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Synthesis, Characterization, Structures and Comparative Electrochemical Study of 2,4-Bis(trimethylsilylethynyl)thiophene Coordinated Carbonylcobalt Units

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The reaction between 2,4-dibromothiophene and trimethylsilylacetylene (TMSA) in the presence of $Pd(PPh_3)_4$, CuI and triethylamine gave rise to the formation of 2,4-bis(trimethylsilylethynyl)thiophene (**2,4T**) and 4-bromo-2-(trimethylsilylethynyl)thiophene (**2,4T′**). Complexes **1**, **2**, **3** or **1′** were obtained by direct reaction between $Co_2(CO)_8$ and **2,4T** or **2,4T′**, respectively. (Diphenylphosphanyl)methane-substituted alkyne carbonyl complexes **4**, **5**, **6** and **2′** were prepared by substitution reaction of carbonyl ligands in the presence of Me_3NO at the $Co_2(CO)_6$ units of **1**, **2**, **3** and **1′**, respectively. Desilylation of the non-metallated and metallated alkynes in **4**, **5** and **6** occurred on treatment with KOH or tetrabutylammonium fluoride to give **7**, **8** and **9**. Crystals of **2′** suitable for single-crystal X-ray diffraction were grown, and the molecular structure of this compound is discussed. A comparative electrochemical study of these complexes in relation to analogous derivatives obtained from the organic ligand 2,5-bis(trimethylsilylethynyl)thiophene (**2,5T**) is reported.

Introduction

Recently, the search for molecular systems that are able to transmit electronic effects between two or more remote sites efficiently has become an area of increasing endeavour.[1] The interest in this kind of complexes is due, in part, to the stabilising influence of the metal atom on reactive unsaturated carbon chains and polycarbon ligands[1,2] and, on the other hand, to their potential optoelectronic properties as non-linear optical and electroluminescent materials[3] or in the construction of molecular-scale electronic devices.[4,5] Thus, alkynyl or polyynediyl bridging ligands have been shown to be particularly efficient in allowing the passage of electronic effects between redox-active centres[6,7] and therefore the electronic properties can be modified by changing both, metal fragments and/or alkyne ligands.[4b,4d,7b,8] This electronic communication through such potential molecular wires is often evaluated by examining the redox response of electroactive groups.[5i,5j,8a,9]

In recent studies we have shown that complexes, where the redox centres are either $Co_2(CO)_6$, $Co_2(CO)_4$(dppm) or $Co_2(CO)_4$(dppa) linked by 1,3,5-tris(trimethylsilylethynyl)benzene,[7a] 1,4-bis(trimethylsilyl)butadiyne[7b] and 2,5-bis(trimethylsilylethynyl)thiophene (**2,5T**)[7d] ligands, present electronic communication between the metal centres. In order to study the effect of the position of the alkynyl substituents on the thiophene ring on the electronic communication between $Co_2(CO)_6$ and $Co_2(CO)_4$(dppm) moieties, we report here the synthesis, characterization and the redox properties of these units linked by the organic ligand 2,4-bis(trimethylsilylethynyl)thiophene (**2,4T**).

Results and Discussion

Synthesis and Spectroscopic Characterization

A similar procedure described for 2,5-bis(trimethylsilylethynyl)thiophene (**2,5T**)[10] has been used in our laboratory for the syntheses of the new ligand 2,4-bis(trimethylsilylethynyl)thiophene (**2,4T**). By the coupling reaction of 2,4-dibromothiophene with excess of TMSA [in the presence of $Pd(PPh_3)_4$, CuI and triethylamine] 2,4-bis(trimethylsilylethynyl)thiophene (**2,4T**) (33% yield) and 4-bromo-2-(trimethylsilylethynyl)thiophene (**2,4T′**) (35% yield) were obtained, both as stable yellow oils. Large amounts of a catalyst [5% mol $Pd(PPh_3)_4$ and 10% mol CuI] and higher temperature and reaction time (75 °C for 20 d) were required, causing a side reaction of the terminal acetylene, TMSA, to

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afford 1,4-bis(trimethylsilyl)-1,3-butadiyne. Such side reactions were often observed in reactions with less reactive aryl bromides.[11] This synthesis needed a longer reaction time than that to obtain the analogous ligand **2,5T**, because the thiophene positions more suitable to an oxidative addition are 2 and 5. Also, from 2,6-dibromopyridine,[12] under Sonogashira coupling conditions, reasonable yields of both, the partially and fully substituted compounds containing the TMSA group were obtained. Complexes **1**, **2**, **3** or **1′** were obtained by direct reaction between $Co_2(CO)_8$ and **2,4T** or **2,4T′**, respectively.

In order to stabilise the dicobalt units, we have employed the dppm ligand (the small bite angle of dppm was expected to lead to the formation of bridged dicobalt complexes). Thus, dppm-substituted alkyne carbonyl complexes **4**, **5**, **6** and **2′** could only be prepared by substitution reaction of two or four carbonyl ligands in the presence of Me_3NO at the $Co_2(CO)_6$ units of complexes **1**, **2**, **3** and **1′**, respectively (Scheme 1), because of the poor yields obtained by direct reaction between the alkyne and "$Co_2(CO)_6$(phosphane)" under thermal conditions for the analogous complexes from **2,5T**.[7d] The FT-IR spectral changes of these reactions were monitored until the $\nu_{C\equiv O}$ bands of the parent complex had disappeared.

On the basis of the isolated yield for **4** and **5**, it can be observed that the preference of the $Co_2(CO)_4$(dppm) units for coordination at the alkyne in 2-position of the thiophene ring is two times greater than that for the 4-position. This preference is also observed for the analogous complexes **1** and **2** with $Co_2(CO)_6$ units (see Exp. Sect.). Moreover, compound **5**, in $CDCl_3$ solution at room temp. for 48 h, led to **4** (**4** was never observed to yield **5**), and complex **6** decomposed to afford **4** and **5** in a 7:1 ratio [determined by thin-layer chromatography (TLC) using hexane/CH_2Cl_2 (5:4) as eluent]. These results can be explained by simple steric or electronic effects.

As both positions have the same substituent on the alkyne ($SiMe_3$), it can be expected that the steric demand at the end-caps are similar. Then, the preference of the $Co_2(CO)_4X$ [X = $(CO)_2$ or dppm] moieties to coordinate the alkyne in position 2 can be explained by electronic factors. In agreement with this, the electron density on the triple bond of the alkyne in position 4 is higher than on the alkyne in position 2, as judged by the ^{13}C NMR shifts for the alkyne C atoms; this situation should disfavor the attachment of the Co atoms to the C≡C group in position 4, since back-donation from the Co d-orbitals to the π*-MO of an electron-poor ligand is the stabilizing factor in the bonding.[13]

However, Diederich et al. obtained in the reaction of $Co_2(CO)_8$ with 1,6-bis(triisopropylsilyl)hexa-1,3,5-triyne the exclusive formation of the compound in which the carbonylcobalt fragment is coordinated to the central C≡C triple bond, which was attributed to the presence of the bulky triisopropylsilyl end-caps.[2c]

Removal of the TMS protecting group from **4** and **5** was accomplished by treatment with saturated solutions of KOH in degassed methanol at room temp. to give the terminal diyne compounds **7** and **8**, respectively, isolated as unstable red solids. Complex **9** was synthesized from **6** when stronger desilylation conditions were used (8 equiv. of Bu_4NF in wet THF).

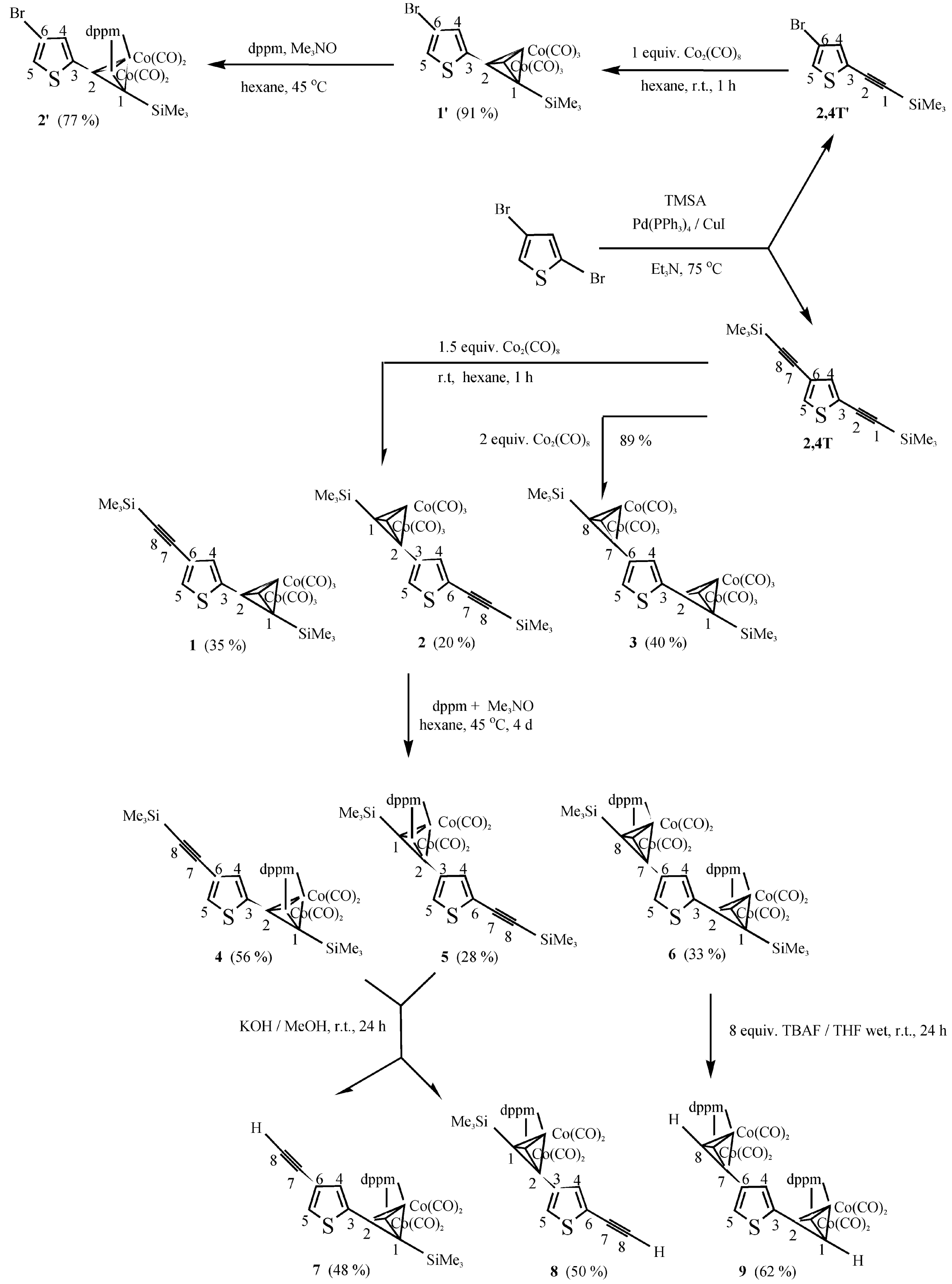
All these compounds have been characterized by spectroscopic data (IR, UV/Vis, ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR, MS) and elemental analysis, details of which are given as Supporting Information, and X-ray crystallography (for **2′**).

The IR spectra of the organic ligands **2,4T** [2165 (w), 2152 (w) cm^{-1}] and **2,4T′** [2156 (w) cm^{-1}] show weak absorption bands, typically $\nu_{C\equiv C}$ stretches of the alkynyl units, in the characteristic range of diynyl complexes (two $\nu_{C\equiv C}$ stretches at ca. 2060–2200 cm^{-1}) and monoynyl complexes (one $\nu_{C\equiv C}$ stretch at ca. 2090–2150 cm^{-1}). The ^1H NMR spectra of both ligands show two doublet signals due to the thiophene ring protons with coupling constants that are consistent with their chemical formulations. In the ^{13}C NMR spectra for **2,4T** and **2,4T′**, the signals belonging to the thiophene ring (C^3, C^4, C^5 and C^6) and the alkynyl units (C^1, C^2, C^7 and C^8) can be observed, and the assignments were made on the basis of the δ values and two-dimensional NMR experiments (HMBC and HMQC).

The IR spectra of the (alkyne)cobalt complexes exhibit three strong absorptions in the carbonyl stretching region (2090–2024 cm^{-1}) except for compound **3** (four absorptions) due to the asymmetry of the molecule; in dppm-substituted alkyne complexes **4**–**9** and **2′** these absorptions lie at lower frequencies (2027–1950 cm^{-1}), and the spectral patterns are similar to those observed for previously reported (alkyne) cobalt and (substituted alkyne)cobalt complexes.[1a,1c,2c,7,14] Complexes **1**, **2**, **4** and **5** contain an uncomplexed C≡C triple bond, which gives a $\nu_{C\equiv C}$ weak absorption at ca. 2157 cm^{-1}. For **7** and **8** this absorption could not be observed, but a $\nu_{\equiv C-H}$ one at ca. 3301 cm^{-1} is exhibited. The absence of $\nu_{C\equiv C}$ in the region of 2150 cm^{-1} (for **6** and **9**) and $\nu_{\equiv C-H}$ around 3300 cm^{-1} (for **9**) indicates that the alkynyl bond loses its triple-bond character and both alkyne linkages are coordinated to $Co_2(CO)_4$(dppm) units.

The NMR spectroscopic data, which have been recorded in several solvents, are consistent with the overall geometry established in the solid state for complex **2′** (Figure 1) and with the proposed structures (Scheme 1).

In ^1H NMR spectra, the chemical shifts for the $SiMe_3$ and C≡CH protons are found to be very sensitive to cobalt complexation on the adjacent alkyne bond, and they show a significant downfield shift with respect to the free ligands in accordance with the reduction of the C≡C triple-bond character.[15] The signals of all ring protons in the $Co_2(CO)_6$-substituted alkyne complexes are shifted downfield slightly from those of the corresponding alkynylated thiophenes, due to the strong electron-withdrawing effect of the carbonylcobalt moieties. In addition, the values of the ^1H-^1H coupling constants of $J_{HH} \approx 1.3$ Hz for the thiophene proton signals are in accordance with their non-adjacent positions (Table 1). For dppm complexes **4**–**8** and **2′** the diastereotopic protons of the –CH_2– group are coupled with



Scheme 1.

the P atoms; thus, they appear as two double triplets with $J_{\mathrm{HH}} \approx 13.3$ Hz and $J_{\mathrm{PH}} \approx 10.5$ Hz, except in **6**, where the inequivalent $Co_2(CO)_4$(dppm) moieties display four signals in the ^1H and $^1H\{^{31}P\}$ NMR spectra in CD_2Cl_2. Also, in **9**, the two moieties $Co_2(CO)_4$(dppm) are inequivalent, and this is reflected in the ^1H NMR spectrum. This spectrum

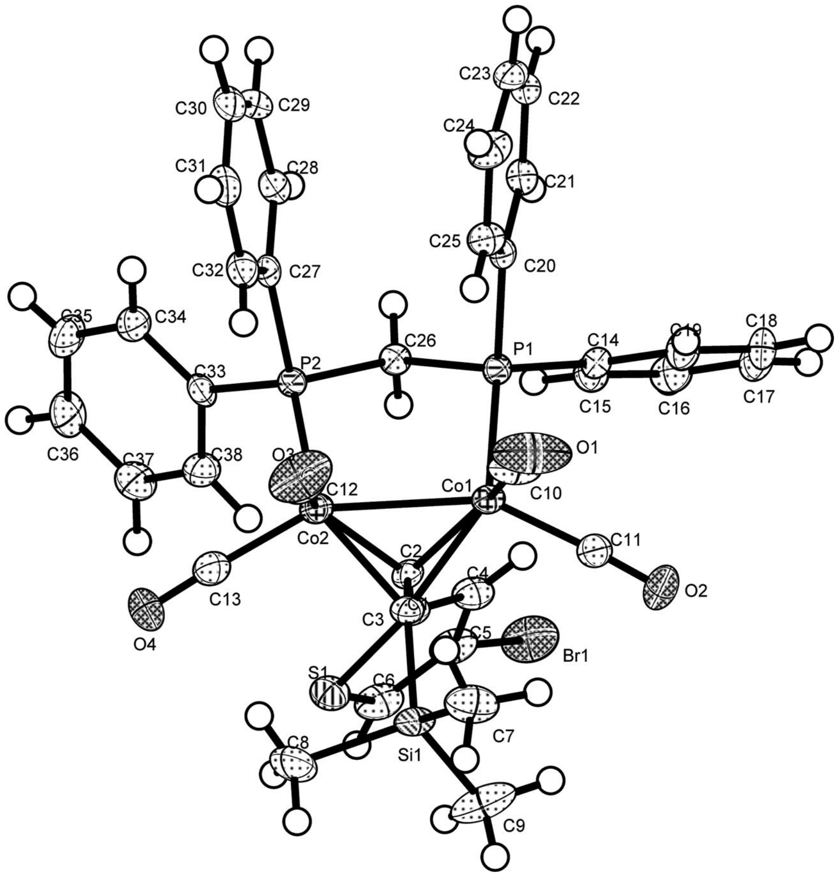


Figure 1. ORTEP diagram of **2′**, with 50% ellipsoids.

shows two resonances for the terminal "alkyne" protons, $–(C–C)_{coord}–H$ in the region δ = 5.72–5.80 ppm, and they are coupled with the P atoms like in similar compounds.[7d,16] As expected,[15,17] because of the reduction in the C≡C triple-bond character, there is a downfield shift in the signal positions of these terminal protons with respect to those of the free ligand (δ = 3.32 and 2.99 ppm).

The ^{31}P NMR spectra for **4**, **5**, **7** and **8** present a broad singlet, while for **6** and **9**, which contain two inequivalent $Co_2(CO)_4$(dppm) units, two broad singlets appear. All of them are shifted to higher frequencies (ca. 35 ppm) with respect to that of the free ligand because of the coordination.

The ^{13}C NMR chemical shifts of the carbonyl groups in all the complexes appear as one (**1**, **2**, **3** and **1′**), two (**4**, **5**, **7**, **8** and **2′**) or four (**6** and **9**) signals at $\delta \approx$ 200 and 207 ppm, suggesting that they are rapidly interchanging on the NMR scale. The carbon resonances of the free and coordinated acetylene carbon atoms can be assigned on the basis of the magnitude of the J_{CP} coupling constants, chemical shifts and in comparison with analogous complexes.[1c,2c,7,18] Thus, for **4** and **5**, in $CDCl_3$ and CD_2Cl_2, the C^1, C^2 and C^3 atoms display similar triplets with ^{13}C-^{31}P coupling constants of $J_{CP} \approx$ 10.1, 8.9 and 3.0 Hz, respectively. The replacement of the $–SiMe_3$ group by a proton results in a significant deshielding of the C^1, C^2, C^7 and C^8 atoms. The thiophene carbon signals appear between δ = 120 and 150 ppm (Table 2).

Compound **6** exhibits low solubility in $CDCl_3$ and CD_2Cl_2, and for that reason the ^{13}C NMR spectrum was recorded in [D$_8$]THF. The unambiguous assignment of its carbon atoms has been carried out by comparison with published data of analogous compounds[7d] and by using the ^{13}C NMR spectra of **4** and **5** in the same solvent in addition to HMQC and HMBC spectroscopy (these experiments have also been performed for the rest of the complexes) (Figure 2).

All compounds gave satisfactory mass spectrometric data; thus, the positive FAB mass spectra show the respective molecular ions or [M^+ – CO], as well as peaks corresponding to the consecutive loss of the CO ligands. The UV/Vis spectra of all complexes exhibit broad low-intensity absorption bands with λ between 520 and 558 nm attributed to the d-d transitions. For **3**, **6**, and **9**, the presence of the second $Co_2(CO)_6$ or $Co_2(CO)_4$(dppm) unit results in a redshift of these absorption bands. These spectra, for complexes **4**–**9** and **2′**, are dominated by the characteristic UV bands below 380 nm associated with π-π* transitions within the phenyl groups of the bis(phosphane) ligand. In addition, strong absorptions are observed around 231, 250 and 276 nm attributed to π-π* transition associated with the thiophene ring.

Table 1. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, ppm) data for the compounds **1**–**9** and **2,4T**.

	H^4	H^5	–C≡CH	–C–CH	–C≡CSiMe$_3$	–C–CSiMe$_3$
2,4T	7.21 (d) J_{HH} = 1.3 Hz	7.32 (d) J_{HH} = 1.3 Hz	–	–	0.25 (s), 0.24 (s)	–
1	7.22 (d) J_{HH} = 1.3 Hz	7.42 (d) J_{HH} = 1.3 Hz	–	–	0.25 (s)	0.39 (s)
2	7.24 (d) J_{HH} = 1.4 Hz	7.26 (s br)	–	–	0.26 (s)	0.38 (s)
	7.27 (d)[a] J_{HH} = 1.5 Hz	7.31 (d)[a] J_{HH} = 1.5 Hz			0.25 (s)[a]	0.39 (s)[a]
3	7.31 (d) J_{HH} = 1.4 Hz	7.33 (d) J_{HH} = 1.4 Hz	–	–	–	0.40 (s), 0.38 (s)
	7.34 (d)[a] J_{HH} = 1.2 Hz	7.39 (d)[a] J_{HH} = 1.2 Hz				0.41 (s), 0.39 (s)[a]
4	6.57 (d) J_{HH} = 1.3 Hz	7.28 (s br)	–	–	0.28 (s)	0.36 (s)
	6.58 (d)[a] J_{HH} = 1.4 Hz	7.31 (d)[a] J_{HH} = 1.4 Hz			0.28 (s)[a]	0.38 (s)[a]
	6.52 (s br)[b]	7.37 (s br)[b]			0.24 (s)[b]	0.36 (s)[b]
5	6.77 (d) J_{HH} = 1.4 Hz	6.63 (d) J_{HH} = 1.4 Hz	–	–	0.29 (s)	0.33 (s)
	6.76 (d)[a] J_{HH} = 1.5 Hz	6.67 (d)[a] J_{HH} = 1.5 Hz			0.29 (s)[a]	0.34 (s)[a]
	6.74 (s br)[b]	6.71 (s br)[b]			0.25 (s)[b]	0.32 (s)[b]
6	6.68 (d) J_{HH} = 1.3 Hz	7.27 (d) J_{HH} = 1.4 Hz	–	–	–	0.36 (s), 0.35 (s)
	6.68 (d)[a] J_{HH} = 1.4 Hz	7.26 (d)[a] J_{HH} = 1.4 Hz				0.36 (s), 0.35 (s)[a]
	6.75 (s br)[b]	7.35 (s br)[b]				0.385 (s), 0.381(s)[b]
7	6.67 (d) J_{HH} = 1.3 Hz	7.31 (d) J_{HH} = 1.3 Hz	2.99 (s)	–	–	0.38 (s)
8	6.87 (d) J_{HH} = 1.4 Hz	6.64 (d) J_{HH} = 1.4 Hz	3.32 (s)	–	–	0.33 (s)
9	7.43–7.15	7.43–7.15	–	5.80 (dt) J_{HH} = 8.2 Hz J_{PH} = 6.2 Hz 5.72 (t) J_{PH} = 6.7 Hz	–	–

[a] CD_2Cl_2. [b] [D$_8$]THF.

Table 2. ^{13}C NMR (500 MHz, $CDCl_3$, 25 °C, ppm) data for the compounds **1**–**9** and **2,4T**.

	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8
2,4T	99.4 (s)	99.0 (s)	122.2 (s)	134.9 (s)	130.6 (s)	123.2 (s)	96.5 (s)	94.1 (s)
1	81.0 (s br)	93.4 (s br)	141.9 (s)	131.0 (s)	130.4 (s)	123.2 (s)	99.2 (s)	94.2 (s)
2	80.0 (s br)[a]	97.7 (s br)[a]	139.0 (s)[a]	134.2 (s)[a]	125.9 (s)[a]	124.6 (s)[a]	96.9 (s)[a]	100.1(s)[a]
3	80.7 (s br)	93.8 (s br)	143.0 (s)	130.3 (s)	124.7 (s)	139.5 (s)	97.1 (s br)	79.4 (s br)
	81.3 (s br)[a]	94.5 (s br)[a]	143.1 (s)[a]	130.8 (s)[a]	125.2 (s)[a]	139.9 (s)[a]	97.7 (s br)[a]	80.0 (s br)[a]
4	89.7 (t) J_{CP} = 10.5 Hz	93.3 (t) J_{CP} = 9.2 Hz	147.8 (t) J_{CP} = 2.7 Hz	128.9 (s)	128.3 (s)	122.1 (s)	100.4 (s)	92.9 (s)
	89.7 (t)[a] J_{CP} = 10.0 Hz	93.8 (t)[a] J_{CP} = 9.4 Hz	148.2 (t)[a] J_{CP} = 3.1 Hz	129.1 (s)[a]	128.6 (s)[a]	122.6 (s)[a]	100.4 (s)[a]	92.3 (s)[a]
	88.5 (m)[b]	93.5 (m)[b]	147.5 (t)[b] J_{CP} = 2.7 Hz	128.8 (s)[b]	128.3 (s)[b]	122.3 (s)[b]	100.3 (s)[b]	91.9 (s)[b]
5	87.9 (t) J_{CP} = 9.9 Hz	97.9 (t) J_{CP} = 8.3 Hz	143.7 (t) J_{CP} = 3.2 Hz	134.8 (s)	122.1 (s)	123.2 (s)	97.6 (s)	98.6 (s)
	87.9 (t)[a] J_{CP} = 10.0 Hz	98.4 (t)[a] J_{CP} = 8.8 Hz	144.1 (t)[a] J_{CP} = 2.9 Hz	135.0 (s)[a]	122.6 (s)[a]	123.7 (s)[a]	97.7 (s)[a]	99.1 (s)[a]
	86.8 (m)[b]	98.0 (m)[b]	143.6 (t)[b] J_{CP} = 3.2 Hz	134.4 (s)[b]	122.3 (s)[b]	123.2 (s)[b]	97.4 (s)[b]	97.8 (s)[b]
6	87.9 (m)[b]	93.3 (m)[b]	149.5 (t)[b] J_{CP} = 2.7 Hz	120.6 (s)[b]	126.0 (s)[b]	145.1 (t)[b] J_{CP} = 2.7 Hz	98.2 (m)[b]	87.2 (m)[b]
7	89.6 (m)	93.2 (m)	148.3 (t) J_{CP} = 3.2 Hz	128.5 (s) 128.6 (s)		121.0 (s)	79.2 (s)	76.2 (s)
8	88.0 (m)	97.9 (m)	143.9 (t) J_{CP} = 2.7 Hz	135.2 (s)	122.3 (s)	122.0 (s)	77.2 (s)	81.1 (s)
9	74.5 (m)[a]	83.2 (m)[a]	147.3 (m)[a]	121.7 (s)[a]	128.9 (s)[a]	143.9 (m)[a]	89.4 (m)[a]	75.2 (m)[a]

[a] CD_2Cl_2. [b] [D$_8$]THF.

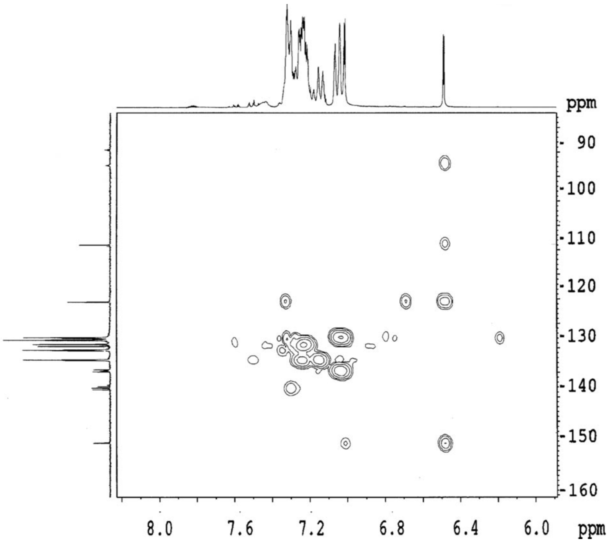


Figure 2. HMBC NMR (500 MHz, CDCl$_3$, 25 °C, ppm) spectra for complex **2′**.

Table 3. Selected bond lengths [Å] and angles [°] for **2′**.

C(1)–C(2)	1.358(4)	C(11)–Co(1)	1.767(3)
C(1)–Si(1)	1.853(3)	C(12)–O(3)	1.142(4)
C(1)–Co(2)	1.969(2)	C(12)–Co(2)	1.794(3)
C(1)–Co(1)	1.985(2)	C(13)–O(4)	1.139(3)
C(2)–C(3)	1.450(3)	C(13)–Co(2)	1.781(3)
C(2)–Co(1)	1.943(2)	C(26)–P(1)	1.831(2)
C(2)–Co(2)	1.975(2)	C(26)–P(2)	1.843(2)
C(5)–Br(1)	1.894(3)	Co(1)–P(1)	2.2221(7)
C(10)–O(1)	1.138(3)	Co(2)–P(2)	2.2256(7)
C(10)–Co(1)	1.797(3)	Co(1)–Co(2)	2.4850(5)
C(11)–O(2)	1.141(3)		
C(2)–C(1)–Si(1)	141.71(19)	C(1)–C(2)–C(3)	136.0(2)
C(6)–C(5)–Br(1)	123.7(2)	C(4)–C(5)–Br(1)	121.5(2)
C(11)–Co(1)–C(2)	97.81(11)	C(11)–Co(1)–C(10)	99.79(14)
C(11)–Co(1)–C(1)	101.12(11)	C(10)–Co(1)–C(2)	143.70(12)
C(2)–Co(1)–C(1)	40.44(10)	C(10)–Co(1)–C(1)	104.70(12)
C(10)–Co(1)–P(1)	106.82(9)	C(11)–Co(1)–P(1)	99.37(9)
C(1)–Co(1)–P(1)	138.51(7)	C(2)–Co(1)–P(1)	101.25(7)
C(1)–Co(1)–Co(2)	50.78(7)	C(2)–Co(1)–Co(2)	51.20(7)
C(10)–Co(1)–Co(2)	102.62(11)	C(11)–Co(1)–Co(2)	147.76(8)
C(13)–Co(2)–C(12)	101.48(14)	C(13)–Co(2)–C(1)	102.53(11)
C(12)–Co(2)–C(1)	98.35(11)	C(13)–Co(2)–C(2)	102.79(11)
C(12)–Co(2)–C(2)	135.73(12)	C(1)–Co(2)–C(2)	40.28(10)
C(13)–Co(2)–P(2)	98.79(9)	C(12)–Co(2)–P(2)	111.69(9)
C(1)–Co(2)–P(2)	138.56(8)	C(2)–Co(2)–P(2)	100.46(7)
C(13)–Co(2)–Co(1)	151.05(9)	C(12)–Co(2)–Co(1)	95.39(10)
C(1)–Co(2)–Co(1)	51.34(7)	C(2)–Co(2)–Co(1)	50.06(7)
P(1)–Co(1)–Co(2)	96.00(2)	P(2)–Co(2)–Co(1)	96.55(2)
P(1)–C(26)–P(2)	107.97(12)		

Crystal Structure of 2′

The single-crystal X-ray structure determination of 2-{Co$_2$(CO)$_4$(μ-dppm)[μ$_2$-η^2-(SiMe$_3$C$_2$)]}-4-(Br)-C$_4$H$_2$S (**2′**) confirms the structure presented in Scheme 1. Compound **2′** consists of a monosubstituted 4-bromo-2-(trimethylsilylethynyl)thiophene ligand with a dimetallic Co unit at the 2-position. The dimetallic Co moiety has two terminal carbonyl ligands on the Co atoms, bridging dppm and trimethylsilylethynyl groups. This geometry has been observed in other carbonylcobalt dimetallic complexes possessing a bridging acetylene ligand.[19] The geometric parameters for **2′** are summarized in Table 5. Table 3 contains selected bond lengths and angles. An ORTEP plot indicating the atom-labelling scheme is given in Figure 1. Complex **2′** crystallizes in the monoclinic space group *P*2$_1$/*c*, with one molecule in the asymmetric unit, but contains no crystallographic symmetry.

A highly distorted tetrahedron is formed by the coordination of the dicobalt unit with the ethynyl carbon atoms, with a Co(1)–Co(2) bond length of 2.4850(5) Å, and the average Co–C bond length was determined to be 1.968(2) Å. The Co–Co distance is comparable to those reported for the compounds 2,5-{Co$_2$(CO)$_4$(μ-dppm)[μ$_2$-η^2-(SiMe$_3$C$_2$)]}$_2$C$_4$H$_2$S[7d] and [Co$_2$(CO)$_4$(μ-dppm){μ$_2$-η^2-(SiMe$_3$C$_2$)}]$_2$(SiMe$_3$C≡C)(1,3,5-C$_6$H$_3$)[7a] and may be considered typical for this type of clusters.[14d,20]

The coordination geometry of the Co atom is similar to a pyramid with a pentagonal-shaped base, where the Co atom is in the centre of the pyramid. The distortion of the pyramid is due to the constrained tetrahedron comprised of Co(1)–Co(2)–C(1)–C(2), as well as the bridging of the dppm ligand. The carbonyl moieties coordinate to the Co atoms in the sterically least hindered sites, thus making up the pyramid. The apex of the pyramid is one of the carbonyl groups, and the base is comprised of the carbonyl group, one of the phosphorus atoms of the dppm ligand, the two ethynyl carbon atoms, and the other Co atom. The bond lengths of the apex carbonyl groups to the Co atoms, C(10)–Co(1) and C(12)–Co(2), are 1.797(3) and 1.794(3) Å, respectively. These bond lengths are statistically not different from those of the base carbonyl groups to the Co atoms, which are 1.767(3) and 1.781 Å, for C(11)–Co(1) and C(13)–Co(2), respectively. The dihedral angle Co(1)–C(1)–C(2)–Co(2) was determined to be –84.5(7)°, whereas the dihedral angle C(1)–Co(1)–Co(2)–C(2) was determined to be –52.8(13)°. The bite angle of the dppm ligand was found to be 108.0(12)°, which is consistent with analogous bite angles of dppm in Co–Co complexes.[21]

The C(1)–C(2) bond length of the bridging ethynyl ligand, 1.358(4) Å, is consistent with reported ethynyldicobalt complexes.[22] This reflects the loss of triple-bond character as a result of coordination of the acetylenic moiety to the Co$_2$ unit. The change in hybridisation at C(1)–C(2) is also reflected in the C(1)–C(2)–C(3) angle of 136.0(2)° and the C(2)–C(1)–Si(1) angle of 141.7(19)°.

The bond lengths of the Co atoms to the phosphorus atoms of the dppm ligand are 2.222(7) Å and 2.226(7) Å for Co(1)–P(1) and Co(2)–P(2), respectively. The average P–C distances of the bridging dppm ligand, 1.835(2) Å are normal;[23] the P–C bond lengths are statistically equivalent. All other bond lengths and angles are comparable to those reported for similar structures.[7] The average carbonyl C≡O bond length was determined to be 1.140(3) Å, where all of the bond lengths are sufficiently similar. In addition, the Br–C(5) bond length is 1.894(3) Å and the C(6)–C(5)–Br and C(4)–C(5)–Br angles are 123.7(2)° and 121.5(2)°, respectively. The thiophene ring is essentially planar with a root mean square deviation of 0.0045 Å. There does not appear to be any intramolecular hydrogen bonding within the molecule.

Electrochemical Studies

The electrochemical behaviour of **1**, **2′** and **3**–**9** in CH_2Cl_2 solution was studied by means of cyclic voltammetry (CV) and square wave voltammetry (SWV) techniques. A preliminary study of **1** and **3**–**6** was previously published.[24] Table 4 presents data of $E_{1/2}$ [$E_{1/2} = (E_{pa} + E_{pc})/2$] for the electrochemical reduction and oxidation of **1**, **2′** and **3**–**9**. The organic ligands **2,4T** and **2,4T′** do not show any oxidation or reduction peaks in the potential range between –1.8 V and +1.5 V vs. Fc*+/Fc* (Fc* = decamethylferrocene) in CH_2Cl_2.

Table 4. Electrochemical data for **1**, **2′** and **3**–**9**.[a]

	$E_{1/2}$ for reduction	$\Delta E_{1/2}$ (red)	$E_{1/2}$ for oxidation	$\Delta E_{1/2}$ (ox)
1	–0.99[b]		1.24[b]	
2′	–1.54[b]		0.70	
3	–1.00[b], –1.08[b]	0.08	1.21[b], 1.29[b]	0.08
4	–1.56[b]		0.69	
5	–1.60[b]		0.68	
6	–1.58[b], –1.72[b]	0.14	0.65, 0.77	0.12
7+8[c]	–1.52[b]		0.69	
9	–1.52[b], –1.64[b]	0.12	0.63, 0.73	0.10

[a] In V vs. Fc*+/Fc* in CH_2Cl_2 solution. Data are taken from CV and SWV at 25 °C, unless otherwise stated. [b] From CV and SWV at –30 °C. [c] Equimolecular mixture of compounds **7** and **8**.

Electrochemistry of 1 and 3

CV and SWV of the $Co_2(CO)_6C_2$ derivative **1** at room temp. show chemically irreversible oxidation and reduction waves at moderate sweep rates (EC processes). Thus, when the sweep is reversed after CV reduction, no coupled anodic peak is observed, but a new small one appears at +0.12 V (irreversible). This behaviour indicates that the decomposition of $\mathbf{1}^-$ yields, among other fragments, $Co(CO)_4^-$ (oxidised at 0.12 V).[6d,7,25] The stability of $\mathbf{1}^-$ is greatly enhanced when low temperature decreases the rate of the following chemical reaction, and at –30 °C chemical reversibility is almost completely attained.

Decreasing temperature to –30 °C and increasing the sweep rate to 2 V/s allowed to observe a very small coupled reduction peak on sweep reversal after $\mathbf{1}^+$ formation. The stability of $\mathbf{1}^+$ is lower than that observed for the related cation derived from 2-[$Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}(SiMe_3C_2)\}$]-5-($Me_3SiC{\equiv}C)C_4H_2S$ ($i_{pc}/i_{pa} \approx 0.55$ at –30 °C and 0.1 V/s).[7d] This result is in agreement with the higher overall π-conjugation[26] in complexes containing **2,5T** (λ_{max} = 331 nm)[27] as compared to those of **2,4T** (λ_{max} = 277 nm). $E_{1/2}$(ox) and $E_{1/2}$(red) for **1** are very similar to those of the corresponding **2,5T** derivative, indicating that the position of the $–C_2SiMe_3$ substituent on the thiophene ring does not have a significant influence on the electrochemical processes.

Compound **3**, with two "almost" equivalent dicobalt redox centers, shows two consecutive monoelectronic reductions and oxidations to achieve $\mathbf{3}^{2-}$ and $\mathbf{3}^{2+}$, respectively. At room temp., reduction of **3** is chemically completely irreversible; however, at –30 °C the chemical stability of the reduced species is greatly enhanced, and two distinct and almost completely reversible reduction waves are observed in CV (Figure 3). The ratio i_{pa}/i_{pc} approaches 1 as the sweep rate increases. As regarding oxidation, two quasi-reversible waves are also observed, i_{pc}/i_{pa} increasing as the temperature decreases.

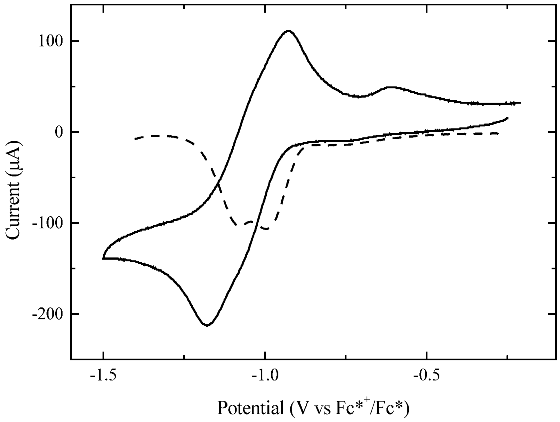


Figure 3. Cyclic (—) and square wave (- - -) voltammograms for the reduction of **3** in CH_2Cl_2 containing 0.15 M $TBAPF_6$ at –30 °C on a glassy carbon working electrode. CV: v = 0.5 V s^{-1}. SWV: scan increment = 2 mV, SW amplitude = 25 mV, frequency = 15 Hz.

Electrochemistry of 2′ and 4–9

Compounds **2′** and **4**–**9** contain $Co_2(CO)_4(dppm)C_2$ redox centers. The dppm ligand increases the electronic density and makes oxidations easier (less positive $E_{1/2}$) and reductions more difficult (more negative $E_{1/2}$) as observed in Table 4.

The $E_{1/2}$(ox) values are quite similar for all the compounds containing a single $Co_2(dppm)(CO)_4C_2$ redox center, independent of the nature of the other substituent on the thiophene ring (–Br in **2′**, $–C_2SiMe_3$ in **4**–**5** and $–C_2H$ in **7**–**8**) or the location of the $Co_2(dppm)(CO)_4C_2$ unit (position 2 or 4). It should be noted that **7** and **8** could not be isolated, and that an equimolecular mixture of both compounds was used for the electrochemical measurements. A single oxidation and a single reduction peak were obtained for that mixture, indicating that both compounds are oxidised and reduced at almost the same potential value. In the case of $E_{1/2}$(red), differences are not too strong among **2′**, **4**, **5** and **7+8**, but it seems that the presence of a $–C_2SiMe_3$ substituent makes reduction slightly more difficult ($E_{1/2}$ more negative), as a result of the higher electron-donating properties of the $–SiMe_3$ group as compared to –H. The bidentate ligand dppm greatly increases the chemical stability of the cations (oxidations of the compounds with one redox center are chemically completely reversible at 25 °C and 0.1 V/s) and the anions (reductions are quasi-reversible at 25 °C and completely reversible a –30 °C) (Figure 4). Potential values and stability trends agree with those of related **2,5T** compounds.[7d]

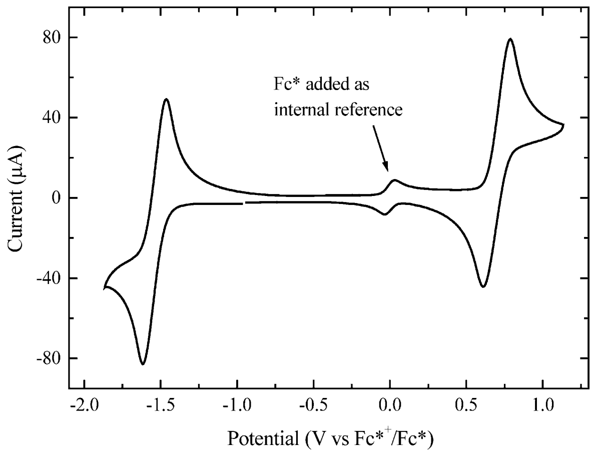


Figure 4. Cyclic voltammogram for the reduction and oxidation of **4** at –30 °C in CH_2Cl_2 containing 0.15 M $TBAPF_6$ on a glassy carbon working electrode at $v = 0.05\ V s^{-1}$.

6 and **9** contain two $Co_2(dppm)(CO)_4C_2$ centers and show two consecutive monoelectronic oxidations and reductions. Chemical reversibility is greatly approached at –30 °C (Figure 5), allowing the determination of $E_{1/2}$. Analogous compounds, in which the ligand is **2,5T**, show a greater stability of the corresponding anions and cations, in agreement with the general trends observed in the synthesis of both sets of compounds (**2,4T** and **2,5T** derivatives) and the higher overall π-conjugation of **2,5T**, as the C^3–C^4 bond in a thiophene ring is known to have less double-bond character than the C^2–C^3 bond.[28]

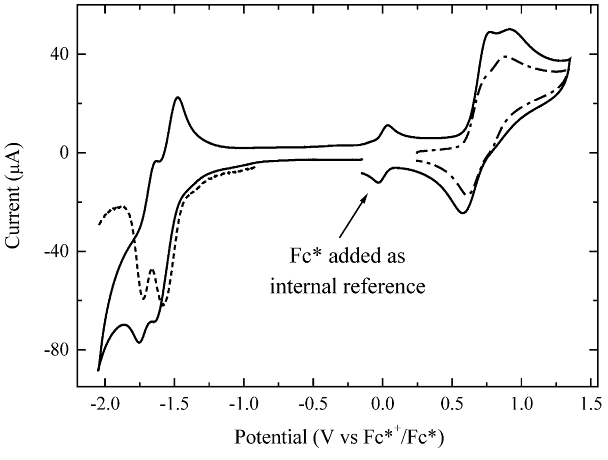


Figure 5. Voltammograms for the reduction and oxidation of **6** in CH_2Cl_2 containing 0.15 M $TBAPF_6$. (–) CV at –30 °C on a glassy carbon working electrode, $v = 0.1\ V s^{-1}$. (-··-) CV at 25 °C on a Pt working electrode, $v = 0.1\ V s^{-1}$. (- - -) SWV at –30 °C on a glassy carbon working electrode, scan increment = 2 mV, SW amplitude = 25 mV, frequency = 60 Hz.

The difference between $E_{1/2}$ of consecutive waves in compounds with two equivalent redox centers, $\Delta E_{1/2}$, is usually regarded as an estimation of the amount of electronic interaction between those centers through the bridging ligand.[9a] The two redox centers in **3**, **6** and **9** are not completely equivalent, and the observed $\Delta E_{1/2}$ could be due to intrinsic differences; however, results obtained with **4**–**5** and **7**–**8** (very scarce influence of the position of the redox center on the thiophene ring) allow to assume that most of $\Delta E_{1/2}$ is due to a low-intensity electronic interaction between the centers. The $\Delta E_{1/2}$ values observed for **3**, **6** and **9** can thus be compared to those measured for the related compounds 2,5-$[Co_2(CO)_6\{\mu_2\text{-}\eta^2\text{-}(SiMe_3C_2)\}]_2C_4H_2S$ [$\Delta E_{1/2}$(red) = 0.11 V; $\Delta E_{1/2}$(ox) = 0.24 V], 2,5-$[Co_2(CO)_4(\mu\text{-dppm})\{\mu_2\text{-}\eta^2\text{-}(SiMe_3C_2)\}]_2C_4H_2S$ [$\Delta E_{1/2}$(red) = 0.13 V; $\Delta E_{1/2}$(ox) = 0.29 V] and 2,5-$[Co_2(CO)_4(\mu\text{-dppm})\{\mu_2\text{-}\eta^2\text{-}(HC_2)\}]_2C_4H_2S$ [$\Delta E_{1/2}$(red) = 0.13 V; $\Delta E_{1/2}$(ox) = 0.20 V], respectively.[7d] All $\Delta E_{1/2}$ values (including those of the present work) indicate that a moderate electronic interaction is established through the aromatic ligand backbone, and the complexes belong to group II in the Hush–Robin–Day classification of mixed-valence compounds.[29] Data for the **2,4T** and **2,5T** derivatives show that the $\Delta E_{1/2}$(ox) values are significantly larger for the latter. This seems to indicate that the HOMO (depopulated by oxidation) of the **2,5T** derivatives shows a greater π-delocalization than the HOMO of the **2,4T** derivatives and than the LUMO (populated by reduction) in both groups, in agreement[26] with the higher conjugation observed in **2,5T** derivatives, where the λ_{max} value is less blue-shifted relative to that of **2,4T** compounds. The differences in $\Delta E_{1/2}$ indicate a significant contribution of through-bond electronic interactions as compared to through-space ones in these compounds.

Conclusion

The overall π-conjugation of **2,4T** derivatives is smaller than that of the analogous **2,5T** derivatives, and this results in a lower stability of the ions derived from **2,4T** and a weaker electronic communication through the aromatic ligand backbone. The derivatives of **2,4T** and **2,5T** with two redox centres belong to group II in the Hush–Robin–Day classification of mixed-valence compounds.

Experimental Section

Reagents and General Techniques: All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under oxygen-free argon. All solvents for synthetic use were dried and distilled under argon by standard procedures.[30] Column chromatography was performed by using silica gel 100 (Fluka) and preparative TLC glass plates coated with silica gel (SDS 60–17 μm, 0.25 mm thick). 2,4-Dibromothiophene (Lancaster Synthesis Inc.); $Me_3SiC{\equiv}CH$ (TMSA), $Co_2(CO)_8$, KOH (Fluka); 1,2-bis(diphenylphosphanyl)methane (dppm), CuI, a solution 1.0 M of tetrabutylammonium fluoride (TBAF) in THF (Aldrich); $NaHCO_3$, $MgSO_4$ (Panreac) and a solution of HCl (35%) (Prolabo) were used as received. Trimethylamine *N*-oxide (Aldrich) was sublimed prior to use and stored under argon. Compound $Pd(PPh_3)_4$[31] was prepared according to the literature. The ^1H, $^1H\{^{31}P\}$, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$ NMR spectra and HMQC and HMBC data were recorded with Bruker AMX-300 and -500 instruments. Chemical shifts were measured relative to either an internal reference of tetramethylsilane or residual protons of the solvents. Infrared spectra were measured with a Perkin–Elmer 1650 infrared spectrometer. Elemental analyses were performed with a Perkin–Elmer 240 B microanalyser. Electronic spectra were recorded with a Unicam UV 4 UV/Vis spectrophotometer. Mass spectra were measured with a VG-Autospec mass spectrometer for FAB and EI. Spectroscopy data are available as Supporting Information. Electrochemical measurements were carried out with a computer-driven Par Mo. 273 electrochemistry system in a three-electrode cell under nitrogen in anhydrous deoxygenated CH_2Cl_2 containing 0.15 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as supporting electrolyte. Cyclic and square wave voltammetry (CV and SWV, respectively) studies were carried out in a three-electrode system. Polycrystalline Pt (0.05 cm^2) or glassy carbon were used as working electrodes; the counter electrode was a Pt gauze and the reference electrode was a silver wire quasi-reference electrode. Decamethylferrocene (Fc*) was used as internal standard, and all potentials in this work are referenced to the Fc^{*+}/Fc^* couple. Under the actual experimental conditions, $E_{1/2}$ of the ferrocene couple (Fc^+/Fc) was +0.55 V vs. Fc^{*+}/Fc^* in CH_2Cl_2 solution. Coulometry of **4** was performed at 1.1 V and 1 mol of electrons per mol of **4** was found to be consumed in the oxidation process. The number of electrons involved in the remaining processes were determined by comparison of peak heights in CV.

Synthesis of 2,4-Bis(trimethylsilylethynyl)thiophene (2,4T) and 4-Bromo-2-(trimethylsilylethynyl)thiophene (2,4T′): To a solution of 2,4-dibromothiophene (3.0 g, 12.4 mmol) in Et_3N (100 mL) was added at 0 °C $Pd(PPh_3)_4$ (0.70 g, 0.62 mmol), CuI (0.23 g, 1.24 mmol) and excess of trimethylsilylacetylene (TMSA) (12.1 g, 17.5 mL, 124 mmol). The resulting mixture was stirred first at room temperature for 0.5 h and finally at 75 °C for 20 d. The solvent was removed under reduced pressure and the residue dissolved in Et_2O (100 mL) and wash with (i) a solution of HCl (10%), (ii) a saturated solution of $NaHCO_3$ and dried ($MgSO_4$). The solvent was evaporated and the residue purified by column chromatography with hexane to yield **2,4T** (1.13 g, 33% yield) and **2,4T′** (1.12 g, 35% yield) as stable yellow oils.

Synthesis of 2-[$Co_2(CO)_6$\{μ_2-η^2-($SiMe_3C_2$)\}]-4-($Me_3SiC{\equiv}C$)C_4H_2S (1), 2-($Me_3SiC{\equiv}C$)-4-[$Co_2(CO)_6$\{μ_2-η^2-($SiMe_3C_2$)\}]C_4H_2S (2) and 2,4-[$Co_2(CO)_6$\{μ_2-η^2-($SiMe_3C_2$)\}]$_2C_4H_2S$ (3): To a solution of **2,4T** (0.90 g, 3.26 mmol) in hexane (100 mL) was added 1.5 equiv. of $Co_2(CO)_8$. The reaction was monitored by FT-IR and ^1H NMR spectroscopy until the signals of the parent compounds **2,4T** and $Co_2(CO)_8$ had disappeared. After the mixture had been stirred at room temp. for 1 h, the solvent was removed under vacuum and the residue purified by thin-layer chromatography (TLC) using hexane as eluent to afford **1** (0.64 g, 35% yield) and **2** (0.36 g, 20% yield) together with **3** (1.24 g, 40% yield) as unstable solids. **3** has also been obtained as the only product in high yield (0.27 g, 89%) from **2,4T** (0.10 g, 0.36 mmol) and 2 equiv. of $Co_2(CO)_8$ and subsequent chromatography with hexane on a silica column.

Synthesis of 2-[$Co_2(CO)_6$\{μ_2-η^2-($SiMe_3C_2$)\}]-4-(Br)-C_4H_2S (1′): By a similar procedure as described above, from **2,4T′** (0.75 g, 2.89 mmol) and 1 equiv. of $Co_2(CO)_8$. After the solvent had been removed under vacuum, the product was eluted with hexane on a silica column to afford **1′** (1.43 g, 91% yield) as an unstable red solid.

Synthesis of 2-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-($SiMe_3C_2$)\}]-4-($Me_3SiC{\equiv}C$)C_4H_2S (4) and 2-($Me_3SiC{\equiv}C$)-4-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-($SiMe_3C_2$)\}]C_4H_2S (5): A solution containing **1** and **2** (1.0 g, 1.78 mmol in a 1.75:1 ratio) in hexane (100 mL) was added dppm (0.68 g, 1.78 mmol) and trimethylamine *N*-oxide (0.40 g, 3.56 mmol). The reaction mixture, monitored by FT-IR spectroscopy until the $\nu_{C\equiv O}$ bands of the parent complexes had disappeared, was stirred at 45 °C for 4 d. Finally, the solvent was removed under vacuum and the residue purified by thin-layer chromatography (TLC) using hexane/CH_2Cl_2 (6:1) to afford **4** (0.56 g, 56% yield) and **5** (0.16 g, 28% yield) as stable dark red solids.

Synthesis of 2,4-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-($SiMe_3C_2$)\}]$_2C_4H_2S$ (6): The same procedure as described above was applied in the preparation of this compound from **3** (0.82 g, 0.97 mmol), dppm (1.94 mmol) and Me_3NO (3.88 mmol). After the solvent had been removed under vacuum, the residue was purified by the same manner. Complex **6** (0.48 g, 33% yield) was obtained as air-stable dark green solid.

Synthesis of 2-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-($SiMe_3C_2$)\}]-4-(Br)-C_4H_2S (2′): A solution of **1′** (0.27 g, 0.50 mmol) and dppm (0.50 mmol) in hexane (50 mL) was prepared. Trimethylamine *N*-oxide (0.11 g, 1.00 mmol) was added and the reaction mixture, monitored by FT-IR spectroscopy, stirred at 45 °C for 4 d. After the solvent had been removed under vacuum, the residue was purified by thin-layer chromatography (TLC) using hexane/CH_2Cl_2 (3:1) to afford **2′** (0.33 g, 77% yield) as stable dark red solid.

Synthesis of 2-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-($SiMe_3C_2$)\}]-4-($C{\equiv}CH$)-C_4H_2S (7) and 2-($C{\equiv}CH$)-4-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-($SiMe_3C_2$)\}]C_4H_2S (8): An equimolecular solution of **4** and **5** in MeOH saturated with KOH was stirred for 24 h at 25 °C. Then the solvent was removed under vacuum and the residue extracted with several portions of Et_2O and purified by chromatography on a hexane-packed silica column (200 g) using hexane/CH_2Cl_2 (1:1) as eluent to afford **7** (48% yield) together with **8** (50% yield) as unstable solids.

Synthesis of 2,4-[$Co_2(CO)_4$(μ-dppm)\{μ_2-η^2-(HC_2)\}]$_2C_4H_2S$ (9): To a solution of **6** (0.48 g, 0.32 mmol) in wet THF (50 mL) was added TBAF (2.56 mL, 1.0 M in THF, 2.56 mmol) and the mixture stirred at room temp. for 24 h. After the solvent had been removed under vacuum, the product was purified by chromatography on a hexane-packed silica column using hexane/CH_2Cl_2 (1:1) as eluent to afford **9** (0.27 g, 62% yield) as unstable dark purplish-red solid.

X-ray Data Collection, Structure Determination and Refinement of 2′: Dark red crystals were obtained by recrystallisation of the complex from CH_2Cl_2/hexane mixtures. A summary of selected crystallographic data for **2′** is given in Table 5. A red single crystal of approximate dimensions 0.25 × 0.12 × 0.09 mm with prismatic shape was mounted on a glass fibre and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd. rotating anode (Cu-K_α radiation, λ = 1.54178 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA.[32] X-ray data were collected at 100 K, with a combination of several runs at different ϕ and 2θ angles. The data were collected using 0.3° wide ω scans, crystal-to-detector distance of 4.0 cm. The raw intensity data frames were integrated with the SAINT program,[33] which also applied corrections for Lorentz and polarization effects. The substantial redundancy in data allowed empirical absorption corrections[34] to be applied using multiple measurements of symmetry-equivalent reflections. A total number of 24250 reflections were collected, and 6989 independent reflections remained after merging R_{int} = 0.0358. The unit-cell parameters were obtained by full-matrix least-squares refinements of the complete data set. The structure was solved and refined using the SHELXTL/PC V 6.10 package.[35] The structure was solved by direct methods, refinement by full-matrix least squares on F^2 using all data (negative intensities included). Weighted R factors (R_w) and all goodness-of-fit (S) are based on F^2; conventional R factors (R) are based on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All scattering factors and anomalous dispersions factors are contained in the SHELXTL 6.10 program library. The H-atom parameters were calculated and atoms were constrained as riding atoms with U_{iso} 20% larger than those of the corresponding C atoms for the phenyl H atoms and 50% larger for the methyl H atoms. CCDC-641070 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Table 3 contains selected bond lengths and angles. Figure 1 presents a molecular diagram of **2′**.

Table 5. Crystal data and structure refinement for compound **2′**.

Empirical formula	$C_{38}H_{33}BrCo_2O_4P_2SSi$
Formula mass	873.50
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit-cell dimensions	a = 16.5425(2) Å
	b = 12.19370(10) Å
	c = 19.1305(2) Å
	β = 93.2610(10)°
Volume	3852.65(7) Å^3
Z	4
Density (calcd.)	1.506 Mg/m^3
Absorption coefficient	9.859 mm^{-1}
F(000)	1768
Crystal size	0.25 × 0.12 × 0.09 mm
θ range for data collection	3.44–70.52°
Index ranges	$-17 \le h \le 19$, $-14 \le k \le 13$, $-21 \le l \le 22$
Reflections collected	24250
Independent reflections	6989 [R(int) = 0.0358]
Completeness to θ = 70.52°	94.9%
Absorption correction	SADABS v. 2.03
Refinement method	full-matrix least squares on F^2
Data/restraints/parameters	6989/0/574
Goodness-of-fit on F^2	1.032
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0330, $wR2$ = 0.0851
R indices (all data)	R_1 = 0.0369, $wR2$ = 0.0874
Largest diff. peak/hole	1.213/–0.798 e Å^{-3}

Supporting Information (see footnote on the first page of this article): IR, UV/Vis, MS, ^{1}H, ^{13}C, ^{31}P NMR spectra and elemental analysis of **1**–**9**, **1′**–**2′**, **2,4T** and **2,4T′**.

Acknowledgments

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