesting that both the hydrogen atoms come from the reactant gas. This was confirmed, finally, by the mass spectrum of tris(heptadeuteriopentane-2,4-dionato)cobalt(III), $[Co(C_5D_7O_2)_3]$, obtained in the presence of H_2 or i-C_4H_{10} as reactant gases: in both cases a peak having *m/z* 108, corresponding to an ion of composition $[C_5D_7O_2 + 2H]^+$, is observed while peaks at higher *m/z* are absent. These facts unambiguously rule out an intramolecular deuterium-transfer process as responsible for the double protonation of acetylacetonate anion. Finally, the presence of a weak signal at *m/z* 358, assigned to $[Co(acac)_3 + 2H]^+$, in the spectrum obtained in the presence of isobutane confirms the hypothesis of a direct transfer of one proton (H^+) and one hydrogen atom ($H^{\bullet}$) from the reactant gas to the cobalt complex.

To our knowledge, this kind of reactivity has no precedent in the literature. Therefore, we sought the origin of the ion at *m/z* 101 as well as of the ions containing two cobalt atoms (see Table 4) by using the method, outlined by Torroni *et al.*,[12] based on the influence exerted by the pressure of the ionizing gas as well as of the sample in the ionization chamber on the ion's relative intensity. As the results obtained by using different gases are almost identical, only the data concerning the ionization of complex **5a** in the presence of D_2 are reported and discussed in details. The relative intensities of the peaks change markedly upon changing the reactant gas pressure as shown in Fig 1. As

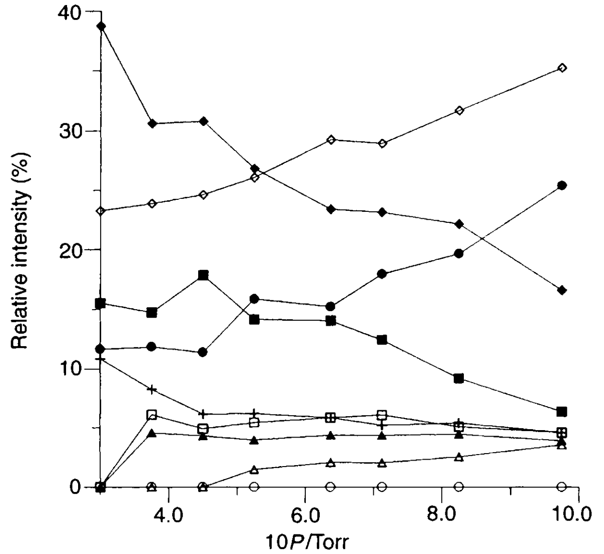


Fig. 1 Variation of relative intensity of ions as a function of total gas pressure in the reaction of $[Co(acac)_3]$ with $[D_3]^+$: (●) $[(acac) + 2D]^+$ (*m/z* 103), (○) $[Co(acac)]^+$ (*m/z* 158), (◆) $[Co(acac)_2]^+$ (*m/z* 257), (◇) $[Co(acac)_2 + D]^+$ (*m/z* 259), (+) $[Co(acac)_3]^+$ (*m/z* 356), (□) $[Co(acac)_3 + D]^+$ (*m/z* 358), (△) $[Co(acac)_3 + 2D]^+$ (*m/z* 360), (▲) $[Co_2(acac)_3]^+$ (*m/z* 415), (■) $[Co_2(acac)_4]^+$ (*m/z* 514)

expected the relative intensity of the ion $[Co(acac)_2 + D]^+$ (*m/z* 259) increases with increasing D_2 pressure, while that of $[Co(acac)_2]^+$ (*m/z* 257) decreases, showing that these two ions are formed *via* different and probably competitive paths. A marked increase with reactant gas pressure is observed in the case of the ion $[acac + 2D]^+$ (*m/z* 103), while the relative intensity of the ion $[Co(acac)_3 + 2D]^+$ (*m/z* 360), observable at rather high D_2 pressures, seems to increase much more slowly. On the other hand, the ions containing two cobalt centres, *i.e.* $[Co_2(acac)_3]^+$ and $[Co_2(acac)_4]^+$, much more abundant at higher **5a** pressures, decrease in relative intensities with increasing D_2 pressure, thus showing that such ions originate from a non-protonated precursor.

On the basis of the above observations, the formation of the monometallic ions could be accounted for by the reaction path outlined in Scheme 1, where the primary reactions are a charge-exchange reaction, a protonation reaction, and the transfer of the $[H_2]^+$ species to the substrate. According to Scheme 1, the origin of the ion at *m/z* 258 is uncertain; thus, in order to explore further the reactivity of complex **5a** with gaseous Brønsted acids we started a study by ITMS aimed first at exploring the possibility that some of the ions observed upon chemical ionization of $[Co(acac)_3]$ could result from the reaction of methane itself with ions deriving from the fragmentation of $[Co(acac)_3]^+$. Thus, we used a scan function which allowed only the ions having *m/z* > 50 to be stored and then to react with CH_4. Adopting reaction times ranging from 1 to 50 ms and methane partial pressures ranging from 0 to 2 × 10^{-4} Torr, a number of mass spectra were registered, none showing the presence of peaks attributable to protonated species. These spectra were quite similar to those obtained with a conventional mass spectrometer, the only difference being the increase in the relative intensities of the peaks associated with bimetallic ions, *i.e.* $[Co_2(acac)_3]^+$ and $[Co_2(acac)_4]^+$. Analogous results were obtained when the same experiments were carried out in the presence of D_2 instead of CH_4.

If a proton-donor species, *e.g.* $[CH_5]^+$ or $[C_4H_9]^+$, is first isolated and then allowed to react with $[Co(acac)_3]$ the formation of protonated species is observed. Fig. 2 shows some typical results obtained operating with $[C_4H_9]^+$: the relative intensity of the peak at *m*/*z* 101, $[acac + 2H]^+$, increases on increasing the reaction time while the intensities of the ions having *m*/*z* 257 and 258, due to $[Co(acac)_2]^+$ and $[Co(acac)_2 + H]^+$, respectively, decrease, this showing unambiguously that the ions having *m*/*z* 101 and 258 have different precursors. The data in Fig. 2 also allow one to hypothesize that the ion $[acac + 2H]^+$ (*m*/*z* 101) could derive from the ions $[Co(acac)_2]^+$ (*m*/*z* 257) and $[Co(acac)_2 + H]^+$ (*m*/*z* 258), or from one of them. However, no peak at *m*/*z* 101 was observed in the mass spectra of the last two ions when they were isolated and allowed to react in the trap.

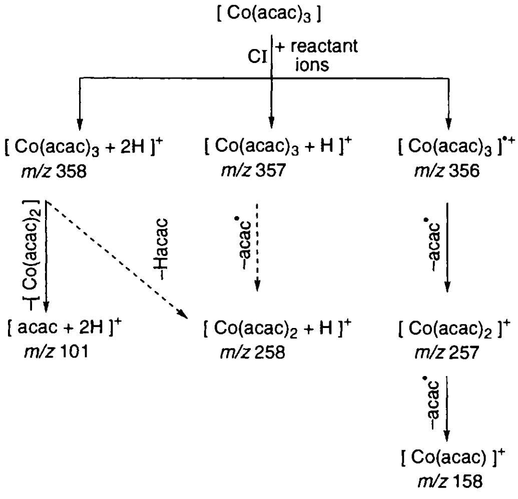
When $[NH_4]^+$ or $[ND_4]^+$ is employed as protonating agent a more selective reaction takes place: no product deriving from charge-exchange reaction is observed and once again the formation of the ions $[acac + 2H]^+$ (*m*/*z* 101) or $[acac + 2D]^+$ (*m*/*z* 103), respectively, is the most important process. Unfortunately, in all cases examined the ion-trap experiments did not allow us to observe the ions at *m*/*z* 357 and 358; therefore, direct evidence for their decomposition reactions is missing.

The formation of species like $[Co(\beta\text{-ket})_3 + H]^+$, $[Co(\beta\text{-ket})_2 + H]^+$ and $[\beta\text{-ket} + 2H]^+$ is observed also in the reactions of Brønsted acids with the complexes **5b**–**5m**. Some relevant data obtained from the study of the reactions of these complexes with CH_5^+ are reported in the Tables 5 and 6. The ion $[acac + 2H]^+$ (*m*/*z* 101) is formed in all cases along with the corresponding R-substituted ion, $[MeC(O)CRC(O)Me + 2H]^+$, unless R is NO_2 or SCN, in which cases further fragmentation occurs as may be deduced by the observation of ions attributable to the loss of NO and HCN, respectively. The most relevant point is undoubtedly the fact that the transfer of $[H_2]^+$ from different gaseous Brønsted acids to tris(β-ketoenolato)cobalt(III) complexes is of general occurrence. We are inclined to conclude that this reaction should be strongly favoured by the particular nature of the reactant substrate, which is characterized by the presence of the β-ketoenolate ligand, which is susceptible to electrophilic attack by Brønsted acids at the intercarbonylic position,[13] and the highly oxidizing cobalt(III) centre.[14] Accordingly, the structure of the initial addition products, *i.e.* $[Co(acac)_3 + 2H]^+$ {in the case of the reaction of $[Co(acac)_3]$ with $[H_2]^+$}, could be tentatively described in terms of the canonical formulae **6**–**8** (Scheme 2) which differ in the location of the unpaired electron or in the oxidation state of the metal centre and are formally the result of the addition of a H• to a β-ketoenolate ligand as well as of the formation of a two-electron, three-centre bond between a proton and an intercarbonylic CH system.[15] Accordingly, the formation of the ion $[acac + 2H]^+$ (*m*/*z* 101) is easily explained by fragmentation of the species **8** (Scheme 3). One could regard the ion $[acac + 2H]^+$ as the product of the addition of a proton to acetylacetone[16] and as such it could be described in terms of structure **9** by analogy to the structure of some β-diketone–transition metal complexes **10**.[17]

Table 5 Relative intensities of the ions $[acac + 2H]^+$ and $[MeC(O)CRC(O)Me + 2H]^+$ in the ion-trap mass spectra of complexes **5b**–**5g***

	Relative intensity (%)					
Ion	R = Cl	Br	NO_2	SCN	Me	Et
$[acac + 2H]^+$	100	80	90	50	100	100
$[MeC(O)CRC(O)Me + 2H]^+$	48	30	0	0	60	90

* Spectra were obtained under chemical ionization conditions by using methane as reactant gas, operating at 0.05 Torr (total pressure); the relative intensities have been evaluated on the basis of the base peak.



Scheme 1

Table 6 Relative intensities of ions $[acac + 2H]^+$ and $[MeC(O)CRC(O)Me + 2H]^+$ in the ion-trap mass spectra of complexes $[Co(acac)\{MeC(O)CRC(O)Me\}_2]$ **5h**–**5m***

	Relative intensity (%)					
Ion	R = Cl	Br	NO_2	SCN	Me	Et
$[acac + 2H]^+$	83	83	90	100	85	100
$[MeC(O)CRC(O)Me + 2H]^+$	100	100	0	0	100	90

* The spectra were obtained under chemical ionization conditions by using methane as reactant gas, operating at 0.05 Torr (total pressure); the relative intensities have been evaluated on the basis of the base peak.

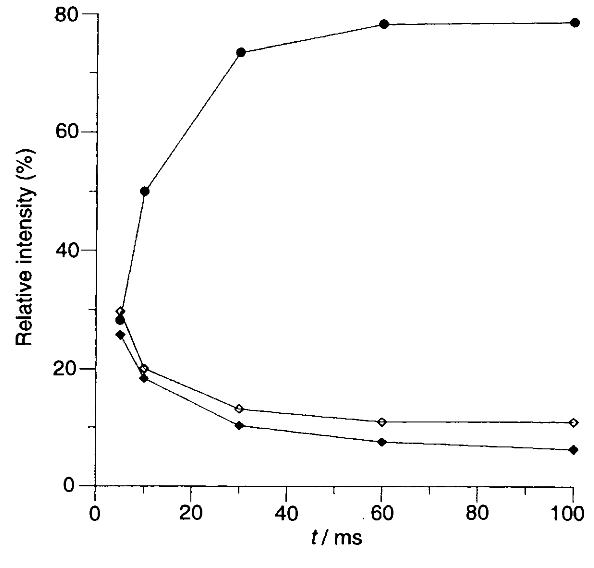
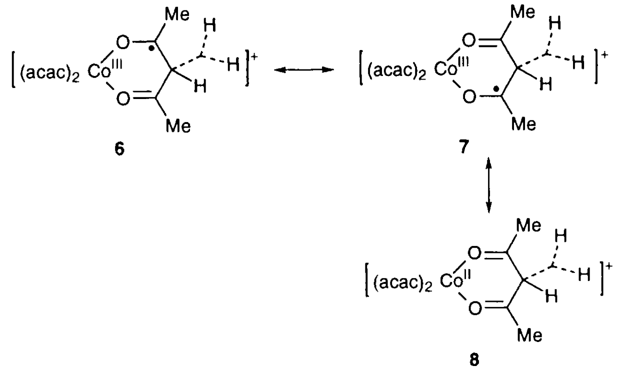
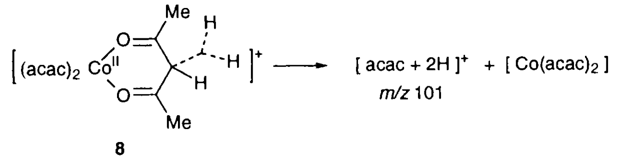


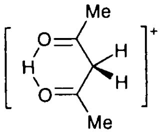
Fig. 2 Variation of relative intensity of ions as a function of reaction time for the reaction of $[Co(acac)_3]$ with $[C_4H_9]^+$: (●) $[acac + 2H]^+$ (*m*/*z* 101), (◆) $[Co(acac)_2]$ (*m*/*z* 257) and (◇) $[Co(acac)_2 + H]^+$ (*m*/*z* 258)



Scheme 2



Scheme 3



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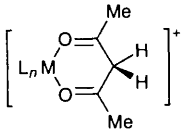


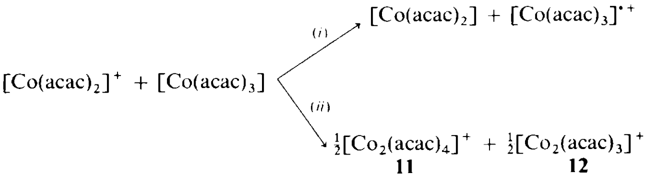
10

ITMS Study of the reaction of $[Co(acac)_2]^+$ with complexes 5a–5g

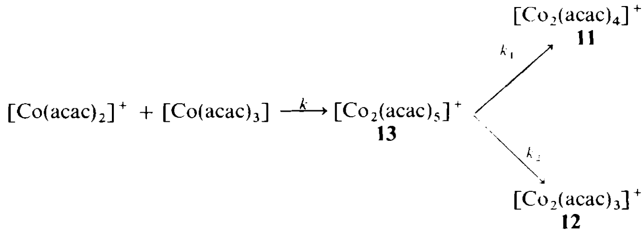
As pointed out in the Introduction, the solution-phase reaction of the ion $[Co(\beta\text{-dik})_2]^+$ with neutral $[Co(\beta\text{-dik})_3]$ has been hypothesized to give rise to radical species and to cobalt(II) derivatives through an intermolecular electron-transfer process [equation (2)]. With the aim of obtaining further evidence for this hypothesis and an insight into the reaction mechanism we started an ITMS study of the gas-phase reaction between $[Co(acac)_2]^+$ with $[Co(acac)_3]^+$. Two reactions were observed, *i.e.* a charge-exchange reaction leading to the formation of the radical cation $[Co(acac)_3]^{\cdot +}$ and a dimerization reaction resulting in the formation of two bimetallic ions, *i.e.* **11** (*m/z* 514) and **12** (*m/z* 415) (Scheme 4).

The charge-transfer reaction is observed only when operating at a rather low buffer gas (He) pressure (10^{-5} Torr) and heating $[Co(acac)_3]$ at 100 °C so as to increase its pressure in the ion trap. This reaction leads to poor product yields when compared with those observed in the dimerization reaction. Under these conditions, however, the high ion concentration in the ion trap prevents an accurate study of the reaction, probably as a consequence of saturation effects. The effect of space charge is in fact a very important consideration in ion-trap operations since it limits the ion concentration which may be achieved. Furthermore, space charge-induced distortion of the stability diagram may occur.[18] Although owing to these reasons a further study of the charge-exchange reaction was precluded, it must be pointed out that the low reaction product yields are most probably due to kinetic factors since the recombination energy of the ion $[Co(acac)_2]^+$ (8.5 eV)[19] is higher than the ionization energy of $[Co(acac)_3]$ (7.8 eV).[20]

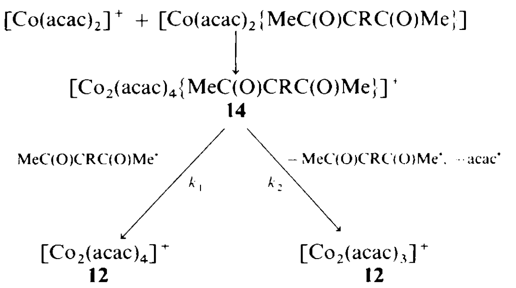
As for the dimerization reaction, the ions produced by complex **5a** on electron impact were allowed to cool for 10 ms; then the ion $[Co(acac)_2]^+$ was isolated and allowed to react with **5a** for a time as long as 900 ms. Two facts give preliminary information on the reaction mechanism: (*a*) when $[Co_2(acac)_4]^+$ **11** and $[Co_2(acac)_3]^+$ **12**, which were formed after 500 ms, were isolated in the ion trap, they were kinetically stable for at least 1000 ms, the mass spectrum showing no other peaks than those at *m/z* 514 (due to **11**) and 415 (due to **12**); (*b*) the buffer gas pressure does markedly influence the **11** : **12** ratio which varies from 20 to 1 : 1 on varying the gas pressure from 5×10^{-5} to 1×10^{-5} Torr. It is important to underline that the rate of disappearance of the precursor ion $[Co(acac)_2]^+$ is not influenced by the buffer gas pressure. These observations are suggestive of the mechanistic path outlined in Scheme 5, where the hypothesized reaction intermediate $[Co_2(acac)_5]^+$ **13**, which was not detected in the course of this study but was recognized by McDonald and Shannon[10a] in the electron-impact mass spectrum of $[Co(acac)_3]$, is assumed to decompose rapidly to **11** and **12** through two parallel reactions. According to the above data, the chemoselectivity of the decomposition reaction of **13** should be influenced by the internal energy of the reactant, the formation of $[Co_2(acac)_4]^+$ **11** being favoured under those experimental conditions which lower the internal energy of **13**, *i.e.* relatively high buffer gas pressure.



Scheme 4 (*i*) Charge exchange reaction; (*ii*) dimerization reaction



Scheme 5



Scheme 6

Interestingly, the ions **11** and **12** are the only bimetallic ions which are formed also when $[Co(acac)_2]^+$ is treated with a variety of heteroleptic complexes of formula $[Co\{MeC(O)CR'C(O)Me\}_2\{MeC(O)Cr_2C(O)Me\}]$, and with the aim of finding a possible role for the substituent R in influencing the reaction kinetics a detailed comparative kinetic study of the reaction of $[Co(acac)_2]^+$ with the complexes $[Co(acac)_2\{MeC(O)CR^2C(O)Me\}]$ **5a–5g** (R^2 = H, Cl, Br, NO_2, SCN, Me or Et) was carried out. In all cases, good pseudo-first-order plots were obtained for the decay of $[Co(acac)_2]^+$ which allowed us to compute the corresponding k_{obs} (see Fig. 3 for the reaction with **5f**). Moreover, the pseudo-first-order rate constants k_1 and k_2 (Scheme 6) can be obtained from plots of ion relative intensity *vs.* $[1 - \exp(k_{obs}t)]$ (see Fig. 4 for the reaction with **5f**). Since the apparatus employed in this study does not allow one to measure the sample pressure with high accuracy, the pseudo-first-order rate constants for the $[Co(acac)_2]^+$ decay were normalized to total ionic current and are reported as k_{rel} in Table 7, together with k_{obs} and the k_1/k_2 ratios. The data show

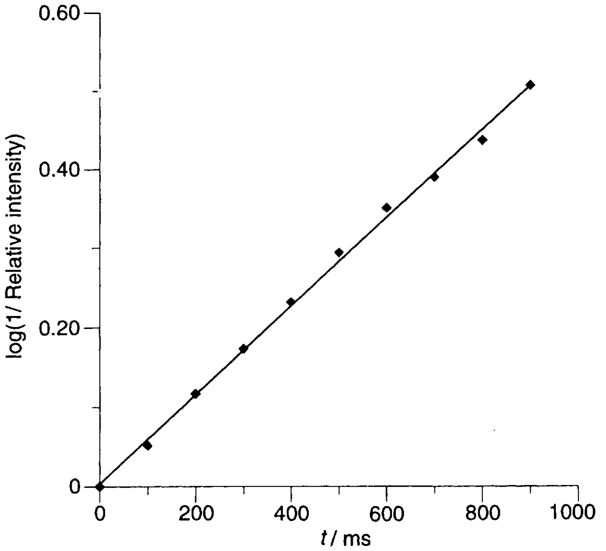


Fig. 3 Reaction of $[Co(acac)_2]^+$ (*m/z* 257) with complex **5f**: $k_{obs} = 5.59 \times 10^{-4} \pm 1.20 \times 10^{-6}$ ms^{-1}; correlation coefficient 0.998

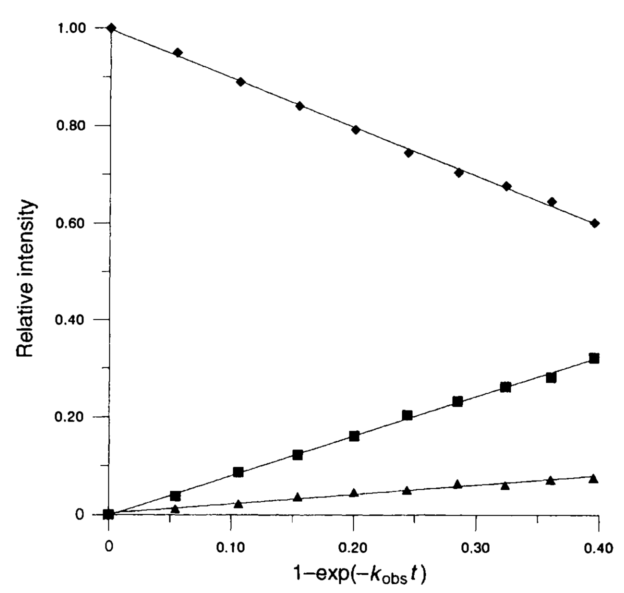


Fig. 4 Reaction of $[Co(acac)_2]^+$ with complex **5f**: variation of the relative intensities of the ions $[Co(acac)_2]^+$ (*m/z* 257) (◆), $[Co_2(acac)_3]^+$ (*m/z* 415) (▲), and $[Co_2(acac)_4]^+$ (*m/z* 514) (■)

clearly that the nature of the substituent R has no definite influence on rate constants, which could imply that the reactant ion $[Co(acac)_2]^+$ does not interact with the substituent R nor with the π-electron system of the R-substituted β-ketoenolate ring of the neutral complex [Co(acac)$_2${MeC(O)CRC(O)Me}]. Instead, the experimental data point to an attack of the ion $[Co(acac)_2]^+$ on one of the unsubstituted β-ketoenolate rings thus giving rise to the hypothesized intermediate **14** (Scheme 6), the subsequent selective fragmentation which can be understood on the basis of the assumption that the R-substituted β-ketoenolyl radicals MeC(O)CRC(O)Me˙ should be more stabilized than are the acetylacetonyl radicals (acac˙) either by inductive or by mesomeric effects exerted by the substituents R.

Table 7 Kinetic parameters of the reactions of $[Co(acac)_2]^+$ with the complexes [Co(acac)$_2${MeC(O)CRC(O)Me}] **5a**–**5g**

Reactant	R	k_{obs}/s^{-1}	k_{rel}*	k_1/k_2
5a	H	0.32	1.00	10
5b	Cl	0.38	1.02	5
5c	Br	0.27	0.89	5
5d	NO_2	0.29	0.87	8
5e	SCN	0.29	0.98	7
5f	Me	0.56	0.96	4
5g	Et	0.42	1.00	5

* k'_{obs} (for a given reaction)/k'_{obs} {for the reaction of $[Co(acac)_2]^+$ with $[Co(acac)_3]$}; where each k'_{obs} is given by the ratio of k_{obs} to the total ion current.

Conclusion

Comparison of the reported data concerning the gas-phase reaction of tris(pentane-2,4-dionato)cobalt(III) with Brønsted acids with those for the corresponding reaction in solution[3] show interestingly some common points: (*a*) protonation of the starting cobalt(III) complex and the formation of a species which can be schematized as $[Co(acac)_3 + H]^+$; (*b*) the significant formation of the ion $[Co(acac)_2]^+$; (*c*) the charge-transfer reaction between $[Co(acac)_2]^+$ and $[Co(acac)_3]$ which results in the formation of the cation radical $[Co(acac)_3]^{\cdot +}$. Two important differences are the observation of products deriving from the $[H_2]^+$ transfer from various Brønsted acids to the starting complex, $[Co(acac)_3]$, and the formation of the bimetallic ions $[Co_2(acac)_4]^+$ and $[Co_2(acac)_3]^+$ from the gas-phase reaction of $[Co(acac)_2]^+$ with the complexes [Co(acac)$_2${MeC(O)CRC(O)Me}].

The kinetic study of this last reaction allows one to get an insight into the reaction mechanism according to which the bimetallic ions could be derived from a common intermediate, $[Co_2(acac)_5]^+$, through two parallel fragmentation reactions. McDonald and Shannon[10a] detected the ions $[Co_2(acac)_4]^+$, $[Co_2(acac)_3]^+$, and $[Co_2(acac)_5]^+$ in the electron-impact mass spectrum of $[Co(acac)_3]$ in 1966, but they left the question on the origin of these ions unanswered. We are now strongly inclined to suggest that the reaction path discussed here could be operative also in the case of the reaction in the condensed phase, this being also in accordance with Schildcrout's findings.[21]

Experimental

Materials

Tris(pentane-2,4-dionato)cobalt(III) **5a**,[22] tris(heptadeuterio-pentane-2,4-dionato)cobalt(III),[22,23] tris(3-ethyl-,[2] tris(3-bromo-[24] and tris(3-chloro-pentane-2,4-dionato)cobalt(III),[24] (3-chloropentane-2,4-dionato)- **5b**,[24] (3-bromopentane-2,4-dionato)- **5c**[24] and (3-nitropentane-2,4-dionato)-(pentane-2,4-dionato)cobalt(III) **5d**,[2] bis(3-chloropentane-2,4-dionato)- **5h**,[24] bis(3-bromopentane-2,4-dionato)- **5i**[24] and bis(3-nitropentane-2,4-dionato)-(pentane-2,4-dionato)cobalt(III) **5j**,[3] tris-(3-nitropentane-2,4-dionato)-,[25] tris(3-thiocyanopentane-2,4-dionato)-[5] and tris(3-methylpentane-2,4-dionato)-cobalt(III)[26] were prepared according to published procedures.

Spectroscopic and analytical measurements

Proton NMR spectra were run at 200 MHz on a Varian Gemini instrument, electron-impact mass spectra on VG Analytical 7070E and Varian MAT 112S apparatus and CI mass spectra using either a Varian MAT 112S or a Finnigan ITMS™ instrument. Gas-phase kinetic studies of ion–molecule reactions were carried out with the latter. Samples were introduced *via* a direct-inlet probe. The ion-source temperature was 150 °C and the electron energy was 70 eV. Microanalyses were performed by the Laboratorio di Microanalisi dell'Istituto di Chimica Organica della Facoltà di Farmacia dell'Università di Pisa.

Preparations

Bis(pentane-2,4-dionato)(3-thiocyanatopentane-2,4-dionato)-5e and (pentane-2,4-dionato)bis(3-thiocyanatopentane-2,4-dionato)-cobalt(III) 5h. Both complexes were obtained by functionalization of tris(pentane-2,4-dionato)cobalt(III) (0.53 g, 1.5 mmol) with a mixture of Pb(SCN)$_2$ and Br$_2$, according to the literature procedure[5] for the preparation of tris(3-thiocyanoatopentane-2,4-dionato)cobalt(III), but using a Pb(SCN)$_2$ to [(Co(acac)$_3$] molar ratio of 1.5 instead of 3 : 1. The reaction mixture was first chromatographed over a column (outside diameter, 20 mm; length, 400 mm) packed with silica gel 60 (230–400 mesh) (Merck), using dichloromethane–benzene–ethyl acetate (6 : 3 : 1 v/v) as eluent. From the first band eluted 220 mg of microcrystalline complex **5e** (0.55 mmol, 36%) were obtained, m.p. 164–165 °C (Found: C, 46.4; H, 4.9; N, 3.4; S, 8.0. $C_{16}H_{20}CoNO_6S$ requires C, 46.5; H, 4.9; N, 3.4; S, 7.8%). ^{1}H NMR (200 MHz, solvent CDCl$_3$, standard SiMe$_4$): δ 2.17 (6 H, s, 2 CH$_3$), 2.23 (6 H, s, 2 CH$_3$), 2.60 (6 H, s, 2 CH$_3$) and 5.55 (2 H, s, 2 H). The second band was further chromatographed over a similar column using dichloromethane–benzene–ethyl acetate (25 : 3 : 1 v/v) as eluent. From the first band eluted a small amount of tris(3-thiocyanatopentane-2,4-dionato)cobalt(III) was obtained, while the second furnished 130 mg of complex **5k** (0.28 mmol, 19%), m.p (decomp.) 160–161 °C (Found: C, 43.5; H, 4.1; N, 6.2; S, 14.0. $C_{17}H_{19}CoN_2O_6S_2$ requires C, 43.4; H, 4.1; N, 6.0; S, 13.6%). ^{1}H NMR: δ 2.23 (6 H, s, 2 CH$_3$), 2.60 (6 H, s, 2 CH$_3$), 2.67 (6 H, s, 2 CH$_3$) and 5.58 (1 H, s, 1 H).

(3-Methylpentane-2,4-dionato)bis(pentane-2,4-dionato)-cobalt(III) 5f. *Method A.* 35% Hydrogen peroxide (0.6 cm^3) and then 3-methylpentane-2,4-dione (160 mg, 1.4 mmol) were added to a stirred mixture of bis(pentane-2,4-dionato)cobalt(II) (350 mg, 1.36 mmol) and absolute ethanol (20 cm^3). The resulting mixture was kept at room temperature for 30 min and then filtered. The solution was evaporated to dryness under reduced pressure and the residue dissolved in dichloromethane–ethyl acetate (1 : 1, 3 cm^3) and then chromatographed over a column (outside diameter, 20 mm; length, 250 mm) packed with silica gel 60 (230–400 mesh) (Merck), using dichloromethane–ethyl acetate (1 : 1 v/v) as eluent. From the first band eluted 35 mg of microcrystalline complex **5f** (0.26 mmol, 19%) were obtained (Found: C, 52.0; H, 6.3. $C_{16}H_{23}CoO_6$ requires C, 51.90; H, 6.25%). ^{1}H NMR: δ 1.91 (3 H, s, 1 CH$_3$), 2.13 (6 H, s, 2 CH$_3$), 2.16 (6 H, s, 2 CH$_3$), 2.24 (6 H, s, 2 CH$_3$) and 5.49 (2 H, s, 2 H).

Method B. A mixture of tris(3-methylpentane-2,4-dionato)-cobalt(III) (199 mg, 0.5 mmol), pentane-2,4-dione (0.10 cm^3, 1 mmol) and dichloromethane (6 cm^3) was stirred at 90 °C for 21 h in a Carius tube (capacity, 25 cm^3). The solution was then chromatographed over a column (outside diameter, 20 mm; length, 300 mm) packed with silica gel 60 (230–400 mesh) (Merck), using dichloromethane–ethyl acetate (1 : 1 v/v) as eluent. From the first band eluted 145 mg of microcrystalline complex **5f** (0.39 mmol, 78%) were obtained.

(3-Ethylpentane-2,4-dionato)bis(pentane-2,4-dionato)-cobalt(III) 5g. *Method A.* 35% Hydrogen peroxide (0.6 cm^3) and 3-methylpentane-2,4-dione (0.2 cm^3, 1.4 mmol) were added to a stirred mixture of [Co(acac)$_2$] (350 mg, 1.36 mmol) and absolute ethanol (20 cm^3). The resulting mixture was kept at room temperature for 30 min and then filtered. The solution was evaporated to dryness under reduced pressure and the residue dissolved in dichloromethane–ethyl acetate (1 : 1, 3 cm^3) and then chromatographed over a column (outside diameter, 20 mm; length, 250 mm) packed with silica gel 60 (230–400 mesh) (Merck), using dichloromethane–ethyl acetate (1 : 1 v/v) as eluent. From the first band eluted 80 mg of microcrystalline complex **5g** (0.47 mmol, 34%) were obtained (Found: C, 53.2; H, 6.6. $C_{17}H_{25}CoO_6$ requires C, 53.15; H, 6.55%). ^{1}H NMR: δ 1.00 (3 H, t, J = 7.3 CH$_3$), 2.13 (6 H, s, 2 CH$_3$), 2.16 (6 H, s, 2 CH$_3$), 2.26 (6 H, s, 2 CH$_3$), 2.29 (2 H, q, J = 7.3 Hz, CH$_2$) and 5.50 (2 H, s, 2 H).

Method B. A mixture of tris(3-ethylpentane-2,4-dionato)-cobalt(III) (65 mg, 0.15 mmol), pentane-2,4-dione (0.03 cm^3, 0.3 mmol) and dichloromethane (3 cm^3) was stirred at 90 °C for 21 h in a Carius tube (capacity, 25 cm^3). The resulting green solution was chromatographed over a column (outside diameter, 20 mm; length, 300 mm) packed with silica gel 60 (230–400 mesh) (Merck), using dichloromethane–ethyl acetate (1 : 1 v/v) as eluent. From the first band eluted 46 mg of microcrystalline complex **5g** (0.12 mmol, 81%) were obtained.

Bis(3-methylpentane-2,4-dionato)(pentane-2,4-dionato)-cobalt(III) 5l. Starting from a mixture of tris(3-methylpentane-2,4-dionato)cobalt(III) (199 mg, 0.5 mmol), pentane-2,4-dione (0.05 cm^3, 0.5 mmol) and dichloromethane (6 cm^3), 150 mg of complex **5l** (0.39 mmol, 78%) were obtained following the procedure described above (Found: C, 53.1; H, 6.6. $C_{17}H_{25}CoO_6$ requires C, 53.15; H, 6.55%). ^{1}H NMR: δ 1.91 (6 H, s, 2 CH$_3$), 2.13 (6 H, s, 2 CH$_3$), 2.15 (6 H, s, 2 CH$_3$), 2.23 (6 H, s, 2 CH$_3$) and 5.49 (1 H, s, 1 H).

Bis(3-ethylpentane-2,4-dionato)(pentane-2,4-dionato)-cobalt(III) 5m. Following the same experimental procedure adopted for the preparation of complex **5l**, but starting from a mixture of tris(3-ethylpentane-2,4-dionato)cobalt(III) (220 mg, 0.5 mmol), pentane-2,4-dione (0.05 cm^3, 0.5 mmol) and dichloromethane (5 cm^3), 148 mg of complex **5m** (0.36 mmol, 72%) were obtained (Found: C, 55.3; H, 7.1. $C_{19}H_{29}CoO_6$ requires C, 55.35; H, 7.10%). ^{1}H NMR: δ 1.00 (6 H, t, 2 CH$_3$), 2.13 (6 H, s, 2 CH$_3$), 2.16 (6 H, s, 2 CH$_3$), 2.26 (6 H, s, 2 CH$_3$), 2.28 (4 H, q, 2 CH$_2$) and 5.49 (1 H, s, 1 H).

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