



The effect of thiophene ring substitution position on the properties and electrochemical behaviour of alkyne–dicobaltcarbonylthiophene complexes

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ARTICLE INFO

Article history:

Received 18 June 2008

Received in revised form 31 July 2008

Accepted 1 August 2008

Available online 12 August 2008

Keywords:

Thiophene

Carbonylcobalt complexes

Electrochemistry

ABSTRACT

A large number of $\text{Co}_2(\text{CO})_6^-$ and $\text{Co}_2(\text{CO})_4(\text{L-L})$ -substituted alkyne complexes (L-L = *dppa* and *dmpm*) have been prepared, characterized and studied by cyclic and square-wave voltammetry. In this paper we report a comparative electrochemical study of 2,5-, 2,4-, 3,4- and 2,3-bis(trimethylsilylethynyl)thiophene dicobalt substituted alkyne complexes, in order to evaluate the extent of the electronic interaction between the “ Co_2C_2 ” redox centres depending on the position of the alkynyl substituent on the thiophene ring.

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1. Introduction

Molecules containing redox-active centres linked by a bridging ligand capable of transmitting electronic effects have become an area of significant research during the last two decades [1]. The interest in these kinds of complexes is due to their possible applications in materials science as non-linear optical systems [2], quasi-one-dimensional conductors [3], electroluminescent devices [4], “molecular” wires [5,6] or as electrochromic devices and electrochemical sensors [7]. Electronic communication through such molecules is often evaluated by the redox response of electroactive groups placed at their termini. The properties of such materials can be modified by changing the metal fragments and/or the bridging ligands [5b,5d,8].

As alkynyl or polyynediyl bridging ligands have been shown to be efficient in allowing the passage of electronic effects between redox-active centres [8e,f,9,10], and therefore the electronic properties and the use of a thiophene-based diethynyl ligand should lower the energy barriers and facilitate electron transfer, we have recently reported the reactivity and the electrochemical behaviour of 2,5- [10b] and 2,4-bis(trimethylsilylethynyl)thiophene [11] derivatives, comparing the effects of the substitution position of the $-\text{C}\equiv\text{C}-\text{SiMe}_3$ groups on the thiophene ring. These results encouraged us to study the analogous 2,3- and 3,4-bis(trimethylsilylethynyl)thiophene ligands that in contrast with the well-studied 2,5-bis(trimethylsilylethynyl)thiophene have received little

attention [12]. Compounds in the present work contain substituents on adjacent positions of the thiophene ring, thus in addition to electronic effects, steric effects are also to be expected.

2. Experimental

2.1. Reagents and general techniques

All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free argon. All solvents for synthetic use were dried and distilled, under an argon atmosphere, by standard procedures [13].

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). 3,4- and 2,3-dibromothiophene (Lancaster Synthesis Inc.); $\text{Me}_3\text{SiC}\equiv\text{CH}$ (TMSA), $\text{Co}_2(\text{CO})_8$, KOH (Fluka); CuI, a solution 1.0 M of tetrabutylammonium fluoride (TBAF) in THF (Aldrich); 1,2-bis(dimethylphosphino)methane (*dmpm*) (Strem); 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. Compounds $\text{Pd}(\text{PPh}_3)_4$ [14] and 1,2-bis(diphenylphosphino)amine (*dppa*) [15] were prepared according to the literature. The ^1H , $^1\text{H}\{^31\text{P}\}$, $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and HMQC and HMBC data were recorded with Bruker AMX-300 and 500 instruments. Chemical shifts were measured relative to 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

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Unicam UV 4 UV-Vis spectrophotometer. Mass spectra were measured with a VG-Autospec mass spectrometer for FAB and EI and with a Reflex III Bruker mass spectrometer for MALDI-TOF. Spectroscopy data are available as [Supplementary material](#). Electrochemical measurements were carried out with a computer driven Par Mo. 273 electrochemistry system in a three-electrode cell under nitrogen atmosphere 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 referred to the Fc^+/Fc^* couple. Under the actual experimental conditions, $E_{1/2}$ of the ferrocene couple (Fc^+/Fc) was +0.55 V versus Fc^+/Fc^* in CH_2Cl_2 solution. Controlled potential electrolysis of **A3** was performed at 0.8 V and one mole of electrons per mole of **A3** 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.

2.2. Synthesis of 3,4- and 2,3-bis(trimethylsilylethynyl)thiophene (**A** and **C**) and X-(trimethylsilylethynyl)-Y-bromothiophene (X = 3, Y = 4 (**B**) and X = 2, Y = 3 (**D**))

To a solution of 3,4- or 2,3-dibromothiophene (3.0 g, 12.4 mmol) in Et_3N (100 mL) was added at 0 °C, $\text{Pd}(\text{PPh}_3)_4$ (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 r.t. for 1/2 h and finally at 75 °C for 20 days. The solvent was removed under reduced pressure and the residue dissolved in Et_2O (100 mL) and washed 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. From 3,4-dibromothiophene, **A** (1.03 g, 30% yield) and **B** (1.12 g, 35% yield) were obtained as stable yellow oils. From 2,3-dibromothiophene, **C** (0.96 g, 28% yield) and **D** (1.32 g, 41% yield) were obtained as stable yellow oils.

2.3. Synthesis of X-[$\text{Co}_2(\text{CO})_6\{\mu_2-\eta^2-(\text{SiMe}_3\text{C}_2)\}$]-Y-($\text{Me}_3\text{SiC}\equiv\text{C}$) $\text{C}_4\text{H}_2\text{S}$ (X = 3, Y = 4 (**A1**); X = 2, Y = 3 (**C1**) and X = 3, Y = 2 (**C2**))

To a solution of **A** (0.90 g, 3.26 mmol) or **C** (0.45 g, 1.63 mmol) in hexane (100 mL) was added 2 equiv. of $\text{Co}_2(\text{CO})_8$. The reaction was monitored by FT-IR and ^1H NMR spectroscopy until the signals of the parent compounds **A** or **C** and $\text{Co}_2(\text{CO})_8$ had disappeared. After the mixture had been stirred at r.t. for 1 h, the solvent was removed under vacuum and the residue purified by column chromatography with hexane. From **A**, **A1** (1.68 g, 92% yield) was obtained as an unstable red solid. From **C**, **C1** (0.55 g, 60% yield) together with **C2** (0.30 g, 33% yield) were obtained as unstable solids.

2.4. Synthesis of X-[$\text{Co}_2(\text{CO})_6\{\mu_2-\eta^2-(\text{SiMe}_3\text{C}_2)\}$]-Y-(Br)- $\text{C}_4\text{H}_2\text{S}$ (X = 3, Y = 4 (**B1**) and X = 2, Y = 3 (**D1**))

By a similar procedure as described above, from **B** or **D** (0.75 g, 2.89 mmol) and 1 equiv. of $\text{Co}_2(\text{CO})_8$. After the solvent had been removed under vacuum, the product was eluted with hexane on a silica column. From **B**, **B1** (1.42 g, 90% yield) was obtained as an unstable red solid. From **D**, **D1** (1.45 g, 92% yield) was obtained as an unstable red solid.

2.5. Synthesis of X-[$\text{Co}_2(\text{CO})_4(\mu\text{-dppa})\{\mu_2-\eta^2-(\text{SiMe}_3\text{C}_2)\}$]-Y-($\text{Me}_3\text{SiC}\equiv\text{C}$) $\text{C}_4\text{H}_2\text{S}$ (X = 3, Y = 4 (**A2**); X = 2, Y = 3 (**C3**) and X = 3, Y = 2 (**C4**))

To a solution of **A1** (0.90 g, 1.60 mmol) or a solution containing **C1** and **C2** (0.75 g, 1.33 mmol in 1.8:1 ratio) in hexane (100 mL) was added 1 equiv. of dppa and 2 equiv. of trimethylamine N-oxide, in each case. The reaction mixture, monitored by FT-IR spectroscopy until the $\nu_{\text{C}\equiv\text{O}}$ bands of the parent complex had disappeared, was stirred at 45 °C for 5 days. Finally, the solvent was removed under vacuum. From **A1**, the residue was purified by chromatography on a hexane-packed silica column using hexane/ CH_2Cl_2 (2:1) to afford **A2** (0.90 g, 63% yield) as a stable dark red solid in addition to **A** (22.1 mg, 5% yield). From **C1** and **C2**, the residue was purified by thin-layer chromatography (TLC) using hexane/ CH_2Cl_2 (3:1) to afford **C3** (0.27 g, 23% yield) and **C4** (0.12 g, 10% yield) as stable dark red solids in addition to **C** (0.15 g, 41% yield).

2.6. Synthesis of X-[$\text{Co}_2(\text{CO})_4(\mu\text{-dppa})\{\mu_2-\eta^2-(\text{SiMe}_3\text{C}_2)\}$]-Y-(Br)- $\text{C}_4\text{H}_2\text{S}$ (X = 3, Y = 4 (**B2**) and X = 2, Y = 3 (**D2**))

The same procedure as describe above was applied in the preparation of these compounds from **B1** or **D1** (0.27 g, 0.50 mmol), dppa (0.19 g, 0.50 mmol) and Me_3NO (0.11 g, 1.00 mmol). 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 (3:1). From **B1**, **B2** (0.30 g, 70% yield) was obtained as a stable dark red solid in addition to **B** (5.1 mg, 4% yield). From **D1**, **D2** (0.20 g, 47% yield) was obtained as a stable dark red solid in addition to **D** (40 mg, 31% yield).

2.7. Synthesis of 3-[$\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})\{\mu_2-\eta^2-(\text{SiMe}_3\text{C}_2)\}$]-4-($\text{Me}_3\text{SiC}\equiv\text{C}$) $\text{C}_4\text{H}_2\text{S}$ (**A3**)

By a similar procedure as described above, from **A1** (0.75 g, 1.33 mmol), dmpm (0.18 g, 0.21 mL, 1.33 mmol) and Me_3NO (0.30 g, 2.66 mmol). The reaction mixture, monitored by FT-IR spectroscopy until the $\nu_{\text{C}\equiv\text{O}}$ bands of the parent complex had disappeared, was stirred at r.t. for 24 h and then at 45 °C for one more day. After the solvent was removed under vacuum, the product was purified by chromatography on a hexane-packed silica column using hexane/ CH_2Cl_2 (2:1) to afford **A3** (0.36 g, 42% yield) as a stable red solid in addition to **A** (77.4 mg, 21% yield).

2.8. Synthesis of X-[$\text{Co}_2(\text{CO})_4(\mu\text{-L-L})\{\mu_2-\eta^2-(\text{SiMe}_3\text{C}_2)\}$]-Y-($\text{C}\equiv\text{CH}$) $\text{C}_4\text{H}_2\text{S}$ (X = 3, Y = 4, L-L = dppa (**A4**) or dmpm (**A5**) and X = 2, Y = 3, L-L = dppa (**C5**))

A solution of **A2** (0.35 g, 0.39 mmol), **A3** (0.34 g, 0.53 mmol) or **C3** (0.25 g, 0.28 mmol) in MeOH saturated with KOH was stirred at r.t. for 24 h. 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 using hexane/ CH_2Cl_2 (1:1) or by thin-layer chromatography (TLC) using hexane/ CH_2Cl_2 (1.5:1). From **C3**, **C5** (87.3 mg, 38% yield) was obtained as an unstable reddish solid. From **A2** and **A3**, **A4** (0.15 g, 48% yield) and **A5** (0.14 g, 46% yield) were obtained, respectively, as unstable red solids. **A4** was also obtained in 39% yield when TBAF (0.44 mL, 1.0 M in THF, 0.44 mmol) was added to a solution of **A2** (0.20 g, 0.22 mmol) in THF/MeOH (10:1), the mixture was stirred at r.t. for 24 h and subsequent chromatography with hexane/ CH_2Cl_2 (1:1) on a silica column was performed.

2.9. Synthesis of 3-[Co₂(CO)₄(μ-dppa){μ₂-η²-(HC₂)}]₂-4-(C≡CH)C₄H₂S (A6)

To a solution of **A2** (0.35 g, 0.39 mmol) in wet THF (100 mL) was added TBAF (1.95 mL, 1.0 M in THF, 1.95 mmol) and the mixture stirred at r.t. for 24 h. After the solvent had been removed under vacuum, the residue was purified by chromatography on a hexane-packed silica column using hexane/CH₂Cl₂ (1:1) and then by thin-layer chromatography (TLC) using hexane/CH₂Cl₂ (4:3), to afford **A6** (0.16 g, 55% yield) as an unstable purple solid. This compound has also been obtained from **A4**, under the same conditions, in a similar yield.

2.10. Synthesis of 3-[Co₂(CO)₄(μ-dppa){μ₂-η²-(HC₂)}]₂-4-[Co₂(CO)₆{μ₂-η²-(HC₂)}]C₄H₂S (A7)

To a solution of **A6** (0.15 g, 0.20 mmol) in hexane (50 mL) was added 1 equiv. of Co₂(CO)₈. The reaction was monitored by FT-IR spectroscopy and the mixture was stirred at r.t. for 1 h. After the solvent had been removed under vacuum, the product was purified by chromatography on a hexane-packed silica column using hexane/CH₂Cl₂ (2:1) to afford **A7** (0.18 g, 87% yield) as an unstable dark red-purple solid.

2.11. X-ray data collection, structure determination and refinement

Dark red crystals of **A2**, **B2** and **D2** were grown by slow evaporation of their respective solutions in *n*-hexane–CH₂Cl₂ at r.t. Suitable crystals were 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 Kα radiation, λ = 1.54178 Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA [16]. The structures were solved and refined using the SHELXTL/PC V 6.10 package [17]. The structures were solved by direct methods, refinement was by full-matrix least-squares on F² using all data (negative intensities included). The H atom parameters were calculated and atoms were constrained as riding atoms with U isotropic 20% larger than those of the corresponding C-atoms for the phenyl H-atoms and the N–H atom, and 50% larger for the methyl H-atoms. CCDC-653921 (**A2**), CCDC-653925 (**B2**) and CCDC-682712 (**D2**) contain the supplementary crystallo-

graphic data for this paper. Final positional parameters, anisotropic thermal parameters, hydrogen atom parameters and structure amplitudes for **A2**, **B2** and **D2** are available as Supplementary material. Crystallographic details are collected in Table 5, while important bond lengths and angles are summarized in Table 6 (for **A2**), Table 7 (for **B2**) and Table 8 (for **D2**). ORTEP plots indicating the atom-labelling schemes are given in Fig. 2 (**A2**), Fig. 3 (**B2**) and Fig. 4 (**D2**).

3. Results and discussion

3.1. Synthesis and spectroscopic characterization

A [12a] and **C** [12b] have been synthesized from coupling reactions of 3,4- and 2,3-dibromothiophene, respectively, with excess of TMSA in the presence of Pd(PPh₃)₄, CuI and triethylamine. In the Pd–Cu catalyzed cross-coupling reactions it is known that the oxidative addition of the organic electrophile to the active Pd(0) catalyst is the critical step for the catalytic process [18]. In agreement with this, the thiophene positions more suitable to an oxidative addition are 2 and 5. Thus, from the less reactive starting materials 3,4- and 2,3-dibromothiophene, we have obtained the desired dialkynyl organic ligands in addition to the respective bromoderivatives, **B** [19] and **D**. Also, the reaction from 2,6-dibromopyridine [20], under Sonogashira coupling conditions, gave reasonable yields of both, the partially and fully substituted compounds containing the TMSA group.

A–D have been completely characterized by spectroscopic data, details of which are given as Supplementary material. IR spectra show weak absorption bands, typically ν_{C≡C} stretches of the alkynyl units, in the characteristic range of diynyl complexes (two ν_{C≡C} stretches at ca. 2060–2200 cm⁻¹) and monoynyl complexes (one ν_{C≡C} stretch at ca. 2090–2150 cm⁻¹). The ¹H NMR spectra exhibit one singlet signal for **A** and two doublet signals for **B**, **C** and **D** due to the thiophene ring protons, with coupling constants that are consistent with their chemical formulae. In the ¹³C NMR spectra the signals belonging to the thiophene ring (C₂, C₃, C₄ and C₅) and the alkynyl units (C₆, C₇, C₈ and C₉) can be observed, and the assignments were made on the basis of the δ values and NMR two-dimensional experiments (HMBC and HMQC). See Schemes A–D for atomic labelling and Tables 1–4 for NMR data.

The C₃–C₄ bond in a thiophene ring is known to have less double bond character than the C₂–C₃ bond [21]. As a consequence, the overall conjugation of 3,4-bis(trimethylsilylethynyl)thiophene is expected to be lower than in 2,5-, 2,3- and 2,4-bis(trimethylsilylethynyl)thiophene. These arguments are supported by the electronic absorption spectra for the ligands (Fig. 1). It can be observed that these molecules have λ_{max} at 331 [22], 311 and 277 nm [11], respectively. However, λ_{max} for 3,4-bis(trimethylsilylethynyl)thiophene (258 nm) is significantly blue-shifted, thus indicating a lesser overall conjugation in this molecule. A similar behaviour takes place in the case of the three diacetylenic dehydrothieno[18]annulenes studied by Sakar and Haley [23], where the electronic spectra of two of them (those in which the thiophene moieties are fused at the 2- and 3-positions to the [18]annulene core) exhibit λ_{max} values at around 428 nm, whereas this value for the third annulene (where two of the thiophene rings are fused to the macrocycle through the 3- and 4-positions) is significantly blue-shifted (401 nm), indicating a lesser overall conjugation as discussed above.

Co₂(CO)₆-substituted alkyne complexes were obtained by direct reaction between Co₂(CO)₈ and the corresponding organic ligand. When 2 equiv. of Co₂(CO)₈ were added to **A** and **C**, only the mono-substituted-cobalt-alkyne compounds could be obtained (Schemes A and C). However, when Co₂(CO)₈ was added to **A6**, complex **A7**

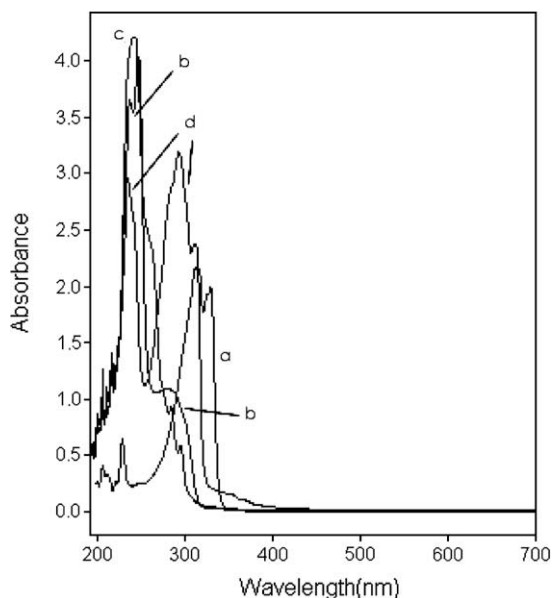


Fig. 1. UV-Vis spectra (CH₂Cl₂, nm) for the organic ligands 2,5- (a), 2,4- (b), 3,4- (c) and 2,3-bis(trimethylsilylethynyl)thiophene (d).

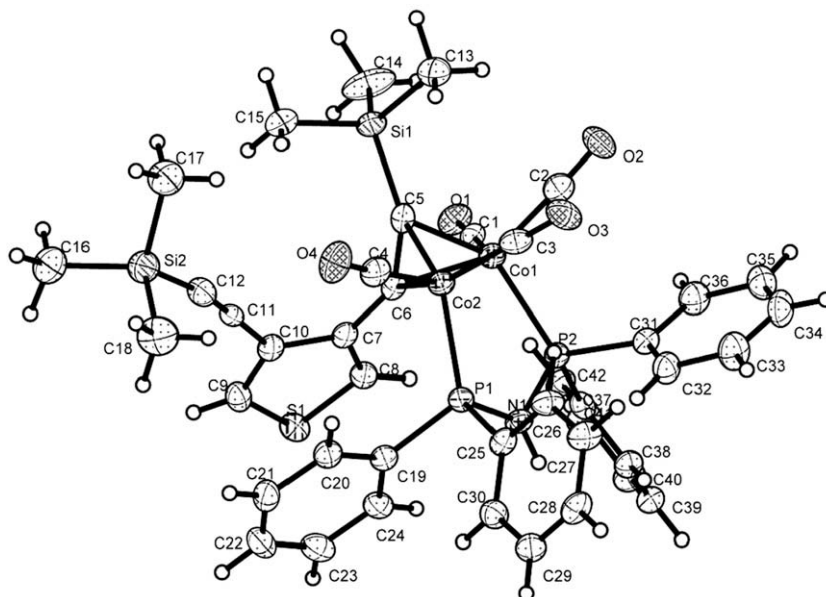


Fig. 2. ORTEP diagram of **A2**, with 50% ellipsoids.

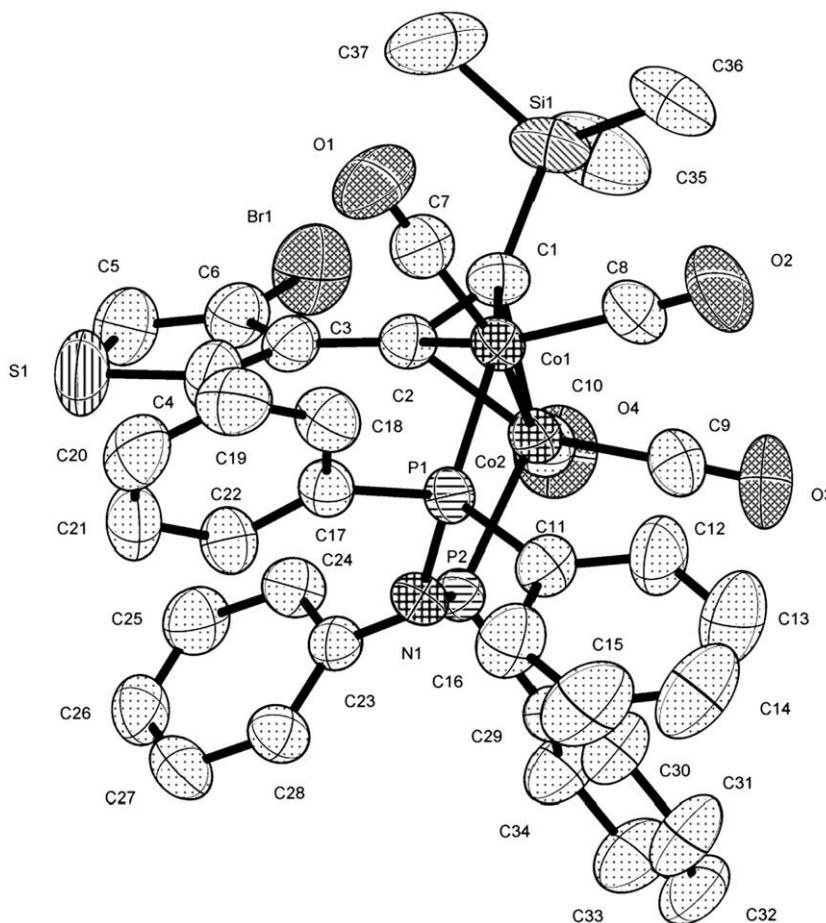


Fig. 3. ORTEP diagram of **B2**, with 50% ellipsoids. Hydrogen atoms have been removed for clarity.

was obtained in 87% yield under the same conditions (Scheme A). It can be explained from the steric hindrance of the $-\text{SiMe}_3$ groups. Thus, the selective synthesis of **A1**, **C1** and **C2** indicates that the addition of " $\text{Co}_2(\text{CO})_6$ " units to alkynes can be controlled. Clearly

one of the factors that influences the degree and position of the metallation is the bulk of the substituents on the alkyne [24]. By a similar manner, it can be observed [10a] that $\text{Co}_2(\text{CO})_8$ reacts with the $-\text{C}\equiv\text{C}-$ free triple-bond in $\text{Co}_2(\text{CO})_4(\text{dppm})\{\mu_2-\eta^2-(\text{Me}_3-$

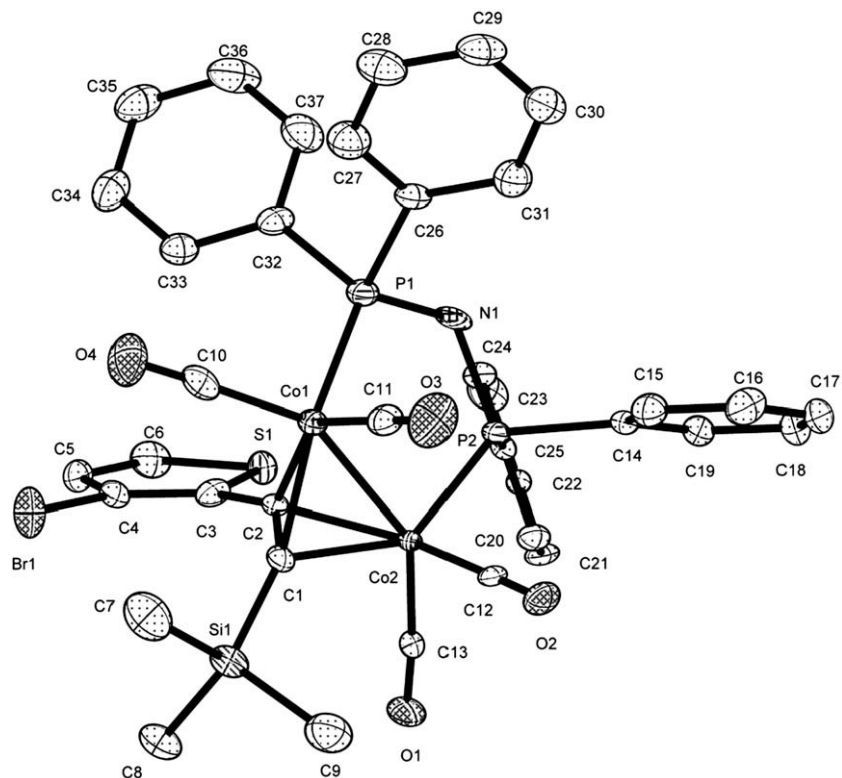
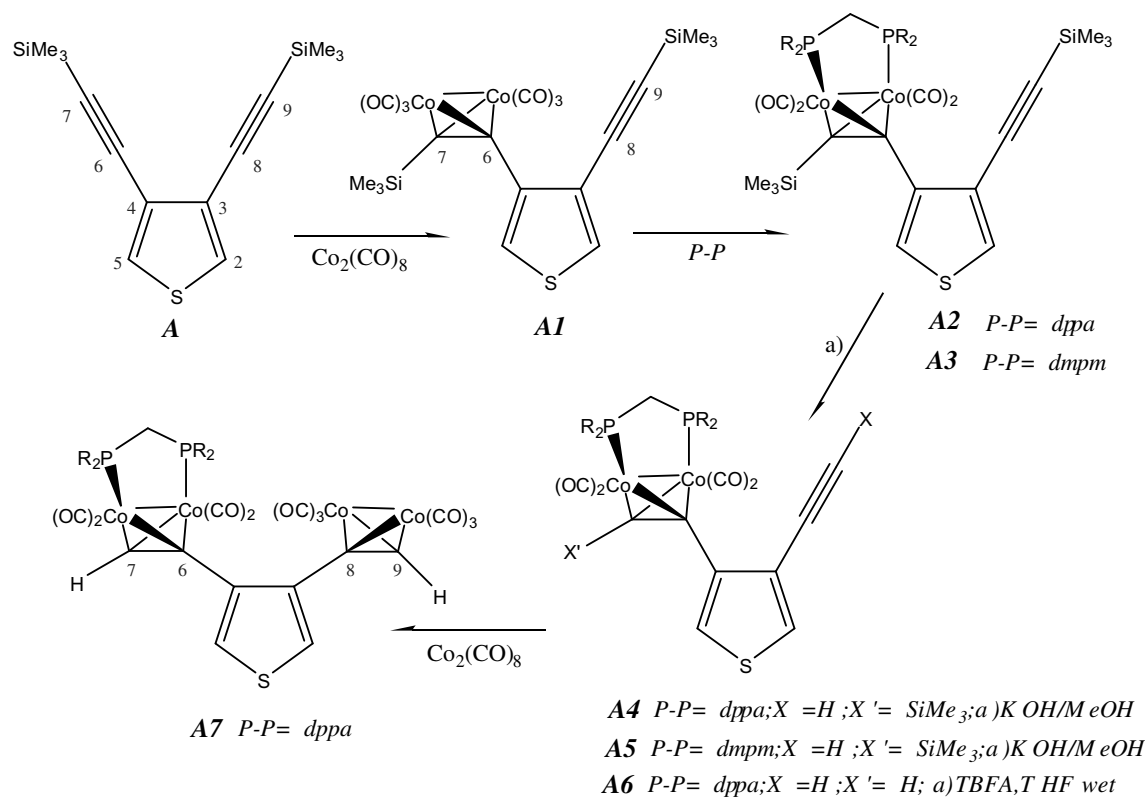


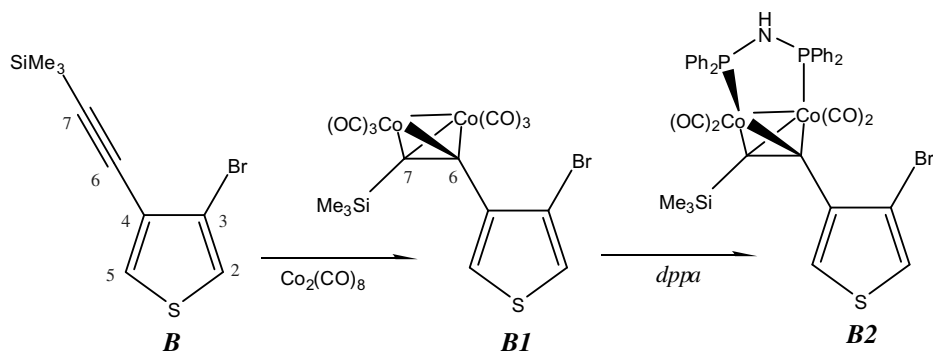
Fig. 4. ORTEP diagram of **D2**, with 50% ellipsoids. Hydrogen atoms have been removed for clarity.



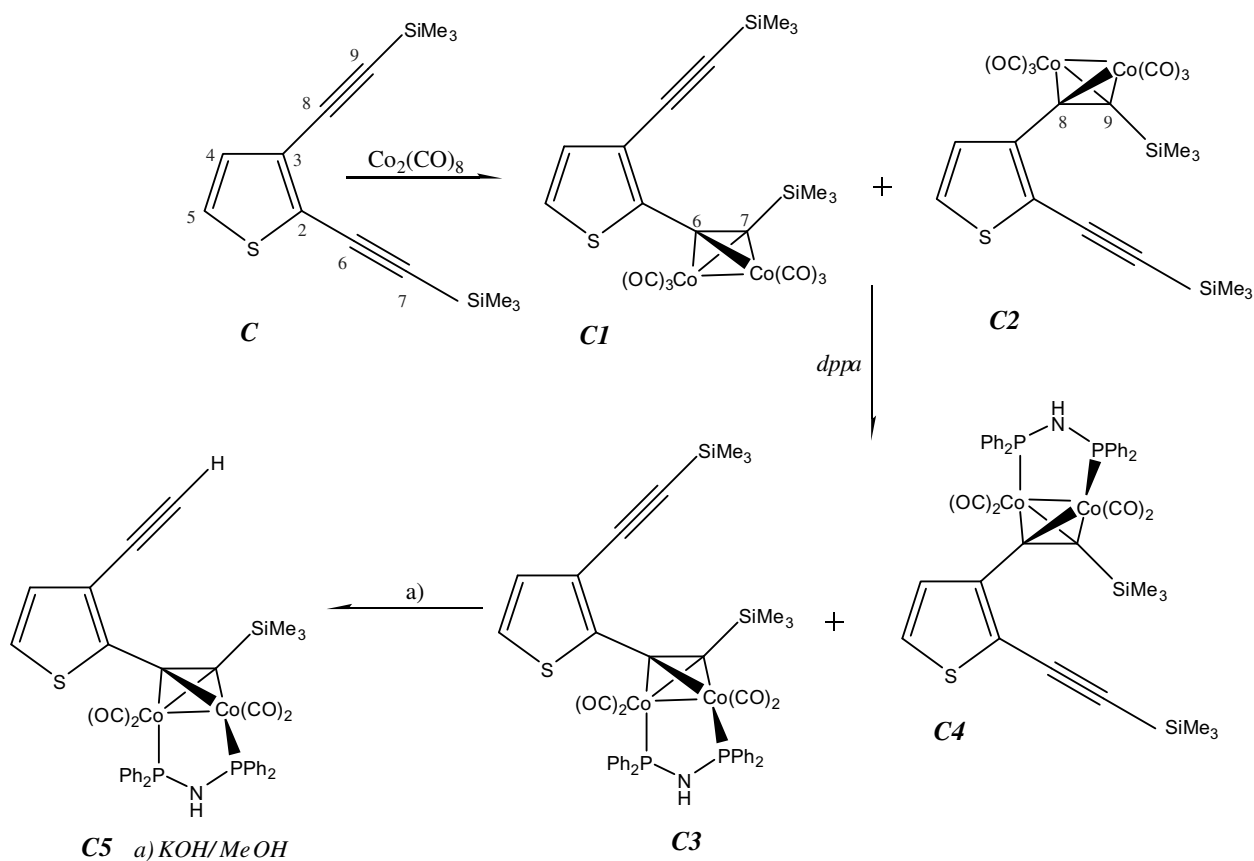
Scheme A.

$\text{SiC}_2\text{)}\text{C}\equiv\text{CX}$ when X = H; however, when X = SiMe₃ the reaction does not take place.

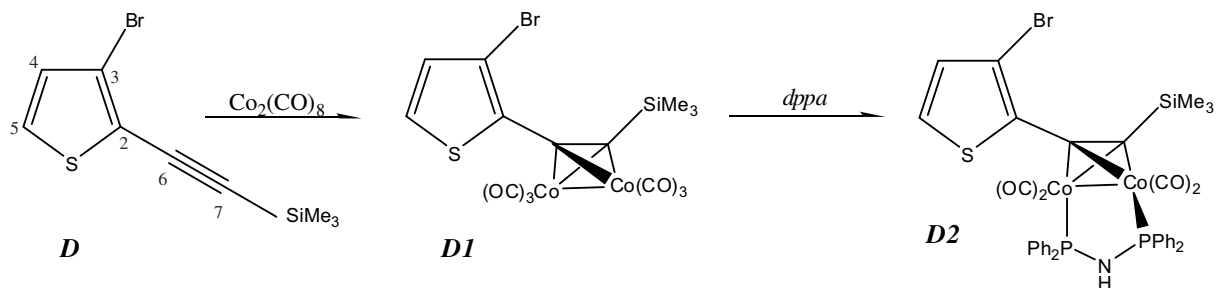
On the basis of the isolated yield for **C1** (60%) and **C2** (33%), it can be observed that the preference of the Co₂(CO)₆ units for coor-



Scheme B.



Scheme C.



Scheme D.

Table 1¹H NMR (300 MHz, CDCl₃, 25 °C, ppm) data for **A**, **B**, **A1–A7** and **B1–B2**

	H ₅	H ₂	–C≡CH	–C ₆ –C ₇ H	–C ₈ –C ₉ H	–C≡CSiMe ₃	–C–CSiMe ₃
A	7.39 (s) 7.44 (s) ^a 7.67 (s) ^b	=H ₅	–	–	–	0.25 (s) 0.27 (s) ^a 0.25 (s) ^b 0.27 (s)	–
B	7.47 (d) <i>J</i> _{HH} = 3.4 Hz 7.51 (d) ^a <i>J</i> _{HH} = 3.4 Hz 7.78 (d) ^b <i>J</i> _{HH} = 3.3 Hz	7.21 (d) <i>J</i> _{HH} = 3.4 Hz 7.27 (d) ^a <i>J</i> _{HH} = 3.4 Hz 7.58 (d) ^b <i>J</i> _{HH} = 3.3 Hz	–	–	–	0.26 (s) ^a 0.24 (s) ^b	–
A1	7.29 (d) <i>J</i> _{HH} = 3.3 Hz	7.57 (d) <i>J</i> _{HH} = 3.3 Hz	–	–	–	0.21 (s)	0.41 (s)
B1	7.44 (d) <i>J</i> _{HH} = 3.2 Hz	7.33 (d) <i>J</i> _{HH} = 3.0 Hz	–	–	–	–	0.42 (s)
A2	6.01 (d) <i>J</i> _{HH} = 3.5 Hz	7.17 (d) <i>J</i> _{HH} = 3.5 Hz	–	–	–	0.15 (s)	0.37 (s)
B2	6.94 (d) <i>J</i> _{HH} = 3.6 Hz	6.21 (d) <i>J</i> _{HH} = 3.6 Hz	–	–	–	–	0.40 (s)
A3	6.80 (d) <i>J</i> _{HH} = 3.4 Hz	7.53 (d) <i>J</i> _{HH} = 3.4 Hz	–	–	–	0.17 (s)	0.30 (s)
A4	6.05 (d) <i>J</i> _{HH} = 3.4 Hz	7.19 (d) <i>J</i> _{HH} = 3.3 Hz	3.03 (s)	–	–	–	0.37 (s)
A5	6.82 (d) <i>J</i> _{HH} = 3.4 Hz	7.53 (d) <i>J</i> _{HH} = 3.4 Hz	3.12 (s)	–	–	–	0.29 (s)
A6	7.50–7.35	7.50–7.35	3.14 (s)	5.73 (t) <i>J</i> _{PH} = 9.3 Hz	–	–	–
A7	7.60–7.39	7.60–7.39	–	5.31 (t) <i>J</i> _{PH} = 10.5 Hz	5.75 (s)	–	–

^a CD₂Cl₂.^b Acetone-*d*₆.

dination at the alkyne in 2-position of the thiophene ring is almost two times greater than that for the 3-position. This preference is also observed in the synthesis of the analogous complexes 2-[Co₂(CO)₆{μ₂-η²-(SiMe₃C₂)}]–4-(Me₃SiC≡C)C₄H₂S and 2-(Me₃SiC≡C)–4-[Co₂(CO)₆{μ₂-η²-(SiMe₃C₂)}]C₄H₂S [11]. This result can be explained by electronic factors, as judged by the ¹³C NMR shifts for the alkyne C-atoms in **C** (Table 4).

In order to enhance the stability of the dicobalt units by bridging effect between the two metal atoms, we have synthesized complexes containing two different phosphine ligands, dp_{pp}a and dmpm. Co₂(CO)₄(L–L)-substituted alkyne complexes were prepared by substitution reaction of two carbonyl ligands in the presence of Me₃NO at the Co₂(CO)₆ units of the parent complexes (Schemes A–D).

By taking advantage of the preferential desilylation of a non-coordinated alkyne group, **A2**, **A3** and **C3** were accomplished by treatment with saturated solutions of KOH in degassed methanol at room temperature to give the terminal diyne compounds **A4**, **A5** and **C5**, respectively. When **A2** was prepared using 2 equiv. of Bu₄NF in THF/MeOH, compound **A4** was isolated too, but in less yield (39%) (see Section 2). Complex **A6** was obtained from **A2** or **A4** when stronger desilylation conditions were used (5 equiv. of Bu₄NF in wet THF). The analogous diprotonated dmpm-compound was synthesized by similar conditions from **A5** and could be observed by IR and ¹H NMR spectroscopies (IR (THF, cm^{−1}): ν_{≡CH} 3303.3 (m), ν_{CO} 2016.5 (s), 1987.2 (vs), 1958.3 (s), 1941.2 (sh). ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.46 (d, *J*_{HH} = 3.2 Hz, H₂), 7.42 (d, *J*_{HH} = 3.3 Hz, H₅), 5.81 (t, *J*_{PH} = 7.6 Hz, –C₇H), 3.18 (s, ≡CH), 2.15 (m, 1H, ABXY, –CH₂–), 2.00 (m, 1H, ABXY, –CH₂–), 1.54 (m, 6H, 2 –PMe), 1.46 (m, 6H, 2 –PMe) ppm). Finally, after being purified by thin-layer chromatography (TLC) using hexane/CH₂Cl₂ (4:3) as eluent, this compound decomposed and it could not be isolated.

All these compounds have been characterized by spectroscopic data (IR, UV–Vis, ¹H, ¹H{³¹P}, ¹³C{¹H}, ³¹P{¹H} NMR and MS) and elemental analysis, details of which were given as [Supplementary material](#).

The IR spectra of Co₂(CO)₆-substituted alkyne complexes exhibit three strong absorptions in the carbonyl stretching region (2090–2022 cm^{−1}); in phosphine-substituted alkyne complexes these absorptions lie at lower frequencies and the spectral patterns are similar to those observed for previously reported cobalt-alkyne and cobalt-substituted-alkyne complexes [8e–f,10,11,20,25–27]. For the dimetallated compound **A7**, the IR carbonyl region results from the overlap of the IR carbonyl stretching bands corresponding to each core. Thus, **A7** exhibits five strong absorptions. The three at lower frequencies (2026, 1995 and 1970 cm^{−1}) belong to the “Co₂(CO)₄(dp_{pp}a)” unit and the two at higher frequencies (2090 and 2054 cm^{−1}) are due to the ‘Co₂(CO)₆’ unit. **A1**, **A2** and **A3** contain an uncomplexed C≡C triple-bond, which gives a ν_{C≡C} weak absorption between 2154 and 2150 cm^{−1}. For **A4**, **A5** and **A6** this value is not observed, but ν_{≡C–H} appears at ca. 3302 cm^{−1}. Similarly, **C1**, **C2**, **C3** and **C4** show a ν_{C≡C} weak absorption at ca.

Table 2¹H NMR (300 MHz, CDCl₃, 25 °C, ppm) data for **C**, **D**, **C1–C5** and **D1–D2**

	H ₅	H ₄	–C≡CH	–C≡CSiMe ₃	–C–CSiMe ₃
C	7.09 (d) <i>J</i> _{HH} = 5.3 Hz	6.96 (d) <i>J</i> _{HH} = 5.3 Hz	–	0.27 (s), 0.28 (s)	–
D	7.16 (d) <i>J</i> _{HH} = 5.4 Hz	6.93 (d) <i>J</i> _{HH} = 5.4 Hz	–	0.28 (s)	–
C1	7.11 (d) <i>J</i> _{HH} = 5.4 Hz	7.03 (d) <i>J</i> _{HH} = 5.4 Hz	–	0.22 (s)	0.41 (s)
D1	7.25 (d) <i>J</i> _{HH} = 5.3 Hz	6.98 (d) <i>J</i> _{HH} = 5.3 Hz	–	–	0.43 (s)
C2	7.14 (d) <i>J</i> _{HH} = 5.3 Hz	6.95 (d) <i>J</i> _{HH} = 5.3 Hz	–	0.23 (s)	0.39 (s)
D2	6.69 (d) <i>J</i> _{HH} = 5.4 Hz	6.60 (d) <i>J</i> _{HH} = 5.4 Hz	–	–	0.39 (s)
C3	6.55 (d) <i>J</i> _{HH} = 5.3 Hz	6.68 (d) <i>J</i> _{HH} = 5.3 Hz	–	0.14 (s)	0.37 (s)
C4	6.50 (d) <i>J</i> _{HH} = 5.3 Hz	5.95 (d) <i>J</i> _{HH} = 5.3 Hz	–	0.15 (s)	0.37 (s)
C5	6.58 (d) <i>J</i> _{HH} = 5.3 Hz	6.69 (d) <i>J</i> _{HH} = 5.3 Hz	3.10 (s)	–	0.36 (s)

Table 3
¹³C NMR (500 MHz, CDCl₃, 25 °C, ppm) data for **A**, **B**, **A1–A7** and **B1–B2**

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉
A	=C ₅	=C ₄	125.1 (s) 125.4 (s) ^a 125.7 (s) ^b	128.8 (s) 129.5 (s) ^a 130.6 (s) ^b	98.2 (s) 98.4 (s) ^a 99.2 (s) ^b	96.6 (s) 97.1 (s) ^a 96.8 (s) ^b	= C ₆	= C ₇
A1	133.6 (s)	123.6 (s)	138.7 (s)	124.8 (s)	95.7 (s br)	81.1 (s br)	100.1 (s)	99.6 (s)
A2	132.2 (s)	122.6 (s)	142.3 (t) <i>J</i> _{CP} = 3.5 Hz	124.2 (s)	95.7 (t) <i>J</i> _{CP} = 8.6 Hz	91.2 (t) <i>J</i> _{CP} = 11.2 Hz	100.8 (s)	98.1 (s)
A3	133.1 (s)	123.0 (s)	145.0 (t) <i>J</i> _{CP} = 4.1 Hz	121.8 (s)	97.3 (t) <i>J</i> _{CP} = 7.8 Hz	86.8 (t) <i>J</i> _{CP} = 10.1 Hz	100.1 (s)	98.9 (s)
A4	131.2 (s)	121.3 (s)	143.5 (t) <i>J</i> _{CP} = 3.5 Hz	124.3 (s)	95.2 (t) <i>J</i> _{CP} = 8.6 Hz	91.4 (t) <i>J</i> _{CP} = 11.1 Hz	79.5 (s)	82.1 (s)
A5	132.0 (s)	121.7 (s)	146.0 (t) <i>J</i> _{CP} = 3.7 Hz	121.8 (s)	96.7 (m) <i>J</i> _{CP} = 17.6 Hz	86.7 (m) <i>J</i> _{CP} = 9.4 Hz	79.1 (s)	82.5 (s)
A6	130.2 (s)	121.4 (t) <i>J</i> _{CP} = 3.1 Hz	144.8 (t) <i>J</i> _{CP} = 2.1 Hz	125.0 (t) <i>J</i> _{CP} = 5.6 Hz	86.2 (t) <i>J</i> _{CP} = 17.6 Hz	74.0 (t) <i>J</i> _{CP} = 9.4 Hz	79.2 (s)	80.5 (s)
A7	129.6 (s)	135.5 (t) <i>J</i> _{CP} = 3.2 Hz	141.1 (t) <i>J</i> _{CP} = 2.7 Hz	129.0 (t) <i>J</i> _{CP} = 5.9 Hz	86.0 (t) <i>J</i> _{CP} = 17.9 Hz	75.1 (t) <i>J</i> _{CP} = 10.1 Hz	81.8 (s)	74.7 (s)
B	122.7 (s) 123.5 (s) ^a 124.8 (s) ^b	113.8 (s) 113.9 (s) ^a 113.7 (s) ^b	124.6 (s) 124.9 (s) ^a 125.1 (s) ^b	129.6 (s) 130.3 (s) ^a 131.6 (s) ^b	97.8 (s) 98.1 (s) ^a 98.8 (s) ^b	97.7 (s) 98.0 (s) ^a 97.9 (s) ^b	–	–
B1	126.5 (s)	112.6 (s)	137.7 (s)	124.6 (s)	95.4 (s br)	82.1 (s br)	–	–
B2	125.3 (s)	111.7 (s)	140.9 (t) <i>J</i> _{CP} = 3.7 Hz	122.9 (s)	95.1 (t) <i>J</i> _{CP} = 8.9 Hz	91.4 (t) <i>J</i> _{CP} = 11.2 Hz	–	–

^a CD₂Cl₂.^b Acetone-*d*₆.**Table 4**
¹³C NMR (500 MHz, CDCl₃, 25 °C, ppm) data for **C**, **D**, **C1–C4** and **D1–D2**

	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉
C	127.1 (s)	127.5 (s)	129.3 (s)	125.7 (s)	98.6 (s)	103.5 (s)	96.2 (s)	98.8 (s)
C1	143.7 (s)	123.1 (s)	133.7 (s)	124.2 (s)	It is not observed	82.3 (m)	100.0 (s)	102.7 (s)
C2	121.5 (s)	140.6 (s)	130.0 (s)	126.4 (s)	97.4 (s)	107.4 (s)	95.4 (m)	80.9 (m)
C3	151.5 (m)	118.2 (s)	133.9 (s)	121.8 (s)		92.97 (m) 92.90 (m)	101.8 (s)	100.0 (s)
C4	117.0 (s)	145.6 (s)	134.2 (s)	124.3 (s)	99.0 (s)	105.4 (s)	95.5 (m)	93.0 (m)
D	120.8 (s)	116.6 (s)	129.9 (s)	126.9 (s)	95.5 (s)	103.4 (s)	–	–
D1	136.2 (s)	113.7 (s)	132.2 (s)	126.0 (s)	91.5 (m)	83.2 (m)	–	–
D2	142.5 (t) <i>J</i> _{CP} = 3.5 Hz	107.5 (s)	131.3 (s)	123.1 (s)	91.2 (t) <i>J</i> _{CP} = 8.2 Hz	92.6 (t) <i>J</i> _{CP} = 10.5 Hz	–	–

2143 cm⁻¹. As expected, for **C5** this $\nu_{C=C}$ value (2088 cm⁻¹) is lower. In addition, **C5** exhibits a ν_{C-H} absorption at ca. 3300 cm⁻¹.

All NMR data are consistent with overall geometry established in the solid state for **A2**, **B2** and **D2** (Figs. 2–4) and with the proposed structures (Schemes A–D) and comparable to those of the known cobalt-substituted 2,5- [10b] and 2,4-bis(trimethylsilylethynyl)thiophene [11] complexes. The ¹H and ¹³C{¹H} NMR data of all the complexes are summarized in Tables 1–4.

In ¹H NMR spectra, the chemical shifts for the SiMe₃ 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 in the C≡C triple-bond character [28]. Thus, the acetylenic proton of complexes **A4**, **A5** and **A6** (one “Co₂C₂” unit) appears as a singlet signal at ca. 3.10 ppm, while in **A7** (two “Co₂C₂” units) the coordination of Co₂(CO)₆ to the alkyne is evident from the downfield shift of the terminal proton in the ¹H NMR spectrum (at 5.75 ppm). In **A6** the –(C–C)_{coord}–H signal is coupled with the two chemically equivalent P-atoms and it appears as a triplet with ¹H–³¹P coupling constant of *J* = 9.3 Hz like in other similar compounds [10b,11,29]. This resonance can also be observed in **A7** as a triplet signal at a similar value. The ¹H NMR spectra of **A3** and **A5** show two doublet signal resonances of the thiophene protons together with those due to the methyl (at ca. δ = 1.45 and

1.35 ppm) and the diastereotopic protons of the methylene (at ca. δ = 2.20 and 1.96 ppm) of the dmpm ligand, which are coupled with the P-atoms, and they appear as double triplets with *J*_{HH} at ca. 13.4 Hz and *J*_{PH} at ca. 10.3 Hz. For dppe-complexes the proton of –NH group is coupled with the two chemically equivalent P-atoms and it appears as triplet with ¹H–³¹P coupling constant of *J* ≈ 6.1 Hz.

The ¹³C NMR chemical shifts of the carbonyl groups in all the complexes appear as one, two or three signals at around δ = 200, 204 and 207 ppm, suggesting that they are rapidly interchanging on the NMR scale. The unambiguous assignments of all carbon atoms has been carried out by using homonuclear and heteronuclear two-dimensional correlation spectroscopy experiments (HMOC and HMBC) and by comparison of their spectral data with those of the known cobalt-substituted 2,5- [10b] and 2,4-bis(trimethylsilylethynyl)thiophene [11] complexes. The carbon resonances of the free and coordinated acetylene carbon atoms were easily observed and their *J*_{CP} coupling constants values and chemical shifts show in the range of analogous compounds (δ = 74–101 ppm) (Tables 3 and 4) [8e–f,10,11,26b,30]. For **A2–A4** and **B2**, the C₄, C₆, and C₇ atoms display similar triplets with ¹³C–³¹P coupling constants of *J*_{CP} ≈ 10.9, 8.5 and 3.7 Hz, respectively. A similar behaviour is observed for the C₃, C₄, C₅, C₆ and C₇ atoms in **A6** and **A7** (Table 3).

Table 5
Crystal data and structure refinement for the compounds **A2**, **B2** and **D2**

	A2	B2	D2
Empirical formula	C ₄₂ H ₄₁ Co ₂ NO ₄ P ₂ SSi ₂	C ₃₇ H ₃₂ BrCo ₂ NO ₄ P ₂ SSi	C ₃₇ H ₃₂ BrCo ₂ NO ₄ P ₂ SSi
Formula weight	891.80	874.50	874.50
Temperature (K)	100(2)	293(2)	100(2)
Wavelength (Å)	1.54178	1.54178	1.54178
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Pbca</i>	<i>P2(1)/c</i>	<i>P2(1)/n</i>
Unit cell dimensions			
<i>a</i> (Å)	21.5580(3)	13.1423(3)	15.9429(2)
α (°)	90	90	90
<i>b</i> (Å)	13.3336(2)	22.6036(5)	12.24850(10)
β (°)	90	99.164(2)	99.0490(10)
<i>c</i> (Å)	29.3262(3)	13.1801(2)	19.1976(2)
γ (°)	90	90	90
Volume (Å ³)	8429.69(19)	3865.35(14)	3702.18(7)
<i>Z</i>	8	4	4
<i>D</i> _{calc} (mg/m ³)	1.405	1.503	1.569
Absorption coefficient (mm ⁻¹)	8.224	9.835	10.268
<i>F</i> (000)	3680	1768	1768
Crystal size (mm ³)	0.09 × 0.07 × 0.03	0.10 × 0.05 × 0.02	0.30 × 0.21 × 0.10
Theta range for data collection	3.01–70.70°	3.41–70.60°	2.81–70.44°
Index ranges	–21 ≤ <i>h</i> ≤ 24, –14 ≤ <i>k</i> ≤ 14, –35 ≤ <i>l</i> ≤ 32	–12 ≤ <i>h</i> ≤ 16, –26 ≤ <i>k</i> ≤ 27, –15 ≤ <i>l</i> ≤ 16	–18 ≤ <i>h</i> ≤ 19, –13 ≤ <i>k</i> ≤ 14, –23 ≤ <i>l</i> ≤ 22
Reflections collected	36724	34480	22812
Independent reflections [<i>R</i> _{int}]	7616 [0.0679]	7128 [0.0427]	6639 [0.0550]
Completeness to theta = 70.70°	94.0%	96.2%	93.9%
Absorption correction	Semi-empirical from equivalents (SADABS v. 2.03)	Semi-empirical from equivalents (SADABS v. 2.03)	Semi-empirical from equivalents (SADABS v. 2.03)
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7616/0/651	7128/0/537	6639/0/559
Goodness-of-fit on <i>F</i> ² (GOF)	1.027	1.009	1.062
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0401, <i>wR</i> ₂ = 0.0929	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0943	<i>R</i> ₁ = 0.0458, <i>wR</i> ₂ = 0.1111
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0594, <i>wR</i> ₂ = 0.1028	<i>R</i> ₁ = 0.0512, <i>wR</i> ₂ = 0.1024	<i>R</i> ₁ = 0.0540, <i>wR</i> ₂ = 0.1154
Largest difference peak and hole (e Å ⁻³)	0.632 and –0.303	0.418 and –0.571	3.069 and –0.619

Table 6
Selected bond lengths (Å) and angles (°) for **A2**

C(1)–O(1)	1.152(4)	C(5)–C(6)	1.352(4)	C(11)–C(12)	1.145(4)
C(1)–Co(1)	1.762(3)	C(5)–Si(1)	1.851(3)	C(12)–Si(2)	1.864(4)
C(2)–O(2)	1.141(4)	C(5)–Co(2)	1.976(3)	Co(1)–P(2)	2.2123(9)
C(2)–Co(1)	1.805(3)	C(5)–Co(1)	1.991(3)	Co(2)–P(1)	2.1917(9)
C(3)–O(3)	1.147(4)	C(6)–C(7)	1.459(4)	N(1)–P(2)	1.703(3)
C(3)–Co(2)	1.783(3)	C(6)–Co(1)	1.972(3)	N(1)–P(1)	1.706(3)
C(4)–O(4)	1.139(4)	C(6)–Co(2)	1.988(3)	Co(1)–Co(2)	2.4592(7)
C(4)–Co(2)	1.786(3)	C(10)–C(11)	1.483(4)		
C(6)–C(5)–Si(1)	151.1(2)	C(5)–C(6)–C(7)	143.3(3)		
C(9)–C(10)–C(11)	121.0(3)	C(7)–C(10)–C(11)	127.1(3)		
C(12)–C(11)–C(10)	177.9(3)	C(11)–C(12)–Si(2)	171.0(3)		
C(1)–Co(1)–C(2)	99.54(14)	C(1)–Co(1)–C(6)	94.84(13)		
C(2)–Co(1)–C(6)	143.59(13)	C(1)–Co(1)–C(5)	98.87(13)		
C(2)–Co(1)–C(5)	104.47(14)	C(6)–Co(1)–C(5)	39.91(12)		
C(1)–Co(1)–P(2)	108.21(10)	C(2)–Co(1)–P(2)	102.26(11)		
C(6)–Co(1)–P(2)	104.68(9)	C(5)–Co(1)–P(2)	137.80(9)		
C(1)–Co(1)–Co(2)	145.68(10)	C(2)–Co(1)–Co(2)	104.21(10)		
C(6)–Co(1)–Co(2)	51.90(8)	C(5)–Co(1)–Co(2)	51.42(9)		
P(2)–Co(1)–Co(2)	90.64(3)	C(3)–Co(2)–C(4)	99.04(15)		
C(3)–Co(2)–C(5)	109.38(13)	C(4)–Co(2)–C(5)	99.85(13)		
C(3)–Co(2)–C(6)	140.30(14)	C(4)–Co(2)–C(6)	109.31(13)		
C(5)–Co(2)–C(6)	39.90(12)	C(3)–Co(2)–P(1)	106.83(10)		
C(4)–Co(2)–P(1)	102.43(11)	C(5)–Co(2)–P(1)	133.38(9)		
C(6)–Co(2)–P(1)	93.84(9)	C(3)–Co(2)–Co(1)	91.29(10)		
C(4)–Co(2)–Co(1)	151.79(10)	C(5)–Co(2)–Co(1)	51.95(8)		
C(6)–Co(2)–Co(1)	51.33(9)	P(1)–Co(2)–Co(1)	99.51(3)		
P(2)–N(1)–P(1)	120.20(15)				

The ³¹P{¹H} NMR spectra for all of the phosphine-substituted compounds, show one broad single resonance that is shifted to higher frequencies (ca. 13 and 93 ppm for dmpm and dppa-complexes, respectively) with respect to that of the free ligand because

of the coordination. The UV–Vis spectra of all complexes exhibit broad low-intensity absorption bands with λ between 531 and 566 nm attributed to the d–d transitions. These spectra, for dppa-complexes, are dominated by the characteristic UV band at

ca. 330 nm associated with $\pi-\pi^*$ transitions within the phenyl groups of the bisphosphine ligand. In addition, strong absorptions are observed around 231, 255 and 280 nm attributed to $\pi-\pi^*$ transition associated with the thiophene ring. All compounds gave satisfactory mass spectrometric data.

3.2. Crystal and molecular structures of **A2**, **B2** and **D2**

Single-crystal X-ray diffraction studies were performed on complexes **A2**, **B2** and **D2**. These structural studies serve the obvious purpose of confirming the structures presented in Schemes A–D. The thermal ellipsoid plots shown in Figs. 2–4 depict the structures determined in this work. Crystal data and structure refinements are given in Table 5, and selected bond lengths and angles in Tables 6–8 for **A2**, **B2** and **D2**, respectively.

Compound **A2** consists of a disubstituted thiophene ring with a trimethylsilyl ethyne at the 3- and 4-positions and one bimetallic Co unit. The bimetallic Co moiety has two terminal CO ligands on the Co atoms, bridging dppa ligand and one of the trimethylsilyl ethynyl ligands. The X-ray structure of **A2** shows that the “Co₂C₂” core adopts the usual pseudo-tetrahedral geometry with the alkyne vector lying essentially perpendicular to the Co–Co vector. This geometry has been observed in other carbonyl cobalt bimetallic complexes possessing a bridging acetylene ligand [31]. The Co–Co bond length (2.459(7) Å) found in **A2** is in the region expected for other dicobalt systems that are bridged by perpendicular alkyne ligands, indicating the presence of a metal–metal bond [27b,32] and is similar to Co–Co lengths found in the related μ -alkyne complexes [Co₂(CO)₄(μ -dppm){ μ_2 - η^2 -(SiMe₃C₂)}]₂(SiMe₃C≡C)(1,3,5-C₆H₃) [8e], 2,5-[Co₂(CO)₄(μ -dppm){ μ_2 - η^2 -(SiMe₃C₂)}]₂C₄H₂S

Table 7
Selected bond lengths (Å) and angles (°) for **B2**

C(1)–C(2)	1.345(4)	C(6)–Br(1)	1.885(4)	C(10)–Co(2)	1.787(3)
C(1)–Co(1)	1.994(3)	C(7)–O(1)	1.138(4)	C(10)–O(4)	1.128(4)
C(1)–Co(2)	1.979(3)	C(7)–Co(1)	1.769(3)	Co(1)–P(1)	2.2084(8)
C(1)–Si(1)	1.844(3)	C(8)–O(2)	1.136(4)	Co(2)–P(2)	2.1901(8)
C(2)–C(3)	1.451(4)	C(8)–Co(1)	1.802(4)	N(1)–P(2)	1.687(2)
C(2)–Co(1)	1.981(3)	C(9)–O(3)	1.136(4)	N(1)–P(1)	1.692(2)
C(2)–Co(2)	1.982(3)	C(9)–Co(2)	1.785(4)	Co(1)–Co(2)	2.4568(6)
C(7)–Co(1)–C(8)	98.86(16)	C(7)–Co(1)–C(2)	98.31(14)		
C(8)–Co(1)–C(2)	141.86(14)	C(7)–Co(1)–C(1)	103.00(14)		
C(8)–Co(1)–C(1)	103.17(15)	C(2)–Co(1)–C(1)	39.54(12)		
C(7)–Co(1)–P(1)	99.73(12)	C(8)–Co(1)–P(1)	105.14(12)		
C(2)–Co(1)–P(1)	105.15(9)	C(1)–Co(1)–P(1)	140.14(9)		
C(7)–Co(1)–Co(2)	149.47(11)	C(8)–Co(1)–Co(2)	103.17(11)		
C(2)–Co(1)–Co(2)	51.71(8)	C(1)–Co(1)–Co(2)	51.52(8)		
P(1)–Co(1)–Co(2)	94.67(2)	C(9)–Co(2)–C(10)	97.41(15)		
C(9)–Co(2)–C(1)	111.19(15)	C(10)–Co(2)–C(1)	103.10(14)		
C(9)–Co(2)–C(2)	143.63(14)	C(10)–Co(2)–C(2)	109.14(13)		
C(1)–Co(2)–C(2)	39.69(12)	C(9)–Co(2)–P(2)	101.45(11)		
C(10)–Co(2)–P(2)	101.24(11)	C(1)–Co(2)–P(2)	135.83(9)		
C(2)–Co(2)–P(2)	97.33(9)	C(9)–Co(2)–Co(1)	94.88(11)		
C(10)–Co(2)–Co(1)	155.06(11)	C(1)–Co(2)–Co(1)	52.08(8)		
C(2)–Co(2)–Co(1)	51.68(8)	P(2)–Co(2)–Co(1)	97.45(2)		
C(5)–C(6)–Br(1)	121.5(3)	C(3)–C(6)–Br(1)	123.8(3)		
Si(1)–C(1)–Co(2)	136.86(17)	C(1)–C(2)–C(3)	141.9(3)		
P(2)–N(1)–P(1)	122.08(16)				

Table 8
Selected bond lengths (Å) and angles (°) for **D2**

C(1)–C(2)	1.350(6)	C(4)–Br(1)	1.891(4)	C(13)–O(1)	1.134(5)
C(1)–Si(1)	1.849(4)	C(10)–O(4)	1.141(5)	C(13)–Co(2)	1.786(4)
C(1)–Co(2)	1.982(4)	C(10)–Co(1)	1.772(4)	N(1)–P(1)	1.690(4)
C(1)–Co(1)	1.976(4)	C(11)–O(3)	1.140(5)	N(1)–P(2)	1.698(3)
C(2)–C(3)	1.454(5)	C(11)–Co(1)	1.800(4)	Co(1)–P(1)	2.1981(11)
C(2)–Co(1)	1.983(4)	C(12)–O(2)	1.142(5)	Co(2)–P(2)	2.2151(11)
C(2)–Co(2)	1.952(4)	C(12)–Co(2)	1.797(4)	Co(1)–Co(2)	2.4478(8)
C(2)–C(1)–Si(1)	145.4(3)	C(1)–C(2)–C(3)	139.4(4)		
C(3)–C(4)–Br(1)	123.2(3)	C(5)–C(4)–Br(1)	121.0(3)		
C(11)–Co(1)–C(2)	142.98(17)	C(10)–Co(1)–C(11)	99.89(18)		
C(11)–Co(1)–C(1)	108.25(17)	C(10)–Co(1)–C(2)	103.84(16)		
C(1)–Co(1)–C(2)	39.88(17)	C(10)–Co(1)–C(1)	100.10(17)		
C(10)–Co(1)–P(1)	101.95(13)	C(11)–Co(1)–P(1)	102.29(13)		
C(1)–Co(1)–P(1)	138.26(12)	C(2)–Co(1)–P(1)	100.11(12)		
C(1)–Co(1)–Co(2)	51.92(11)	C(2)–Co(1)–Co(2)	50.96(11)		
C(10)–Co(1)–Co(2)	150.99(12)	C(11)–Co(1)–Co(2)	96.98(13)		
C(13)–Co(2)–C(12)	101.65(18)	C(13)–Co(2)–C(1)	99.15(17)		
C(12)–Co(2)–C(1)	103.49(17)	C(13)–Co(2)–C(2)	97.26(17)		
C(12)–Co(2)–C(2)	141.64(17)	C(2)–Co(2)–C(1)	40.13(17)		
C(13)–Co(2)–P(2)	103.16(13)	C(12)–Co(2)–P(2)	102.76(13)		
C(1)–Co(2)–P(2)	141.04(12)	C(2)–Co(2)–P(2)	104.99(12)		
C(13)–Co(2)–Co(1)	147.61(13)	C(12)–Co(2)–Co(1)	99.26(12)		
C(1)–Co(2)–Co(1)	51.67(11)	C(2)–Co(2)–Co(1)	52.11(11)		
P(1)–Co(1)–Co(2)	97.27(4)	P(2)–Co(2)–Co(1)	95.95(3)		
P(1)–N(1)–P(2)	122.4(2)				

[10b] and 2-[Co₂(CO)₄(μ-dppm){μ₂-η²-(SiMe₃C₂)}]-4-(Br)-C₄H₂S [11]. However, such a distance is shorter than that in the parent carbonyl, [Co₂(CO)₈], (average 2.52 Å) [33].

The C(5)–C(6) bond length of the bridging ethynyl ligand, 1.352(4) Å, is much longer than the C(11)–C(12) triple-bond value, 1.145(4) Å, and this reflects the loss of triple-bond character as a result of coordination of the acetylenic moiety to the Co₂ fragment. This distance lies in the range 1.33–1.36 Å reported for the alkylenic C–C bond in related dicobalt complexes [27b]. The change in hybridization at C(5) and C(6) is also reflected in the C(5)–C(6)–C(7) angle of 143.3(3)° and C(6)–C(5)–Si(1) angle of 151.1(2)°.

The bond lengths of the apex carbonyl groups to the Co atoms, C(2)–Co(1) and C(3)–Co(2), are 1.805(3) and 1.783(3) Å, respectively. These bond lengths are statistically not different from those of the base carbonyl groups to the Co atoms, which are 1.762(3) and 1.786(3) Å, for C(1)–Co(1) and C(4)–Co(2), respectively. The dihedral angle Co(1)–C(6)–C(5)–Co(2) was determined to be –82.6(9)°, whereas the dihedral angle C(6)–Co(1)–Co(2)–C(5) was determined to be –51.6(15)°. The average P–N distance of the bridging (Ph₂P)₂NH ligand, 1.704(3) Å, is normal; the P–N bond lengths are statistically equivalent. The P–N–P angle is 122.2(15)°. This value is comparable with the average found for bridging (Ph₂P)₂NR ligands of 119.3° [9b,34]. All other bond lengths and angles are comparable to those reported for similar structures [8e–f,10,11,35]. The average carbonyl C≡O bond length was determined to be 1.145(4) Å, where all the bond lengths are sufficiently similar. The thiophene ring is essentially planar with a root mean square deviation of 0.0042 Å. There does not appear to be any intramolecular hydrogen bonding within the molecule.

Compounds **B2** and **D2** consist of a monosubstituted X-trimethylsilylethynyl-Y-bromothiophene ligand (X = 3, Y = 4 (**B2**) and X = 2, Y = 3 (**D2**)) with a bimetallic Co unit at the 3- and 2-position, respectively. It can be observed that **B2** is derived from **A2** by substitution of the –C≡CSiMe₃ group by a Br atom. In general, the structural parameters of the common fragments are the same, within experimental error. The basic structural skeleton of **B2** and **D2** resembles that of **A2** and the cobalt–alkyne complex with the “Co₂C₂” unit linked to a 2-trimethylsilylethynyl-4-bromothiophene ligand [11].

The bond length between Co(1) and Co(2) (2.457(6) Å in **B2** and 2.4478(8) Å in **D2**) is similar to that of **A2** and the bond length between C(1) and C(2) (1.345(4) Å in **B2** and 1.350(6) Å in **D2**) also lies within the expected range for alkyne groups bound to Co₂(CO)₆ units. In addition, the Br–C(6) bond length in **B2** is 1.886(4) Å and the Br–C(4) bond length in **D2** is 1.891(4) Å. C(3)–C(6)–Br and C(5)–C(6)–Br angles in **B2** are 123.8(3)° and 121.5(3)°, respectively. C(3)–C(4)–Br and C(5)–C(4)–Br angles in **D2** are

123.2(3)° and 121.0(3)°, respectively. The thiophene ring in **B2** and in **D2** is also essentially planar with a root mean square deviation of 0.0019 Å and 0.0018 Å, respectively. The remaining interatomic distances and angles in the molecules are normal and compare well with the values reported above.

3.3. Electrochemical studies

The electrochemical behaviour of **A1–A7**, **B1**, **B2**, **C1+C2**, **C5** and **D2** in CH₂Cl₂ solution was studied by means of the cyclic voltammetry (CV) and square-wave voltammetry (SWV) techniques. Table 9 presents data of $E_{1/2}$ ($E_{1/2} = (E_{pa} + E_{pc})/2$) for the electrochemical reduction and oxidation of these compounds. All E values are given versus $E_{1/2}$ of Fc^{+/Fc} (Fc⁺ = decamethylferrocene).

3.3.1. Electrochemistry of compounds containing one Co₂(CO)₆-alkyne redox centre (**A1**, **B1** and **C1 + C2**)

It should be noted that **C1** and **C2** could not be isolated, and that a solution containing **C1** together with **C2** in 1.8:1 ratio, respectively, was used for the electrochemical measurements. A single oxidation and a single reduction peak were obtained for that mixture, indicating that both compounds are oxidized and reduced at almost the same potential value.

A1 and **B1** show irreversible voltammetric oxidation and reduction peaks at room temperature and moderate sweep rates ($v \approx 0.1$ V/s), but partially chemical reversibility is attained in the oxidation process at room temperature and $v = 1$ V/s. The mixture **C1 + C2** shows a partially chemically reversible voltammetric oxidation peak at room temperature and moderate sweep rates ($i_{pc}/i_{pa} = 0.7$ at $v = 0.1$ V/s). The reduction of **C1 + C2** is chemically irreversible at room temperature. This indicates that **A1**⁺, **B1**⁺, **C1**⁺ + **C2**⁺, **A1**[–], **B1**[–] and **C1**[–] + **C2**[–] undergo decomposition processes [8e–f,9d,10,11,36] in solution which are somewhat slower for cations. Sweeping potential beyond ca. 1.2 V involves a serious contamination of the electrode surface by an adsorbed cobalt-containing product, which can be reduced at ca. –0.65 V.

It is noteworthy that ions formed from **A1**, **B1** and **C1 + C2** show a greater overall chemical stability than those from closely related species derived from 2,5- and 2,4-bis(trimethylsilylethynyl)thiophene, probably due to steric reasons [10b,11]. When temperature is –30 °C, the oxidation and reduction processes of **A1**, **B1** and **C1 + C2** appear as chemically partially reversible (Fig. 5), and coupled peaks allow the determination of $E_{1/2}$ as listed in Table 9. Potential values are in the range expected for C₂Co₂(CO)₆ con-

Table 9
Electrochemical data for **A1–A7**, **B1–B2**, **C1 + C2**, **D2** and **C5**^a

	$E_{1/2}$ for reduction	$E_{1/2}$ for oxidation
A1	–1.05 ^b	+1.18 ^b
C1 + C2	–1.07 ^b	+1.18 ^b
B1	–1.02 ^b	+1.19 ^b
A2	–1.59 ^b	+0.57
B2	–1.53 ^b	+0.60
D2	–1.53 ^b	+0.62
A3	–1.74 ^b	+0.50
A4	–1.57 ^b	+0.57
A5	–1.73 ^b	+0.51
C5	–1.49 ^b	+0.60
A6	–1.57 ^b	+0.62
A7	–1.08 ^b ; –1.71 ^b	+0.64, +1.26 ^b

^a Data in V vs. Fc^{+/Fc} in CH₂Cl₂ solution. Data are taken from CV and SWV at 25 °C unless otherwise stated.

^b Data from CV and SWV at –30 °C.

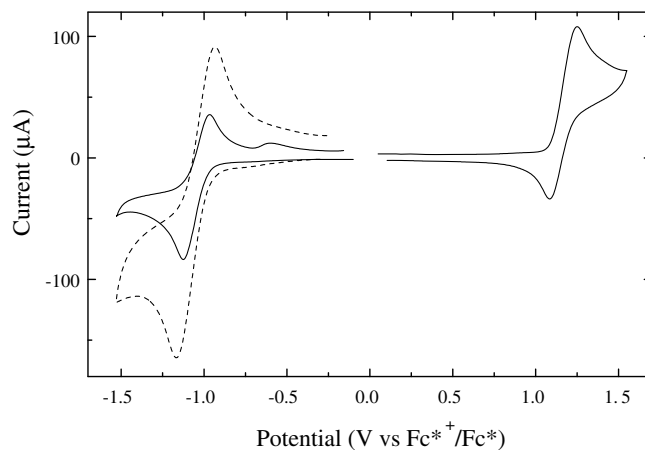


Fig. 5. Cyclic voltammograms for the oxidation and reduction of **A1** in CH₂Cl₂ containing 0.2 M TBAPF₆ at –30 °C on a glassy carbon working electrode. (–) $v = 0.1$ V/s; (– –) $v = 0.5$ V/s.

taining compounds [8e–f, 10b, 11, 36d, 36f]. A comparison of $E_{1/2}$ values with those of related species 2-[Co₂(CO)₆{μ₂-η²-SiMe₃C₂}]–5-(Me₃SiC≡C)C₄H₂S ($E_{1/2}(\text{ox}) = 1.23$ V; $E_{1/2}(\text{red}) = -1.01$ V) [10b] and 2-[Co₂(CO)₆{μ₂-η²-(SiMe₃C₂)}]–4-(Me₃SiC≡C)C₄H₂S ($E_{1/2}(\text{ox}) = 1.24$ V; $E_{1/2}(\text{red}) = -0.99$ V) [11] shows that **A1** and **C1** + **C2** are significantly easier to oxidize and more difficult to reduce. This fact is related to the proximity of the electron-donating substituent –C₂SiMe₃ and will also be evident for phosphine-containing compounds.

3.3.2. Electrochemistry of compounds containing one Co₂(CO)₄(phosphine)-alkyne redox centre (**A2–A6**, **B2**, **C5** and **D2**)

All C₂Co₂(CO)₄dppa or C₂Co₂(CO)₄dmpm containing compounds **A2–A6**, **B2**, **C5** and **D2** show chemically completely reversible (in the 0.01–10 V/s range of sweep rates) monoelectronic oxidation processes at room temperature (Fig. 6), with $E_{1/2}$ in the 0.50–0.62 V range (Table 9), characteristic of this kind of compounds in which the chelating phosphine stabilizes cations (and anions) against decomposition, and makes the redox centre much more electron-rich and easier to be oxidized, as compared with related C₂Co₂(CO)₆ compounds. i_p increases linearly with $v^{1/2}$ as corresponds to diffusion-controlled processes. Reductions are partially chemically reversible at room temperature, but i_{pa} equals i_{pc} at –30 °C (Fig. 7). $E_{1/2}(\text{red})$ are in the –1.53 to –1.74 V range of potential (Table 9). The higher basicity and electron-donating capacity of dmpm as compared to dppa [37] is reflected in the very significantly less positive $E_{1/2}(\text{ox})$ and more negative $E_{1/2}(\text{red})$ of **A3** and **A5** than values for **A2**, **A4**, **A6**, **B2**, **C5**, and **D2**. Compounds **A2** and **A4** have less positive oxidation and more negative reduction potentials than closely related species derived from 2,5-bis(trimethylsilylethynyl)thiophene, as already observed for **A1**. Thus, for 2-[Co₂(CO)₄(μ-dppa){μ₂-η²-SiMe₃C₂}]–5-(Me₃SiC≡C)–C₄H₂S and 2-[Co₂(CO)₄(μ-dppa){μ₂-η²-SiMe₃C₂}]–5-(C≡CH)C₄H₂S, $E_{1/2}(\text{ox})$ are 0.61 V and 0.63 V and $E_{1/2}(\text{red})$ are –1.51 V and –1.50 V, respectively [10b].

Table 9 shows the effect of the higher electron-donating properties of the capping group –SiMe₃ as compared to –H, which makes

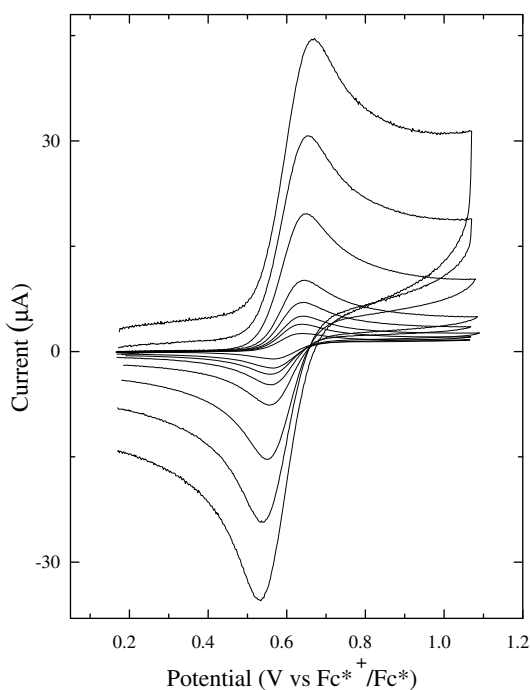


Fig. 6. Cyclic voltammograms for the oxidation of **C5** in CH₂Cl₂ containing 0.2 M TBAPF₆ at 25 °C on a Pt working electrode at different sweep rates: $v = 0.02$ –10 V/s (0.02, 0.05, 0.1, 0.2, 0.5, 2, 5 and 10 V/s).

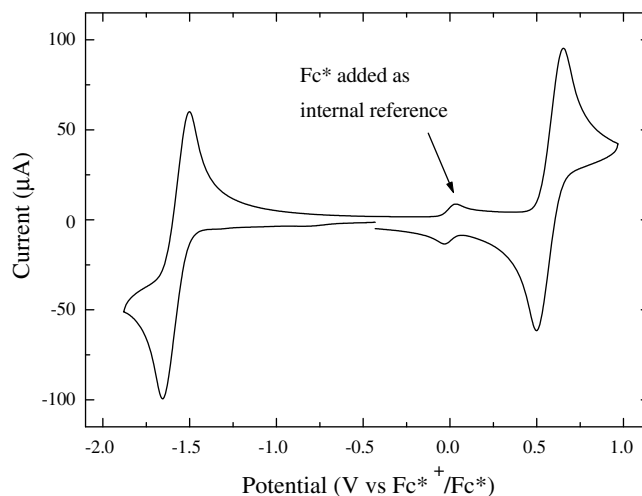


Fig. 7. Cyclic voltammogram for the reduction and oxidation of **A2** in CH₂Cl₂ containing 0.2 M TBAPF₆ at –30 °C and $v = 0.1$ V/s on a glassy carbon working electrode.

C₂SiMe₃ containing compounds easier to oxidize and more difficult to reduce. This is particularly evident for **A6**, which contains two –H capping atoms, one of them directly bonded to the C₂Co₂(CO)₄dppa redox centre.

3.3.3. Electrochemistry of **A7**

One of our goals for this work was to evaluate the electronic communication through 3,4- and 2,3-bis(trimethylsilylethynyl)thiophene, comparing it with those found for 2,4- and 2,5-analogous ligands. Thus, we intended to prepare complexes containing two equal redox centres. Unfortunately, our efforts proved vain and only **A7**, which contains two unequal redox centres (HC₂Co₂(CO)₆ and HC₂Co₂(CO)₄dppa), could be prepared and isolated.

In order to evaluate the electronic communication in **A7**, we cannot only measure the difference in $E_{1/2}$ for the oxidation or the reduction waves ($\Delta E_{1/2}$), as is usually made for compounds containing two equivalent redox centres [36f, 38], but we also have to take into account the intrinsic difference in $E_{1/2}$ values of the C₂Co₂(CO)₆ and the C₂Co₂(CO)₄dppa units, independent of the possible existence of interaction, and which is manifested in the very different $E_{1/2}$ values of **A1** and **A2**, **A4** or **A6**.

Reduction of **A7** in CH₂Cl₂ solution and –30 °C shows a first wave, which is chemically irreversible, at –1.08 V (SWV). This peak can be assigned to the C₂Co₂(CO)₆ redox centre and is followed by a chemically quasi-reversible wave at $E_{1/2} = -1.71$ V, which is in the range of potential values characteristic in C₂Co₂(CO)₄(phosphine) containing compounds. The complete chemical irreversibility of the first reduction peak means that **A7**[–] undergoes a fast homogeneous reaction, and the wave at –1.71 V is due to the reduction of a C₂Co₂(CO)₄(phosphine) containing product of it. Thus, evaluation of the electronic interaction from the reduction behaviour of **A7** is not feasible. However, oxidation of **A7** in CH₂Cl₂ solution at room temperature shows a first monoelectronic completely reversible wave at $E_{1/2} = +0.64$ V, which is attributable to the C₂Co₂(CO)₄dppa redox centre. A second peak, irreversible even at –30 °C, is observed at 1.26 V (SWV), which is a potential value characteristic of C₂Co₂(CO)₆ containing compounds. The chemical reversibility of the first oxidation process indicates that the species, which is oxidized in the second wave is **A7**⁺. Thus, a study based on the comparison of the oxidation data of **A7** with those of **A1** and **A6** could tentatively afford a very preliminary estimation of the degree of electronic interaction between both redox centres in **A7**. In order to achieve a more precise comparison, **A1** should be

replaced by the related compound in which the capping group were –H instead of –SiMe₃ (we will name this species **A1***). Such compound could not be obtained but, taking into account the influence of the capping group (H or SiMe₃) on $E_{1/2}(\text{ox})$ values (see Table 9, compounds **A2** and **A6**) it can be expected that **A1*** were oxidized at a potential value slightly more positive than that of **A1**.

Therefore, if the difference in $E_{1/2}(\text{ox})$ for **A2** and **A6** (50 mV) is extrapolated to **A1** and **A1***, $E_{1/2}(\text{ox})$ for **A1*** would be ca. 1.23 V and therefore $E_{1/2}(\text{A1}^*) - E_{1/2}(\text{A6}) \cong 0.61$ V. Even if we take into account the considerable error margin of these calculations and comparisons, it can be observed that $E_{1/2}(\text{A1}^*) - E_{1/2}(\text{A6}) \cong \Delta E_{1/2}(\text{A7})$. Thus, no electronic interaction is observed between the two “Co₂” redox centres in **A7**. If such interaction exists, it must be very scarce.

This result contrasts with those found for 2,5- [10b] and 2,4-bis(trimethylsilylethynyl)thiophene [11] derivatives with two “Co₂” redox centres (which belong to class II in the Hush-Robinson-Day classification of mixed valence compounds) and agrees with the fact that the C₃–C₄ bond in the thiophene ring possesses less multiple character than C₂–C₃ [21]. Thus, less overall conjugation is to be expected in 3,4-bis(trimethylsilylethynyl)thiophene as compared to the analogous 2,5- and 2,4-ligands. UV–Vis data are in accordance with this result, as discussed above.

Acknowledgments

The authors would like to thank to the Dirección General de Investigación Científica y Tecnológica (Grants No. CTQ2006-10940/BQU) Spain. X-ray diffraction data were collected at the Monocrystal Diffraction Laboratory SIDI. Facultad de Ciencias. Universidad Autónoma de Madrid, Spain.

Appendix A. Supplementary material

CCDC 653921, 653925 and 682712 contains the supplementary crystallographic data for **A2**, **B2** and **D2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.08.005.

References

- (a) R. Nast, *Coord. Chem. Rev.* 47 (1982) 89–124;
(b) M.D. Ward, *Chem. Soc. Rev.* 24 (1995) 121–134;
(c) F. Paul, C. Lapinte, *Coord. Chem. Rev.* 431–509 (1998) 178–180;
(d) U.H.F. Bunz, *J. Organomet. Chem.* 683 (2003) 267–445;
(e) W. Kaim, G.K. Lahiri, *Angew. Chem., Int. Ed.* 46 (2007) 1778–1796. and references therein.
- (a) R.A. Hahn, D. Bloor, *Organic Materials for Non-Linear Optics*, The Royal Society of Chemistry, London, 1989;
(b) G.D. Stucky, S.R. Marder, J. Sohn, *Materials for Nonlinear Optics; Chemical Perspectives*, American Chemical Society, Washington, DC, 1991;
(c) S.R. Marder, in: D.W. Bruce, D. O'Hare (Eds.), *Inorganic Materials*, Wiley, Chichester, 1996, p. 121;
(d) M. Haller, J. Luo, H. Li, T.-D. Kim, Y. Liao, B.H. Robinson, L.R. Dalton, A.K.-Y. Jen, *Macromolecules* 37 (2004) 688–690;
(e) R.D. Nielsen, H.L. Rommel, B.H. Robinson, *J. Phys. Chem. B* 108 (2004) 8659–8667;
(f) M.P. Cifuentes, M.G. Humphrey, J.P. Morrall, M. Samoc, F. Paul, C. Lapinte, T. Roisnel, *Organometallics* 24 (2005) 4280–4288;
(g) M.O. Senge, M. Fazekas, E.G.A. Notaras, W.J. Blau, M. Zawadzka, O.B. Locos, E.M. Ni Mhuircheartaigh, *Adv. Mater.* 19 (2007) 2737–2774;
(h) G.-J. Zhou, W.-Y. Wong, C. Ye, Z. Lin, *Adv. Funct. Mater.* 17 (2007) 963–975.
- (a) G. Frapper, M. Kertesz, *Inorg. Chem.* 32 (1993) 732–740;
(b) P.J. Low, *The Roy. Soc. Chem., Dalton Trans.* (2005) 2821–2824.
- (a) M.L.H. Green, S.R. Marder, M.E. Thomson, J.A. Bandy, D. Bloor, P.V. Kolinsky, R.J. Jones, *Nature* 330 (1987) 360–362;
(b) J.S. Miller, A.J. Epstein, *Angew. Chem., Int. Ed.* 33 (1994) 385–415;
(c) M.S. Khan, M.R.A. Al-Mandhary, M.K. Al-Suti, B. Ahrens, M.F. Mahon, L. Male, P.R. Raithby, C.E. Boothby, A. Koehler, *J. Chem. Soc., Dalton Trans.* (2003) 74–84;
(d) V.W.-W. Yam, K.M.-C. Wong, N. Zhu, *Angew. Chem., Int. Ed.* 42 (2003) 1400–1403;
(e) P. Li, B. Ahrens, N. Feeder, P.R. Raithby, S.J. Teat, M.S. Khan, *J. Chem. Soc., Dalton Trans.* (2005) 874–883;
(f) W.-Y. Wong, *J. Chem. Soc., Dalton Trans.* (2007) 4495–4510.
- (a) P.I. Dosa, C. Erben, V.S. Iyer, K.P.C. Vollhardt, I.M. Wasser, *J. Am. Chem. Soc.* 121 (1999) 10430–10431;
(b) D.T. McQuade, A.E. Pullen, T.M. Swager, *Chem. Rev.* 100 (2000) 2537–2574;
(c) N. Robertson, C.A. McGowan, *Chem. Soc. Rev.* 32 (2003) 96–103;
(d) C.J. Elsevier, J. Reedijk, P.H. Walton, M.D. Ward, *J. Chem. Soc., Dalton Trans.* (2003) 1869–1880;
(e) J. Stahl, J. Bohling, C. James, E.B. Bauer, B. Eike, T.B. Peters, W. Mohr, J.M. Martin-Alvarez, F. Hampel, J.A. Gladysz, A. John, *Angew. Chem., Int. Ed.* 41 (2002) 1871–1876;
(f) L. De Quadras, E.B. Bauer, W. Mohr, J.C. Bohling, T.B. Peters, J.M. Martin-Alvarez, F. Hampel, J.A. Gladysz, *J. Am. Chem. Soc.* 129 (2007) 8296–8309.
- (a) *Molecular and biomolecular electronics* R.R. Birge (Ed.), *Advances in Chemistry Series 240*, American Chemical Society, 1994;
(b) W.P. Kirk, M.A. Reed (Eds.), *Nanostructures and Mesoscopic Systems*, Academic, New York, 1992;
(c) *Molecular electronics: science and technology* A. Aviram (Ed.), *Conference Proceedings No. 262*, American Institute of Physics, New York, 1992;
(d) D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, VCH Publishers, New York, 1995;
(e) R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney, R.G. Osifchin, *Science* 273 (1996) 1690–1693;
(f) D.L. Feldheim, C.D. Keating, *Chem. Soc. Rev.* 27 (1998) 1–12;
(g) R.D. Adams, B. Qu, M.D. Smith, *Inorg. Chem.* 40 (2001) 2932–2934;
(h) M.I. Bruce, K. Costuas, J.-F. Halet, B.C. May, P.J. Low, B.K. Nicholson, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (2002) 383–398;
(i) H. Yao, M. Sabat, R.N. Grimes, F. Fabrizi de Biani, P. Zanello, *Angew. Chem., Int. Ed.* 42 (2003) 1002–1005;
(j) H. Yao, M. Sabat, R.N. Grimes, P. Zanello, F. Fabrizi de Biani, *Organometallics* 22 (2003) 2581–2593;
(k) N. Tanifuji, K. Matsuda, M. Irie, *Mol. Cryst. Liq. Cryst.* 430 (2005) 75–79.
- (a) J. Roncali, *Chem. Rev.* 92 (1992) 711–738;
(b) A. Caballero, A. Tárraga, M.D. Velasco, P. Molina, *J. Chem. Soc., Dalton Trans.* (2006) 1390–1398.
- (a) B.H. Robinson, J. Simpson, in: M. Chanon (Ed.), *Paramagnetic Organometallic Species in Activation: Selectivity Catalysis*, Kluwer, Dordrecht, 1989, p. 357;
(b) J. Roncali, *Chem. Rev.* 97 (1997) 173–205;
(c) R.D. Adams, B. Qu, *Organometallics* 19 (2000) 2411–2413;
(d) H. Jiao, J.A. Gladysz, *New J. Chem.* 25 (2001) 551–562;
(e) C. Moreno, M.L. Marcos, G. Domínguez, A. Arnanz, D.H. Farrar, R. Teeple, A. Lough, J. González-Velasco, S. Delgado, *J. Organomet. Chem.* 631 (2001) 19–28;
(f) M.L. Marcos, M.J. Macazaga, R.M. Medina, C. Moreno, J.A. Castro, J.L. Gómez, S. Delgado, J. González-Velasco, *Inorg. Chim. Acta* 312 (2001) 249–255;
(g) A. Ceccon, S. Santi, L. Orian, A. Bisello, *Coord. Chem. Rev.* 248 (2004) 683–724.
- (a) N. Le Narvor, L. Toupet, C. Lapinte, *J. Am. Chem. Soc.* 117 (1995) 7129–7138;
(b) T. Bartik, B. Bartik, M. Brady, R. Dembinski, J.A. Gladysz, *Angew. Chem., Int. Ed.* 35 (1996) 414–417;
(c) F. Coat, C. Lapinte, *Organometallics* 15 (1996) 477–479;
(d) T.S. Jung, J.H. Kim, E.K. Jang, D.H. Kim, Y.-B. Sim, B. Park, S.C. Shin, *J. Organomet. Chem.* 599 (2000) 232–237.
- (a) R.M. Medina, C. Moreno, M.L. Marcos, J.A. Castro, F. Benito, A. Arnanz, S. Delgado, J. González-Velasco, M.J. Macazaga, *Inorg. Chim. Acta* 357 (2004) 2069–2080;
(b) A. Arnanz, M.L. Marcos, C. Moreno, D.H. Farrar, A.J. Lough, J.O. Yu, S. Delgado, J. González-Velasco, *J. Organomet. Chem.* 689 (2004) 3218–3231.
- A. Arnanz, C. Moreno, M.L. Marcos, J. González-Velasco, S. Delgado, *Eur. J. Inorg. Chem.* (2007) 5215–5225.
- (a) Y. Sugihara, T. Yagi, I. Murata, A. Imamura, *J. Am. Chem. Soc.* 114 (1992) 1479–1481;
(b) Y. Sugihara, R. Miyatake, T. Yagi, *Chem. Lett.* (1993) 933–936;
(c) B. Sahu, I.N.N. Nambhothiri, R. Persky, *Tetrahedron Lett.* 46 (2005) 2593–2597.
- D.D. Perrin, S.L.F. Armarego, D.R. Perrin, *Purification of Laboratory Chemicals*, Pergamon Press, New York, 1980.
- (a) F.A. Cotton, *Inorg. Synth.* 13 (1972) 121;
(b) D.R. Coulson, *Inorg. Synth. (Reagents Transition Met. Complex Organomet. Synth.)* 28 (1990) 107–109.
- V.H. Noeth, L. Meinel, *Z. Anorg. Allg. Chem.* 349 (1967) 225–240.
- SMART v. 5.625, Area-Detector Software Package, Bruker AXS, Madison, WI, 2001.
- Bruker AXS SHELXTL version 6.10, Structure Determination Package, Bruker AXS, Madison, WI, 2000.
- J.A. Mariden, M.M. Haley, *Cross-coupling reactions to sp carbon atoms*, in: A. de Meijere, F. Diederich (Eds.), *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed., Wiley, Weinheim, 2004, pp. 318–345.
- L. Brandsma, H.D. Verkruisje, *Synth. Commun.* 20 (1990) 2275–2277.
- B.H. Dana, B.H. Robinson, J. Simpson, *J. Organomet. Chem.* 648 (2002) 251–269.
- F. Fringuelli, G. Marino, A. Taticchi, G. Grandolini, *J. Chem. Soc., Perkin Trans. 2: Phys. Org. Chem.* 4 (1974) 332–337.

- [22] J. Lewis, N.J. Long, P.R. Raithby, G.P. Shields, W.-Y. Wong, M. Younus, *J. Chem. Soc., Dalton Trans.* (1997) 4283–4288.
- [23] A. Sakar, M.M. Haley, *Chem. Commun.* (2000) 1733–1734.
- [24] (a) M.C.B. Colbert, S.L. Ingham, J.L. Nicholas, N.J. Long, P.R. Raithby, *J. Chem. Soc., Dalton Trans.* (1994) 2215–2216;
(b) P. Jutzi, B. Kleinebeckel, *J. Organomet. Chem.* 545 (1997) 573–576;
(c) D.M. Guldi, M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* 119 (1997) 974–980;
(d) S.M. Draper, M. Delamesiere, E. Champeil, B. Twamley, J.J. Byrne, C. Long, *J. Organomet. Chem.* 589 (1999) 157–167.
- [25] (a) G. Bor, *Spectrochim. Acta* 19 (1963) 1209–1224;
(b) K.M. Nicholas, M.O. Nestle, D. Seyferth, in: H. Alper (Ed.), *Transition Metal Organometallics in Organic Synthesis*, vol. 2, Academic Press, New York, 1978, p. 2;
(c) J.L. Davison, in: P.S. Braterman (Ed.), *Reactions of Coordinated Ligands*, vol. I, Plenum Press, New York, 1986, p. 825;
(d) J. Lewis, B. Lin, M.S. Khan, M.R.A. Al-Mandhary, P.R. Raithby, *J. Organomet. Chem.* 484 (1994) 161–167;
(e) W.-Y. Wong, H.-Y. Lam, S.-M. Lee, *J. Organomet. Chem.* 648 (2000) 70–80.
- [26] (a) R.S. Dickinson, P.J. Fraser, in: F.G.A. Stone, R. West (Eds.), *Advances in Organometallic Chemistry*, vol. 12, 1974, pp. 323–377;
(b) F. Diederich, Y. Rubin, O.L. Chapman, N.S. Goroff, *Helv. Chim. Acta* 77 (1994) 1441–1457;
(c) B. Happ, T. Bartik, C. Zucchi, M.C. Rossi, F. Ghelfi, G. Pályi, G. Váradi, G. Szalontai, I.T. Horváth, A. Chiesi-Villa, C. Guastini, *Organometallics* 14 (1995) 809–819.
- [27] (a) G. Cetini, O. Gambino, R. Rosetti, E. Sappa, *J. Organomet. Chem.* 8 (1967) 149–154;
(b) C.E. Housecroft, B.F.G. Johnson, M.S. Khan, J. Lewis, P.R. Raithby, M.E. Robson, D.A. Wilkinson, *J. Chem. Soc., Dalton Trans.* (1992) 3171–3178.
- [28] (a) S. Aime, L. Milone, R. Rossetti, P.L. Stanghellini, *Inorg. Chim. Acta* 22 (1977) 135–139;
(b) R.K. Harris, *Nuclear Magnetic Resonance Spectroscopy: A Physicochemical View*, Pitman, London, 1983.
- [29] (a) J. Castro, A. Moyano, M.A. Pericas, A. Riera, M.A. Maestro, J. Mahía, *Organometallics* 19 (2000) 1704–1712;
(b) T.J. Snaith, P.J. Low, R. Rousseau, H. Pushmann, J.A.K. Howard, *J. Chem. Soc., Dalton Trans.* (2001) 292–299;
(c) E. Champeil, S.M.J. Draper, *Chem. Soc., Dalton Trans.* (2001) 1440–1447.
- [30] (a) H. Lang, U. Lay, M. Weinmann, *J. Organomet. Chem.* 436 (1992) 265–276;
(b) T. Bartik, B. Happ, M. Iglewsky, H. Badmann, R. Boese, P. Heimbach, T. Hoffmann, E. Wenschuh, *Organometallics* 11 (1992) 1235–1241.
- [31] J.C. Jeffery, R.M.S. Pereira, M.D. Vargas, M.J. Went, *J. Chem. Soc., Dalton Trans.* (1995) 1805–1811, and references therein.
- [32] M.I. Bruce, B.D. Kelly, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.* (1999) 847–852.
- [33] G.G. Sumner, H.P. Klug, L.E. Alexander, *Acta Crystallogr.* 17 (1964) 732–742.
- [34] (a) W. Weng, T. Bartik, M. Brady, B. Bartik, J.A. Ramsden, A.M. Arif, J.A. Gladysz, *J. Am. Chem. Soc.* 117 (1995) 11922–11931;
(b) B. Bartik, R. Dembinski, T. Bartik, A.M. Arif, J.A. Gladysz, *New J. Chem.* 21 (1997) 739–750;
(c) M. Brady, W. Weng, Y. Zhou, J.W. Seyler, A.J. Amoroso, A.M. Arif, M. Boehme, G. Frenking, J.A. Gladysz, *J. Am. Chem. Soc.* 119 (1997) 775–788.
- [35] C. Moreno, J.L. Gómez, R.-M. Medina, M.-J. Macazaga, A. Arnanz, A. Lough, D.H. Farrar, S. Delgado, *J. Organomet. Chem.* 579 (1999) 63–74.
- [36] (a) G.J. Bezems, P.H. Rieger, S.J. Visco, *J. Chem. Soc., Chem. Commun.* (1981) 265–266;
(b) C.M. Arewgoda, P.H. Rieger, B.H. Robinson, J. Simpson, S.J. Visco, *J. Am. Chem. Soc.* 104 (1982) 5633–5640;
(c) D. Osella, J. Fiedler, *Organometallics* 11 (1992) 3875–3878;
(d) D. Osella, L. Milone, C. Nervi, M. Ravera, *J. Organomet. Chem.* 488 (1995) 1–7;
(e) N.W. Duffy, J. McAdam, C. Nervi, D. Osella, M. Ravera, B.H. Robinson, J. Simpson, *Inorg. Chim. Acta* 247 (1996) 99–104;
(f) D. Osella, L. Milone, C. Nervi, M. Ravera, *Eur. J. Inorg. Chem.* (1998) 1473–1477.
- [37] J.R. Sowa, R.J. Angelici, *Inorg. Chem.* 30 (1991) 3534–3537.
- [38] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York, 2001. p. 505.