Synthesis and characterization of diphenyl-2-thienylphosphine derivatives of di- and tricobalt carbonyl complexes[1]

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Abstract

The reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ with the ligand diphenyl-2-thienylphosphine, $PPh_2(C_4H_3S)$, yields the complexes $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (**1**) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (**2**). The related complex $[Co_3(\mu_3CMe)(CO)_9]$ reacts with the same ligand to give $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (**3**) and $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (**4**). Thermolysis of **1** at 80°C leads to partial conversion of **1** into **2**, which is isolated in low yield. Similarly, thermolysis of **3** at 70°C results in partial conversion of **3** to **4**. Coordination of the thienyl unit of the diphenyl-2-thienylphosphine ligand to cobalt could not be detected in these thermolyses. Complexes **1**–**4** have been completely characterized and the crystal structure of complex **4** has been determined. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Cobalt; Carbonyl; Polyfunctional phosphine; Crystal structure

1. Introduction

There is sustained interest in the investigation of the organometallic chemistry of thiophenes [1–3] with the aim of elucidating the mechanisms of commercial catalytic hydrodesulfurization reactions [1–4]. Thiophenes themselves are relatively poor ligands for transition metals and, in an attempt to circumvent this limitation, the ligand diphenyl-2-thienylphosphine [5] has been employed as a means of introducing the thiophene group into a transition metal complex. Some complexes have been synthesized in which this ligand acts as a simple tertiary phosphine [6,7], donating via the phosphorus atom only, but it has recently been demonstrated that diphenyl-2-thienylphosphine can also act as a bidentate ligand, coordinating to rhenium through both the phosphorus and sulfur atoms in the complex $[Re_2(CO)_8\{\mu\text{-}PPh_2(C_4H_3S)\}]$ [8]. Furthermore, reaction with $[Ru_3(CO)_{12}]$ results in C–H bond cleavage and bimetallic products are isolated in which the thiophene moiety of the ligand forms a σ, η^2-vinyl type bridge between two metal atoms with phosphorus coordinating to the third center [8]. Thermolysis of these complexes can effect P–C bond scission, leaving the C_4H_2S residue coordinated as a μ_4-thiophyne ligand [8].

We are interested in the preparation of new polynuclear molybdenum, ruthenium, osmium, cobalt, rhodium, iridium and mixed-metal complexes containing thiophene ligands. Our aim is to establish possible coordination modes of thiophene and its derivatives in complexes containing several metal atoms, and to correlate the structures and reactivities of such complexes to intermediates and mechanisms of hydrodesulfurization processes. Here we report the preparation of new cobalt clusters into which thiophene has been introduced via the agency of the diphenyl-2-thienylphosphine ligand. Thiophene-containing cobalt complexes

are of particular interest since cobalt is currently employed as a promoter [4,9] in the molybdenum-catalyzed hydrodesulfurization of petroleum feedstocks.

2. Results and discussion

2.1. Reaction of [Co₂{μ-C₂(CO₂Me)₂}(CO)₆] with PPh₂(C₄H₃S)

The thermal reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ with an excess of $PPh_2(C_4H_3S)$ in toluene led to the formation of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (1) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (2) in a 24 and 40% yield, respectively. Both complexes have been characterized by IR, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, mass spectrometry and microanalysis. The FAB mass spectra and microanalytical data are in agreement with the proposed formulae, as are the IR data which are in accord with those collected for other mono- and bis-substituted alkyne dicobalt carbonyl complexes [10]. In the ^{13}C-NMR spectrum of 1, resonances at δ 203.9 and δ 199.3 with intensities in the approximate ratio 2:3 are assigned to the carbon atoms of the CO groups on the substituted and unsubstituted cobalt atoms, respectively. (Fig. 1a) indicates that the $Co(CO)_3$ group of 1 should give rise to separate resonances for axial and equatorial carbonyl ligands if the static structure is maintained in solution. The ^{13}C-NMR data suggest, however, that in solution at 293 K a fluxional process occurs which renders all the carbonyl ligands at a given metal center equivalent

on the NMR timescale. Mechanisms involving localized site exchange [11] or metal fragment reorientation [12] have been discussed previously for such complexes and the findings here are consistent with either proposal. As may be expected, only one resonance was detected for the CO ligands in the ^{13}C-NMR spectrum of 2.

2.2. Reaction of [Co₃(μ₃-CMe)(CO)₉] with PPh₂(C₄H₃S)

Mild heating of $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ in the presence of an excess of $PPh_2(C_4H_3S)$ gave $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3) and $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (4) in a 23 and 32% yield, respectively. The FAB mass spectrometric and microanalytical data are consistent with the suggested formulae and the IR spectra of 3 and 4 are typical of alkylidyne tricobalt carbonyl complexes with one and two phosphine (or phosphite) ligands, respectively [13]. The carbon atoms of the CO groups in 3 give rise to a single, broad peak in the ^{13}C-NMR spectrum at δ 204.1, which remains even when the spectrum is recorded at 183 K. A low-energy fluxional process clearly operates to render all the carbonyl ligands equivalent. Such a process requires exchange of carbonyls between axial and equatorial positions and between cobalt atoms.

The static structure of 4 (Fig. 1b) indicates that all carbonyl ligands are inequivalent but only two signals are observed in the ^{13}C-NMR spectrum of this complex. The two resonances appear at δ 210.2 and δ 204.0 with intensities in the approximate ratio 4:3. This result is consistent with a fluxional process featuring localized exchange of axial and equatorial carbonyls but not delocalized exchange of carbonyls between cobalt atoms. On the basis of the integration of the signals, the upfield resonance is assigned to the carbonyl ligands at the unsubstituted cobalt atom and the resonance that occurs at lower field is thus attributed to the carbonyls of the substituted cobalt centres.

2.3. The molecular structure of [Co₃(μ₃-CMe)(CO)₇ {PPh₂(C₄H₃S)}₂] (4)

It was possible to grow crystals of 4 suitable for X-ray diffraction experiments and the crystal structure was determined in order to confirm the proposed structure. The molecular structure of $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (4) is shown in Fig. 2; it corresponds to the expected static structure depicted in (Fig. 1b). Relevant bond lengths and angles are reported in Table 1 and fractional coordinates for all non-hydrogen atoms are listed in Table 2. The cluster core consists of an almost equilateral Co_3 triangle capped by the μ_3-ethylidyne moiety. The two diphenyl-2-thienylphosphine ligands are coordinated in equatorial positions on Co(1) and Co(2), *trans* to metal–metal

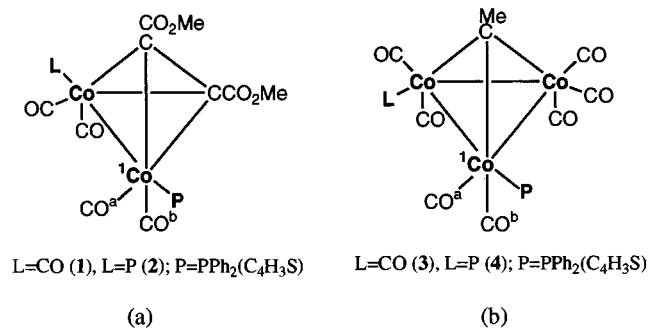Fig. 1. (a) Proposed static molecular structures of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (1) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (2). In 1, a fluxional process involving localised site exchange [11] or non-dissociative reorientation about Co(1) [12] will render carbonyls a and b equivalent. (b) Proposed static molecular structures of $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3) and $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (4). In 3, carbonyls a and b may be rendered equivalent by dissociative localised site exchange or non-dissociative reorientation about Co(1). In 4, the same carbonyls can be rendered equivalent by dissociative localised site exchange but not by non-dissociative reorientation about Co(1).
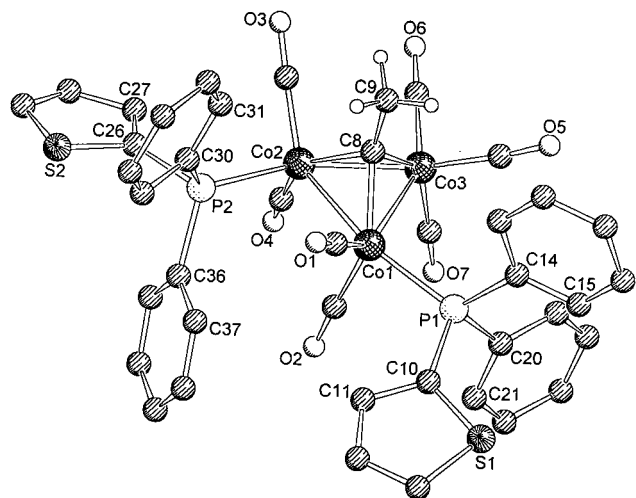
Fig. 2. A SCHAKAL [16] drawing of the molecular structure of [Co$_3$(μ_3-CMe)(CO)$_7${PPh$_2$(C$_4$H$_3$S)}$_2$] (**4**) in the solid state, showing the atom numbering scheme. The hydrogens of the phenyl and thienyl rings have been omitted for clarity.

bonds, as has previously been found in the related complex [Co$_3$(μ_3-CMe)(CO)$_7${P(OPh)$_3$}$_2$] [14]. The cobalt atoms complete their pseudo-octahedral coordination spheres with three [Co(3)] or two terminal carbonyl ligands. The Co–Co bond lengths fall in a narrow range (Co(1)–Co(2) = 2.484, Co(1)–Co(3) = 2.488 and Co(2)–Co(3) = 2.480(1) Å, Co–Co$_{ave}$ = 2.484 Å) and are comparable to those found in [Co$_3$(μ_3-CMe)(CO)$_7${P(OPh)$_3$}$_2$] (Co–Co$_{ave}$ = 2.488 Å) [14] and

Table 1
Selected bond lengths (Å) and angles (°) for [Co$_3$(μ_3-CMe)(CO)$_7${PPh$_2$(C$_4$H$_3$S)}$_2$] · 0.5C$_6$H$_{14}$ · H$_2$O (**4**)

Bond length (Å)

Co(1)–Co(2)	2.484(2)	Co(1)–C(8)	1.891(7)
Co(1)–Co(3)	2.488(2)	Co(2)–C(8)	1.927(6)
Co(2)–Co(3)	2.480(1)	Co(3)–C(8)	1.910(7)
Co(1)–P(1)	2.207(2)	C(8)–C(9)	1.495(9)
Co(2)–P(2)	2.217(2)	P(1)–C(20)	1.835(4)
P(1)–C(14)	1.846(4)	P(1)–C(10)	1.816(7)
C(10)–S(1)	1.682(7)	C(12)–C(13)	1.38(1)
S(1)–C(13)	1.75(1)	C(12)–C(11)	1.38(1)
C(10)–C(11)	1.397(9)	P(2)–C(30)	1.833(7)
P(2)–C(36)	1.850(4)	P(2)–C(26)	1.800(9)
C(26)–S(2)	1.69(1)	S(2)–C(29)	1.73(2)
C(29)–C(28)	1.34(2)	C(27)–C(28)	1.41(2)
C(26)–C(27)	1.49(2)	Co(1)–C(1)	1.778(8)
C(1)–O(1)	1.125(8)	Co(1)–C(2)	1.804(7)
C(2)–O(2)	1.142(7)	Co(2)–C(3)	1.750(7)
C(3)–O(3)	1.135(8)	Co(2)–C(4)	1.808(7)
C(4)–O(4)	1.122(8)	Co(3)–C(5)	1.780(7)
C(5)–O(5)	1.127(8)	Co(3)–C(6)	1.770(8)
C(6)–O(6)	1.126(9)	Co(3)–C(7)	1.830(8)
C(7)–O(7)	1.128(8)		

Bond angle (°)

Co(3)–Co(1)–P(1)	101.90(8)	Co(1)–Co(2)–P(2)	99.43(6)
P(1)–Co(1)–C(1)	94.5(2)	P(2)–Co(2)–C(3)	96.1(2)

Table 2
Fractional atomic coordinates ($\times 10^4$) for [Co$_3$(μ_3-CMe)(CO)$_7${PPh$_2$(C$_4$H$_3$S)}$_2$] · 0.5C$_6$H$_{14}$ · H$_2$O (**4**)

	x	y	z
Co (1)	1607 (1)	2629 (1)	7420 (1)
Co (2)	−441 (1)	2530 (1)	6935 (1)
Co (3)	−254 (1)	578 (1)	6924 (1)
P (1)	3007 (2)	2079 (2)	7857 (1)
P (2)	112 (2)	4550 (2)	7103 (1)
C (8)	685 (6)	1881 (6)	6425 (4)
C (9)	1058 (7)	1754 (7)	5612 (4)
C (1)	2761 (7)	3844 (7)	7052 (4)
O (1)	3507 (5)	4579 (5)	6802 (3)
C (2)	1214 (6)	3123 (6)	8383 (4)
O (2)	985 (5)	3415 (5)	9002 (3)
C (3)	−1402 (7)	2054 (6)	6060 (4)
O (3)	−2009 (5)	1726 (5)	5484 (3)
C (4)	−1438 (6)	2350 (6)	7727 (4)
O (4)	−2054 (5)	2189 (5)	8218 (3)
C (5)	518 (7)	−376 (6)	6529 (4)
O (5)	975 (5)	−989 (5)	6240 (3)
C (6)	−1766 (8)	−336 (7)	6387 (5)
O (6)	−2714 (6)	−918 (6)	6030 (4)
C (7)	−598 (7)	359 (6)	7903 (4)
O (7)	−801 (6)	248 (6)	8512 (3)
S (1)	5624 (3)	3317 (3)	8833 (2)
C (10)	4356 (6)	3405 (6)	8448 (4)
C (11)	4500 (7)	4632 (6)	8655 (4)
C (12)	5620 (9)	5456 (8)	9109 (5)
C (13)	6404 (9)	4918 (12)	9259 (5)
C (14)	3822 (4)	1393 (4)	7140 (2)
C (15)	4484 (5)	763 (5)	7339 (3)
C (16)	5168 (5)	345 (5)	6798 (4)
C (17)	5190 (5)	557 (5)	6057 (3)
C (18)	4528 (5)	1186 (5)	5858 (2)
C (19)	3844 (5)	1604 (4)	6400 (2)
C (20)	2415 (4)	1030 (4)	8513 (2)
C (21)	2334 (5)	1534 (3)	9284 (2)
C (22)	1776 (5)	755 (4)	9778 (2)
C (23)	1299 (5)	−529 (4)	9501 (3)
C (24)	1380 (5)	−1033 (3)	8730 (3)
C (25)	1938 (5)	−254 (4)	8236 (2)
C (36)	787 (4)	5477 (4)	8104 (2)
C (37)	2088 (4)	6004 (5)	8328 (3)
C (38)	2546 (5)	6581 (5)	9104 (3)
C (39)	1704 (7)	6631 (5)	9655 (2)
C (40)	403 (6)	6104 (5)	9431 (3)
C (41)	−56 (4)	5527 (4)	8655 (3)
C (26)	−1238 (9)	4855 (9)	6936 (6)
C (27)	−2628 (13)	4025 (12)	6884 (7)
C (28)	−3326 (14)	4720 (13)	6850 (8)
C (29)	−2636 (19)	5915 (19)	6838 (11)
S (2)	−1018 (6)	6303 (6)	6906 (4)
C (30)	1138 (9)	5304 (8)	6404 (5)
C (31)	1110 (9)	4626 (6)	5657 (5)
C (32)	1876 (9)	5218 (7)	5130 (4)
C (33)	2670 (9)	6487 (7)	5350 (5)
C (34)	2698 (9)	7165 (6)	6097 (5)
C (35)	1932 (10)	6573 (8)	6624 (4)
C (411)	−1179 (10)	5096 (11)	7111 (8)
C (421)	−2430 (11)	4191 (8)	7032 (7)
C (431)	−3434 (8)	4516 (10)	6987 (8)
C (441)	−3185 (9)	5745 (11)	7022 (8)
C (451)	−1934 (11)	6650 (8)	7102 (7)
C (461)	−930 (8)	6326 (10)	7146 (8)

Table 2 *(Continued)*

	x	y	z
C (452)	1203 (9)	5385 (7)	6471 (5)
C (462)	1150 (10)	4914 (7)	5680 (5)
C (472)	2021 (12)	5808 (10)	5319 (4)
C (482)	2717 (10)	6886 (9)	5813 (4)
S (3)	2359 (6)	6905 (6)	6741 (4)
C (42)	4899 (22)	71 (21)	386 (11)
C (43)	4338 (19)	558 (19)	1114 (13)
C (44)	4251 (26)	1577 (24)	1790 (15)
O (8)	4360 (11)	3727 (8)	4899 (8)

the parent cluster $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ $(Co\text{-}Co_{ave} = 2.468(5)$ Å) [15]. The triply bridging ethylidyne carbon is virtually equidistant from the three cobalt atoms $(Co(1)\text{-}C(8) = 1.891(7)$, $Co(2)\text{-}C(8) = 1.927(6)$, $Co(3)\text{-}C(8) = 1.910(7)$, $Co\text{-}C(8)_{ave}$ 1.909 Å), which is analogous to what is found in the aforementioned $[Co_3(\mu_3\text{-}CMe)(CO)_7\{P(OPh)_3\}_2]$ $(Co\text{-}C(Me)_{ave}$ 1.907 Å). The methyl hydrogen atoms are staggered with respect to the Co_3 plane. The Co–P interactions $(Co(1)\text{-}P(1) = 2.207(2)$, $Co(2)\text{-}P(2) = 2.217(2)$ Å) are normal and slightly longer than those reported for $[Co_3(\mu_3\text{-}CMe)(CO)_7\{P(OPh)_3\}_2]$ $(2.137$ and $2.141(2)$ Å) [14].

The arrangement of the phosphine substituents in the diphenyl-2-thienylphosphine ligands deserves some attention in view of the potential of the S atoms belonging to the thienyl rings to coordinate to metal centres. Both the thienyl rings are almost coplanar with the Co_3 plane; the dihedral angles between the $Co(1)\text{-}Co(2)\text{-}Co(3)$ and the C_4H_3S rings are 12.2(3) and 20.2(3)° for the rings containing S(1) and S(2), respectively. The sulfur atoms S(1) and S(2) are directed away from the Co atoms. Using the program SCHAKAL [16], various conformations of the diphenyl-2-thienylphosphine ligand were modelled. Even after a rotation of 180° around the P–C(thienyl) axes, the distances of the sulfur atoms from the closest Co atoms are 3.54 [Co(2)–S(2)] and 3.65 Å [Co(1)–S(1)]. Furthermore, there is orientational disorder between one phenyl group and the thienyl ring attached to P(2). The modelling indicated that rotation of the $PPh_2(C_4H_3S)$ cone by 180° around the Co–P axis and subsequent rotation of the thienyl group by 180° around the P–C(thienyl) axis will bring the S atom within bonding distance of the vicinal cobalt atom. The diphenyl-2-thienyl phosphine might act as a bidentate ligand through the two heteroatoms but the preferred orientation of the thienyl sulfur inside the phosphine cone prevents its coordination to a metal centre, as has also been found in $[Ru_3(\mu\text{-}H)\{\mu\text{-}PPh_2(C_4H_2S)\}(CO)_8\{PPh_2(C_7H_3S)\}]$ [8].

2.4. Thermolysis of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2\text{-}(C_4H_3S)\}]$ (1) and $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3)

Thermolyses of **1** and **3** were undertaken in attempts to coordinate the thienyl moieties of the diphenyl-2-thienylphosphine ligands. Thermolysis of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (**1**) at 80°C leads to partial conversion of the starting material to the corresponding bis-substituted complex, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (**2**), which is isolated in a 9% yield. A similar conversion is observed when $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (**3**) is heated at 70°C; 70% of the starting complex is recovered along with a 13% yield of the bis-substituted derivative $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (**4**). Higher temperatures result in substantial decomposition of the complexes in both reactions. Products containing a bridging bidentate $PPh_2(C_4H_3S)$ ligand were not obtained. Compounds **1** and **3** have a fairly low thermal stability and under prolonged thermolysis, gradual decomposition of the sample is likely, releasing phosphine into the reaction mixture. Recombination of liberated phosphine with the starting complex (**1** or **3**) may then generate the bis-substituted complex. This process is expected to be facile under the conditions employed.

2.5. Reaction of 1 and 3 with BuLi and PPh_2Cl

In order to investigate the reactivity of the thienyl moiety of the coordinated ligand, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\text{-}(CO)_5\{PPh_2(C_4H_3S)\}]$ (**1**) and $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2\text{-}(C_4H_3S)\}]$ (**3**) were each reacted with ^nBuLi followed by addition of PPh_2Cl in an attempt to lithiate the thienyl group and add PPh_2 to create a diphosphine. In both cases, this reaction causes substantial conversion of the starting material to the corresponding bis-substituted complex. It is likely that, even at low temperatures, the butyl anion attacks a carbonyl ligand of the cluster(s). Initially, this leads to decomposition of the cluster, liberating $PPh_2(C_4H_3S)$. Subsequently, facile BuLi assisted CO substitution can occur on the starting material by the freed phosphine, leading to the bis-substituted complex. Products containing a $(PPh_2)_2(C_4H_2S)$ ligand were not observed.

3. Summary and conclusion

Mono- and bis-substituted diphenyl-2-thienylphosphine derivatives of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ and $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ may be prepared in reasonable yields and under mild conditions. However, attempts at coordination of the thienyl moieties of the $PPh_2(C_4H_3S)$ ligands by thermal or chemical activation of the ligands/clusters do not yield any tractable products, ex-

cept in the case of thermolysis of the mono-substituted complexes $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (**1**) or $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (**3**) which results in some disproportionation to yield the corresponding bis-substituted complexes **3** and **4** in low yield. The above-mentioned modelling based on the solid state structure of **4** indicates that the $PPh_2(C_4H_3S)$ ligands may not be predisposed to coordinate in a bridging mode. Furthermore, the relatively low thermal stability of the cobalt complexes used here appears to prevent thermal activation of the diphenyl-2-thienylphosphine. We are presently investigating the reactions of diphenyl-2-thienylphosphine and related ligands with second and third row transition metal complexes/clusters. The resultant complexes are expected to have greater thermal stability than the above-mentioned cobalt species, and thermal activation of the thienylphosphine ligands may thus be feasible.

4. Experimental

All reactions were carried out under an atmosphere of dry, oxygen free nitrogen, using solvents which were freshly distilled from appropriate drying agents. IR spectra were recorded in *n*-hexane or dichloromethane solution in 0.5 mm NaCl cells, using a Bio-Rad FTS 6000 spectrometer. Fast atom bombardment (FAB +) mass spectra were obtained on a JEOL SX-102 instrument; 3-nitrobenzyl alcohol was used as a matrix and CsI as the calibrant. NMR spectra were recorded on a Varian Unity 300 MHz spectrometer using the solvent resonance as an internal standard for the ^{1}H- and ^{13}C-NMR spectra, while H_3PO_4 was used as an external standard for the ^{31}P spectra. Microanalyses were performed by Mikrokemi AB, Uppsala, Sweden. Column chromatography was performed on Merck Kieselgel 60 (70–230 mesh ASTM); products are given in order of decreasing R_f values. The starting materials $Co_2(CO)_8$ (Strem Chemical), $C_2(CO_2Me)_2$ (Acros Organics), CH_3CCl_3 (Aldrich), PPh_2Cl (Acros) and C_4H_4S (Synthetic Chemicals) were used without further purification. The compounds $PPh_2(C_4H_3S)$, $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$, and $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ were prepared by literature methods [8,17,18].

4.1. Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ with $PPh_2(C_4H_3S)$

A sample of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_6]$ (570 mg, 1.33 mmol) and $PPh_2(C_4H_3S)$ (535 mg, 2.00 mmol) were dissolved in toluene (60 cm^3) and heated at 35°C with stirring for 29 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of dichloromethane and adsorbed onto silica. The silica was pumped dry and transferred to the

top of a silica chromatography column. Elution with hexane/acetone (7:3) gave $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}\text{-}(CO)_5\{PPh_2(C_4H_3S)\}]$ (**1**) (213 mg, 24%) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (**2**) (480 mg, 40%). Complex **1**: Anal. Found: C, 48.9%; H, 2.9%; P, 4.8%; S, 4.9%. $Co_2C_{27}H_{19}O_9PS$ Calc.: C, 48.5%; H, 2.9%; P, 4.6%; S, 4.8%. MS (m/z): 668 (M$^+$) and M$^+ - n$CO ($n = 1$–5). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2083 s, 2036 vs, 2024 sh, 1991 w. NMR (CDCl$_3$), ^{1}H, δ 7.7–7.1 (m, 13H, Ph and C$_4$H$_3$S), δ 3.38 (s, 6H, Me); ^{13}C{^{1}H}, δ 203.9 (s, 2CO), δ 199.3 (s, 3CO) δ 169.4 (s, CO_2Me), δ 137.4–128.2 (Ph, C_4H_3S), δ 72.2 (s, C–CO$_2$Me), δ 52.2 (s, CO$_2$*Me*); ^{31}P{^{1}H}, δ 40.0 (s). Complex **2**: Anal. Found: C, 55.6%; H, 3.6%; P, 7.0%; S, 7.0%. $Co_2C_{42}H_{32}O_8P_2S_2$ Calc.: C, 55.5%; H, 3.6%; P, 6.8%; S, 7.1%. MS (m/z): 880 (M$^+$–CO) and M$^+ - n$CO ($n = 2$–4). IR (CH$_2$Cl$_2$, cm^{-1}): ν(CO) 2042s, 2003 m, 1984 m. NMR (CDCl$_3$), ^{1}H, δ 7.6–7.1 (m, 26H, Ph and C$_4$H$_3$S), δ 2.80 (s, 6H, Me); ^{13}C{^{1}H}, δ 205.0 (s, CO), δ 169.4 (s, CO_2Me), δ 137.3–128.0 (Ph, C_4H_3S), δ 68.1 (s, C–CO$_2$Me), δ 51.1 (s, CO$_2$*Me*); ^{31}P{^{1}H}, δ 39.0 (s).

4.2. Reaction of $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ with $PPh_2(C_4H_3S)$

The cluster $[Co_3(\mu_3\text{-}CMe)(CO)_9]$ (470 mg, 1.03 mmol) and $PPh_2(C_4H_3S)$ (414 mg, 1.54 mmol) were dissolved in toluene (60 cm^3) and heated at 35°C with stirring for 24 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of dichloromethane and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/dichloromethane (4:1) gave $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (**3**) (165 mg, 23%) and $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (**4**) (309 mg, 32%). Crystals of **4** were grown by evaporation of a hexane/dichloromethane solution of the complex at -18°C. Complex **3**: Found: C, 45.0%; H, 2.4%; P, 4.5%; S, 4.6%. $Co_3C_{26}H_{16}O_8PS$ Calc.: C, 44.9%; H, 2.3%; P, 4.5%; S, 4.6%. MS (m/z): 640(M$^+$–2CO) and M$^+ - n$CO ($n = 3$–8). IR (*n*-hexane, cm^{-1}): ν(CO) 2078 m, 2052 w, 2034 s, 2022 s, 2014 s, 1994 w, 1989 w, 1970 w. NMR (CD$_2$Cl$_2$), ^{1}H, δ 7.7–7.2 (m, 13H, Ph and C$_4$H$_3$S), δ 3.28 (s, 3H, Me); ^{13}C{^{1}H}, δ 275.6 (s, C–Me), δ 204.1 (s, CO), δ 137.7–128.4 (*Ph*, C_4H_3S), δ 44.4 (s, *Me*); ^{31}P{^{1}H}, δ 39.1 (s). Complex **4**: Anal. Found: C, 52.3%; H, 3.3%; P, 6.6%; S, 6.8%. $Co_3C_{41}H_{29}O_7P_2S_2$ Calc.: C, 52.6%; H, 3.1%; P, 6.6%; S, 6.9%. MS (m/z): 852 (M$^+$–3CO) and M$^+ - n$CO ($n = 4$–7). IR (*n*-hexane, cm^{-1}): ν(CO) 2052 s, 2005 vs, 1997 vs, 1985 s, 1960 w. NMR (CD$_2$Cl$_2$), ^{1}H, δ 7.7–7.1 (m, 26H, Ph and C$_4$H$_3$S), δ 2.92 (s, 3H, Me). NMR (CDCl$_3$), ^{13}C{^{1}H}, δ 277.1 (s, C–Me), δ 210.2 (s, 4CO), δ 204.0 (s, 3CO), δ 137.1–128.1 (Ph, C_4H_3S), δ 42.6 (s, *Me*); ^{31}P{^{1}H}, δ 38.1 (s).

4.3. Thermolysis of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2\text{-}(C_4H_3S)\}]$ (1)

A total of 250 mg of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (0.38 mmol) was dissolved in toluene (60 cm³) and heated at 80°C with stirring for 20 h. After removal of the solvent under vacuum, the residue was dissolved in the minimum quantity of dichloromethane and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/acetone (7:3) gave $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (1) (204 mg, 82%) and $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (2) (32 mg, 9%).

4.4. Thermolysis of $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2\text{-}(C_4H_3S)\}]$ (3)

A total of 233 mg of $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (0.33 mmol) was dissolved in toluene (60 cm³) and heated at 70°C with stirring for 20 h. After removal of the reaction solvent under vacuum, the residue was dissolved in the minimum quantity of dichloromethane and adsorbed onto silica. The silica was pumped dry and transferred to the top of a silica chromatography column. Elution with hexane/dichloromethane (4:1) gave $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3) (163 mg, 70%) and $[Co_3(\mu_3CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (4) (40 mg, 13%).

4.5. Reaction of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2\text{-}(C_4H_3S)\}]$ (1) with BuLi and PPh_2Cl

The mono-substituted dicobalt complex $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (1) (655 mg, 0.98 mmol) was dissolved in THF and cooled to -78°C. Butyl lithium (613 µl 1.6 M in hexane, 0.98 mmol) was added via a syringe. The reaction mixture was allowed to warm to room temperature (r.t.). After cooling once more to -78°C, PPh$_2$Cl (176 µl, 216 mg, 0.98 mmol) was added. The mixture was allowed to warm to r.t. and was stirred at r.t. for 30 min. Thin layer chromatography of a withdrawn aliquot indicated the presence of $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_5\{PPh_2(C_4H_3S)\}]$ (1), $[Co_2\{\mu\text{-}C_2(CO_2Me)_2\}(CO)_4\{PPh_2(C_4H_3S)\}_2]$ (2) and immobile decomposition products only.

4.6. Reaction of $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3) with BuLi and PPh_2Cl

The mono-substituted tricobalt methylidyne complex $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3) (332 mg, 0.48 mmol) was dissolved in THF and cooled to -78°C. BuLi (300 µl 1.6 M in hexane, 0.48 mmol) was added via a syringe. The reaction mixture was allowed to warm to r.t. After cooling once more to -78°C,

PPh$_2$Cl (86 µl, 106 mg, 0.48 mmol) was added. The mixture was allowed to warm to r.t. and was stirred at r.t. for 30 min. Thin layer chromatography of a withdrawn aliquot indicated the presence of $[Co_3(\mu_3\text{-}CMe)(CO)_8\{PPh_2(C_4H_3S)\}]$ (3), $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2]$ (4) and immobile decomposition products only.

4.7. X-ray structure determination of $[Co_3(\mu_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2] \cdot 0.5C_6H_{14} \cdot H_2O$

Crystal data and details of the data collection for $4 \cdot 0.5C_6H_{14} \cdot H_2O$ are given in Table 3. The diffraction experiments were carried out at 193 K on a fully automated Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo$-$K$_\alpha$ radiation. The unit cell parameters were determined by a least-squares fitting procedure using 25 reflections. Data were corrected for Lorentz and polarization effects. No decay correction was necessary. An empirical absorption correction was applied using the azimuthal scan method [19]. The positions of the metal atoms were found by direct methods using the SHELXS 86 program [20] and all the non-hydrogen atoms located from Fourier-difference maps. The methyl H atoms were located in the

Table 3
Crystal data and experimental details for $[Co_3\text{-}CMe)(CO)_7\{PPh_2(C_4H_3S)\}_2] \cdot 0.5C_6H_{14} \cdot H_2O$ (4)

Empirical formula	$C_{41}H_{29}Co_3O_7P_2S_2 \cdot 0.5C_6H_{14} \cdot H_2O$
M	988.52
Temperature (K)	193(2)
Wavelength (Å)	0.71073
Crystal symmetry	Triclinic
Space group	$P\bar{1}$ (no. 2)
Unit cell dimensions	
a (Å)	00.634(9)
b (Å)	12.209(4)
c (Å)	17.718(8)
α (°)	102.75(3)
β (°)	89.69(4)
γ (°)	115.04(3)
V (Å³)	2213(2)
Z	2
$D_{calc.}$ (mg m⁻³)	1.484
μ(Mo$-$K$_\alpha$) (mm⁻¹)	1.328
$F(000)$	1000
Crystal size (mm)	$0.175 \times 0.20 \times 0.27$
θ limits (°)	2–30
Scan mode	ω
Reflections collected	11138 ($\pm h$, $\pm k$, $+l$)
Unique observed reflections ($F_o > 4\sigma(F_o)$]	4201
Goodness of fit on F^2	0.936
R_1 (F)[a], wR_2 (F^2)[b]	0.0601, 0.1648
Weighting scheme	$a = 0.1072$, $b = 0.0000$[b]
Largest diff. peak and hole (e Å⁻³)	1.053 and -0.894

[a] $R_1 = \Sigma \|F_o| - |F_c\| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{0.5}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

Fourier maps but were placed in calculated positions. One hexane molecule sitting around an inversion centre and one water molecule in a general position were also found in the asymmetric unit. The phenyl rings of the phosphine ligands were refined as rigid hexagons (C–C 1.39, C–H 0.93 Å, C–C–C 120°) and the hydrogen atoms were added in calculated positions. During refinement, some atoms of one phenyl ring [C(30)–C(35)] and the thienyl group bonded to P(2) exhibited unrealistic thermal ellipsoids and bond distances. As there was confidence in the quality of the data set, some orientational disorder in the phosphine cone was proposed and a model was constructed incorporating two orientations of the phosphine ligand related by a 120° rotation around the Co–P axis. This model yielded superimposed images of the thienyl and phenyl rings involved; the remaining phenyl group [C(36)–C(41)] was not affected. The successful refinement of the disordered model showed a slightly unbalanced distribution of the phenyl and thienyl groups; the most populated conformation (0.56) is shown in Fig. 2. The final refinement on F^2 proceeded by full matrix least-squares calculations (SHELXL93) [21] using anisotropic thermal parameters for all non-hydrogen atoms with the exception of the disordered thienyl and phenyl rings and hexane molecule. The methylene and the phenyl H atoms were assigned an isotropic thermal parameter 1.2 times U_{eq} of the carbon atoms to which they were attached.

5. Supplementary material

A complete list of bond lengths and angles as well as tables of hydrogen coordinates and anisotropic displacement parameters for all atoms have been deposited with the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK. Structure factors are available from the authors.

Acknowledgements

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