

## Syntheses, structures and comparative electrochemical study of $\pi$ -acetylene complexes of cobalt

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### Abstract

The preparation and characterization of the complexes  $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})]_2(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{H})$  (**2**),  $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})]_2(\mu\text{-}\eta^2\text{-HC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{H})$  (**3**),  $\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$  (**4**),  $\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CH})$  (**5**),  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})]_2(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{SiMe}_3)$  (**6**) and  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})]_2(\mu\text{-}\eta^2\text{-HC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{SiMe}_3)$  (**7**) are described. A comparative electrochemical study of all these complexes and the related  $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})]_2(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{SiMe}_3)$  (**1**),  $\text{Co}_2(\text{CO})_4(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CH})$  and  $\text{Co}_2(\text{CO})_4(\mu\text{-dppm})(\mu\text{-}\eta^2\text{-HC}_2\text{C}\equiv\text{CH})$  is presented by means of the cyclic and square-wave voltammetry techniques. Crystals of **2** and **3** suitable for single-crystal X-ray diffraction were grown and the molecular structures of these compounds are discussed.

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**Keywords:**  $\pi$ -Acetylene; Cobalt carbonyl complexes; Electrochemistry

### 1. Introduction

Carbon rich organometallic containing polyynes and acetylenic arrays continue to garner attention and increased research interest. Polyynediyl bridging ligands have been shown to be specially efficient in allowing the passage of electronic effects between redox active centres [1] and this raises possibilities for the generation of wire-like polyynyl materials with electronic properties tuned by both the end-capping and  $\pi$ -bound metal fragments [1c,2]. Interactions between identical mononuclear or cluster-based redox active groups bridged by ynyl and polyynyl spacers have been studied extensively [3], and it has been concluded that the strong electronic communi-

cation in these systems is a result of efficient mixing between filled metal fragment and polyyne-based orbitals.

The redox chemistry of  $\text{Co}_2$ -alkyne is well known and communication between these redox centres has been demonstrated for several systems [4].

We have previously reported the electrochemical behaviour of the complex, synthesized by Diederich [5],  $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})]_2(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{SiMe}_3)$  (**1**), showing the existence of electronic communication [1h]. Here, in order to evaluate the influence of the carbon chain end groups and the influence of a more basic and less steric demanding phosphine ligand on the cobalt atoms, we report the electrochemical study of the complexes  $[\text{Co}_2(\text{CO})_4(\mu\text{-L-L})]_2(\mu\text{-}\eta^2\text{-RC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{R}')$  ( $\text{L-L} = \text{dppm}$ ,  $\text{R} = \text{H}$ ,  $\text{R}' = \text{SiMe}_3$ , **2**,  $\text{R}, \text{R}' = \text{H}$ , **3**;  $\text{L-L} = \text{dmpm}$ ,  $\text{R}, \text{R}' = \text{SiMe}_3$ , **6**) together with that of the individual components,  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CR})$  ( $\text{R} = \text{SiMe}_3$ , **4**,  $\text{R} = \text{H}$ , **5**). The results are

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compared with those obtained, in our laboratory, for alkynylthiophene and alkynylbenzene analogous complexes [1h,1j,6]. The X-ray structures of **2** and **3** are given.

## 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 Ar. All solvents for synthetic use were reagent grade. Hexane, tetrahydrofuran (THF) were dried and distilled over sodium in the presence of benzophenone under an Ar atmosphere. Also under Ar, CH<sub>2</sub>Cl<sub>2</sub> and acetone were dried and distilled over CaH<sub>2</sub> and CaCl<sub>2</sub>, respectively. Methanol (Aldrich) was stored over molecular sieves (4 Å) under Ar. All solvents were bubbled with Ar for 1 h after distillation and then stored under Ar, or degassed by means of at least 3 freeze–pump–thaw cycles after distillation and before use. Column chromatography was performed by using Alfa neutral alumina at activity II and silica gel 100 (Fluka). Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel 60 (Merck). Co<sub>2</sub>(CO)<sub>8</sub>, 1,4-bis(trimethylsilyl)butadiyne (MeSiC≡CC≡CSiMe<sub>3</sub>) (Fluka), Cu(OAc)<sub>2</sub> (Prolabo), 1,2-bis(dimethylphosphino)methane (Strem) and 1,2-bis-(diphenylphosphino)methane, pyridine, tetrabutylammonium fluoride (Bu<sub>4</sub>NF) (Aldrich) were used as received. Trimethylamine *N*-oxide (Me<sub>3</sub>NO) (Aldrich) was sublimed prior to use and stored under Ar. The compounds, Co<sub>2</sub>(CO)<sub>6</sub>(μ-η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>C≡CSiMe<sub>3</sub>) [7], Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)(μ-η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>C≡CH) [5], [Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)]<sub>2</sub>(μ-η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>(C≡C)<sub>2</sub>C<sub>2</sub>SiMe<sub>3</sub>) (**1**) [5], were prepared according to literature procedures. All reagents were used without further purification unless otherwise noted. The <sup>1</sup>H, <sup>31</sup>P and <sup>13</sup>C NMR spectra were recorded on a Bruker AMX-300 or 500 instrument. Chemical shifts were measured relative either to an internal reference of tetramethylsilane or to residual protons of the solvents. Infrared spectra were measured on a Perkin–Elmer 1650 infrared spectrometer. Elemental analyses was performed by the Microanalytical Laboratory of the University Autónoma of Madrid on a Perkin–Elmer 240 B microanalyzer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB or Malyd by the Mass Laboratory of the University Autónoma of Madrid.

### 2.2. Synthesis of [Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)]<sub>2</sub>(μ-η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>(C≡C)<sub>2</sub>C<sub>2</sub>H) (**2**) and [Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)]<sub>2</sub>(μ-η<sup>2</sup>-HC<sub>2</sub>(C≡C)<sub>2</sub>C<sub>2</sub>H) (**3**)

To [Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)]<sub>2</sub>(μ-η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>(C≡C)<sub>2</sub>C<sub>2</sub>-SiMe<sub>3</sub>) (0.11 g, 0.07 mmol) in THF/MeOH (10:1)

(22 mL) was added 1.0 M Bu<sub>4</sub>NF in THF (70 μL, 0.07 mmol). The mixture was stirred for 24 h and was monitored by TLC (SiO<sub>2</sub>). The solution was concentrated and chromatographed by TLC (SiO<sub>2</sub>) using hexane/acetone (2:1) as eluent. The TLC gave a brown band and two violet bands. The brown band, isolated from the top of the plate, yielded the starting [Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)]<sub>2</sub>(μ-η<sup>2</sup>-Me<sub>3</sub>SiC<sub>2</sub>(C≡C)<sub>2</sub>C<sub>2</sub>-SiMe<sub>3</sub>) compound. The first violet band gave the product **2** as a dark-violet solid (0.028 g, 27% yield). The second violet band was identified as [Co<sub>2</sub>(CO)<sub>4</sub>(μ-dppm)]<sub>2</sub>(μ-η<sup>2</sup>-HC<sub>2</sub>(C≡C)<sub>2</sub>C<sub>2</sub>H) (0.02 g, 20% yield).

(**2**) FT-IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): ν<sub>C–H</sub> 3306 (w); ν<sub>C≡C</sub> 2068 (vw); ν<sub>CO</sub> 2029 (s), 2007 (vs), 1979 (s). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 7.46–7.08 (m, 40H, Ph); 6.14 (s, br, 1H, ≡C–H); 4.08–3.95 (m, B of ABX<sub>2</sub>, 1H, P–CH<sub>2</sub>–P (SiMe<sub>3</sub>)); 3.68–3.52 (m, B of ABX<sub>2</sub>, 1H, P–CH<sub>2</sub>–P (≡C–H)); 3.48–3.38 (m, A of ABX<sub>2</sub>, 1H, P–CH<sub>2</sub>–P (≡C–H)); 3.37–3.23 (m, A of ABX<sub>2</sub>, 1H, P–CH<sub>2</sub>–P (SiMe<sub>3</sub>)); 0.438 (s, 9H, –SiMe<sub>3</sub>). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, ppm): δ 40.55 (s, 2P, ≡C–H); 37.12 (s, 2P≡C–SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 206.3 (m, CO), 203.8 (m, CO), 202.8 (m, CO), 200.9 (m, CO); 136.4 (t, J<sub>CP</sub> = 23.1 Hz, *i*-Ph), 135.6 (t, J<sub>CP</sub> = 21.4 Hz, *i*-Ph), 134.8 (t, J<sub>CP</sub> = 19.3 Hz, *i*-Ph), 134.3 (t, J<sub>CP</sub> = 18.1 Hz, *i*-Ph), 131.9 (t, J<sub>CP</sub> = 6.2 Hz, *o*-Ph), 131.5 (t, J<sub>CP</sub> = 6.2 Hz, *o*-Ph), 130.8 (t, J<sub>CP</sub> = 6.4 Hz, *o*-Ph), 130.5 (t, J<sub>CP</sub> = 6.2 Hz, *o*-Ph), 129.3 (s, *p*-Ph), 129.2 (s, *p*-Ph), 129.1 (s, *p*-Ph), 128.9 (s, *p*-Ph), 127.9 (m, *m*-Ph), 127.7 (t, J<sub>CP</sub> = 4.8 Hz, *m*-Ph), 127.5 (t, J<sub>CP</sub> = 4.7 Hz, *m*-Ph); 90.5 (m, C<sub>2</sub>), 86.5 (s br, C<sub>3</sub>), 82.4, 82.1 (s, C<sub>4</sub>, C<sub>5</sub>), 80.2 (m, C<sub>8</sub>), 65.9 (m, C<sub>7</sub>); 39.4 (t, J<sub>CP</sub> = 19.0 Hz, P–CH<sub>2</sub>–P), 37.6 (t, J<sub>CP</sub> = 20.3 Hz, P–CH<sub>2</sub>–P); 0.44 (s, –SiMe<sub>3</sub>). MS (FAB<sup>+</sup>, *m/z*): 1342.1 (M<sup>+</sup> – 2CO); 1286.1 (M<sup>+</sup> – 4CO); 1230.1 (M<sup>+</sup> – 6CO); 1202.1 (M<sup>+</sup> – 7CO); 1174.1 (M<sup>+</sup> – 8CO). Anal. Calc. for C<sub>69</sub>H<sub>54</sub>O<sub>8</sub>-Co<sub>4</sub>P<sub>4</sub>Si: C, 59.2; H, 3.9. Found: C, 58.9; H, 4.1%.

(**3**) FT-IR (CHCl<sub>3</sub>, cm<sup>-1</sup>): ν<sub>C–H</sub> 3303 (w); ν<sub>C≡C</sub> 2100 (w); ν<sub>CO</sub> 2022 (s), 2002 (vs), 1972 (s), 1951 (sh, w). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm): δ 7.46–7.12 (m, 40H, Ph); 6.13 (s, br, 2H, ≡C–H); 3.66–3.53 (m, B of ABX<sub>2</sub>, 2H, P–CH<sub>2</sub>–P); 3.44–3.32 (m, A of ABX<sub>2</sub>, 2H, P–CH<sub>2</sub>–P). <sup>31</sup>P NMR (121 MHz, CDCl<sub>3</sub>, ppm): δ 40.34 (s, 2P). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 206 (s, CO); 135.6 (t, *i*-Ph), 134.2 (t, *i*-Ph), 131.3 (t, J<sub>CP</sub> = 6.8 Hz, *o*-Ph), 130.2 (t, J<sub>CP</sub> = 6.4 Hz, *o*-Ph), 128.8 (s, *p*-Ph), 128.6 (s, *p*-Ph), 127.5 (t, J<sub>CP</sub> = 4.2 Hz, *m*-Ph), 127.2 (t, J<sub>CP</sub> = 4.1 Hz, *m*-Ph); 86.8 (s, C<sub>3</sub>, C<sub>6</sub>), 81.8 (s, C<sub>4</sub>, C<sub>5</sub>); 37.5 (t, J<sub>CP</sub> = 20.1 Hz, P–CH<sub>2</sub>–P). MS (Malyd, ditranol) *m/z*: 1326.9 (M<sup>+</sup> + H); 1101.9 (M – 8CO). Anal. Calc. for C<sub>66</sub>H<sub>46</sub>O<sub>8</sub>Co<sub>4</sub>P<sub>4</sub>: C, 59.8; H, 3.5. Found: C, 59.5; H, 3.6%.

### 2.3. Synthesis of $[Co_2(CO)_4(\mu-dppm)]_2(\mu-\eta^2-HC_2(C\equiv C)_2C_2H)$ (**3**)

To  $[Co_2(CO)_4(\mu-dppm)]_2(\mu-\eta^2-Me_3SiC_2(C\equiv C)_2C_2-SiMe_3)$  (0.21 g, 0.14 mmol) in wet THF (30 mL) was added 1.0 M  $Bu_4NF$  in THF (0.29 mL, 0.29 mmol). The solution was stirred for 24 h and was monitored by TLC ( $SiO_2$ ). The solvent was evaporated under vacuum and the residue was dissolved in  $CH_2Cl_2$  and purified by TLC ( $SiO_2$ ) using hexane/ $CH_2Cl_2$  (1:4) as eluent. The product **3** was obtained as a violet solid (0.18 g, 97% yield).

### 2.4. Synthesis of $Co_2(CO)_4(\mu-dmpm)-(\mu-\eta^2-Me_3SiC_2C\equiv CSiMe_3)$ (**4**)

A mixture of  $Co_2(CO)_6(\mu-\eta^2-Me_3SiC_2C\equiv CSiMe_3)$  (2.00 g, 4.16 mmol) and 1,2 bis(dimethylphosphino)methane (0.57 g, 4.16 mmol) in hexane (100 mL) was prepared. Immediately  $Me_3NO$  (0.92 g, 8.32 mmol) was added and the reaction mixture was stirred and heated at 40 °C until the reaction was seen to be completed by IR spectroscopy and no starting material remained (6 h). After removal of the solvent under vacuum, the residue was dissolved with  $CH_2Cl_2$  and purified by column chromatography on  $SiO_2$  packed in hexane. Hexane/ $CH_2Cl_2$  (1:1) eluted a red band which yielded **4** as a red solid (2.21 g, 95% yield). FT-IR (hexane,  $cm^{-1}$ ):  $\nu_{C\equiv C}$  2108 (vw);  $\nu_{CO}$  2024 (s), 1998 (vs), 1972 (s), 1956 (m).  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm):  $\delta$  2.79 (dt,  $J_{HH} = 13.5$  Hz,  $J_{PH} = 11.1$  Hz, 1H, P- $CH_2$ -P), 2.03 (dt,  $J_{HH} = 13.5$  Hz,  $J_{PH} = 10.1$  Hz, 1H, P- $CH_2$ -P); 1.54 (t,  $J_{PH} = 3.3$  Hz, 6H, -P-Me), 1.46 (t,  $J_{PH} = 3.8$  Hz, 6H, -P-Me); 0.27 (s, 9H,  $Me_3SiC-$ ); 0.16 (s, 9H,  $\equiv CSiMe_3$ ).  $^{31}P$  NMR (121 MHz,  $CDCl_3$ , ppm):  $\delta$  13.8 (s br, 2P).  $^{13}C$  (125 MHz,  $CDCl_3$ , ppm):  $\delta$  206.7 (m, CO), 202.6 (m, CO); 108.3 (s,  $C_3$ ), 99.9 (s,  $C_4$ ), 84.4 (t,  $C_1$ ); 40.2 (t,  $J_{CP} = 21.7$  Hz, P- $CH_2$ -P); 20.9 (t,  $J_{CP} = 11.0$  Hz, -Me), 17.7 (t,  $J_{CP} = 16.8$  Hz, -Me); 1.0 (s,  $Me_3SiC-$ ); 0.2 (s,  $\equiv CSiMe_3$ ). MS ( $FAB^+$ ,  $m/z$ ): 559.8 ( $M^+$ ); 531.8 ( $M^+ - CO$ ); 503.8 ( $M^+ - 2CO$ ); 575.8 ( $M^+ - 3CO$ ); 547.8 ( $M^+ - 4CO$ ). Anal. Calc. for  $C_{19}H_{32}O_4Co_2P_2Si_2$ : C, 40.7; H, 5.7. Found: C, 40.5; H, 6.0%.

### 2.5. Synthesis of $Co_2(CO)_4(\mu-dmpm)-(\mu-\eta^2-Me_3SiC_2C\equiv CH)$ (**5**)

To  $Co_2(CO)_4(\mu-dmpm)(\mu-\eta^2-Me_3SiC_2C\equiv CSiMe_3)$  (1.01 g, 1.80 mmol) in THF/MeOH (10:1) (100 mL) was added 1.0 M  $Bu_4NF$  in THF (3.6 mL, 3.6 mmol). The mixture was stirred at room temperature for 24 h and then poured into hexane (160 mL) and saturated aqueous NaCl solution. The organic phase was dried over  $MgSO_4$  and evaporation afforded **5** as a red solid (0.79 g, 90% yield). FT-IR (hexane,  $cm^{-1}$ ):  $\nu_{C-H}$  3302 (w);  $\nu_{C\equiv C}$  2068 (vw);  $\nu_{CO}$  2021 (s), 1993 (vs), 1964 (s).

$^1H$  NMR (300 MHz,  $CDCl_3$ , ppm):  $\delta$  3.45 (s, 1H,  $\equiv C-H$ ); 2.70 (dt,  $J_{HH} = 11.8$  Hz,  $J_{PH} = 11.7$  Hz, 1H, P- $CH_2$ -P), 2.05 (dt,  $J_{HH} = 11.8$  Hz,  $J_{PH} = 10.4$  Hz, 1H, P- $CH_2$ -P); 1.56 (s br, 6H, -PMe), 1.46 (s br, 6H, -PMe); 0.27 (s, 9H,  $Me_3SiC-$ ).  $^{31}P$  NMR (121 MHz,  $CDCl_3$ , ppm):  $\delta$  13.6 (s br, 2P).  $^{13}C$  (125 MHz,  $CDCl_3$ , ppm):  $\delta$  206.9 (m, CO), 202.7 (m, CO); 86.4 (t,  $C_3$ ), 84.2 (s br,  $C_1$ ), 81.5 (s,  $C_4$ ), 76.9 (s br,  $C_2$ ); 40.7 (t,  $J_{CP} = 22.0$  Hz, P- $CH_2$ -P); 17.6 (t,  $J_{CP} = 17.1$  Hz, Me), 11.7 (t,  $J_{CP} = 22.0$  Hz, Me); 0.2 (s,  $Me_3SiC-$ ). MS ( $FAB^+$ ,  $m/z$ ): 487.8 ( $M^+$ ); 459.8 ( $M^+ - CO$ ); 431.8 ( $M^+ - 2CO$ ); 403.8 ( $M^+ - 3CO$ ); 375.8 ( $M^+ - 4CO$ ). Anal. Calc. for  $C_{16}H_{24}O_4Co_2P_2Si$ : C, 39.4; H, 4.9. Found: C, 39.1; H, 5.2%.

### 2.6. Synthesis of $[Co_2(CO)_4(\mu-dmpm)]_2(\mu-\eta^2-Me_3SiC_2(C\equiv C)_2C_2SiMe_3)$ (**6**)

To  $Co_2(CO)_4(\mu-dmpm)(\mu-\eta^2-Me_3SiC_2C\equiv CH)$  (0.10 g, 0.2 mmol) in dry pyridine (10 mL) anhydrous  $Cu(OAc)_2$  (0.36 g, 2.0 mmol) was added and the mixture reaction stirred at room temperature for 2 h and monitored by TLC ( $SiO_2$ ). The solvent was evaporated, the solid extracted with  $CH_2Cl_2$ , and the resulting solution concentrated and chromatographed by TLC ( $SiO_2$ ) using hexane/ $CH_2Cl_2$  (1:1) as eluent. A brown-reddish band gave the product **6** (0.12 g, 60% yield). FT-IR (hexane,  $cm^{-1}$ ):  $\nu_{C\equiv C}$  2102 (vw);  $\nu_{CO}$  2014 (s), 1995 (vs), 1963 (s).  $^1H$  NMR (500 MHz,  $CDCl_3$ , ppm):  $\delta$  2.72 (dt,  $J_{HH} = 13.6$  Hz,  $J_{PH} = 10.8$  Hz, 1H, P- $CH_2$ -P), 2.09 (dt,  $J_{HH} = 13.7$  Hz,  $J_{PH} = 10.2$  Hz, 1H, P- $CH_2$ -P); 1.56 (t,  $J_{PH} = 3.3$  Hz, 6H, -PMe), 1.48 (t,  $J_{PH} = 3.8$  Hz, 6H, -PMe); 0.28 (s, 18H, 2  $Me_3SiC-$ ).  $^{31}P$  NMR (121 MHz,  $CDCl_3$ , ppm):  $\delta$  13.2 (s br, 4P).  $^{13}C$  (125 MHz,  $CDCl_3$ , ppm):  $\delta$  206.4 (m, CO), 202.4 (m, CO); 87.3 (t,  $J_{CP} = 5.0$  Hz,  $C_3$ ,  $C_6$ ), 86.6 (t,  $J_{CP} = 11.5$  Hz,  $C_1$ ,  $C_8$ ), 81.5 (s,  $C_4$ ,  $C_5$ ), 76.4 (m,  $C_2$ ,  $C_7$ ); 41.1 (t,  $J_{CP} = 21.7$  Hz, P- $CH_2$ -P); 20.8 (t,  $J_{CP} = 11.6$  Hz, Me), 18.1 (t,  $J_{CP} = 16.9$  Hz, Me); 0.6 (s,  $Me_3SiC-$ ). MS ( $FAB^+$ ,  $m/z$ ): 974.1 ( $M^+$ ); 918.1 ( $M^+ - 2CO$ ); 890.1 ( $M^+ - 3CO$ ); 862.1 ( $M^+ - 4CO$ ); 834.1 ( $M^+ - 5CO$ ); 806.1 ( $M^+ - 6CO$ ); 778.1 ( $M^+ - 7CO$ ); 750.1 ( $M^+ - 8CO$ ). Anal. Calc. for  $C_{32}H_{46}O_8Co_4P_4Si_2$ : C, 39.4; H, 4.7. Found: C, 39.1; H, 4.9%.

### 2.7. Synthesis of $[Co_2(CO)_4(\mu-dmpm)]_2(\mu-\eta^2-HC_2(C\equiv C)_2C_2H)$ (**7**)

To  $[Co_2(CO)_4(\mu-dmpm)]_2(\mu-\eta^2-Me_3SiC_2(C\equiv C)_2C_2-SiMe_3)$  (0.032 g, 0.033 mmol) in THF/MeOH (10:1) (22 mL) was added 1.0 M  $Bu_4NF$  in THF (0.066 mL, 0.066 mmol). The mixture was stirred for 1.30 h and was monitored by TLC ( $SiO_2$ ). The solution was concentrated and chromatographed by TLC ( $SiO_2$ ) using hexane/ $CH_2Cl_2$  (2:1) as eluent. A violet band gave the

compound **7** as a violet solid (0.011 g, 40% yield). FT-IR ( $\text{CH}_2\text{Cl}_2$ ,  $\text{cm}^{-1}$ ):  $\nu_{\text{C-H}}$  3302 (w);  $\nu_{\text{C}\equiv\text{C}}$  2100 (vw);  $\nu_{\text{CO}}$  2015 (s), 1996 (vs), 1970 (s).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  5.80 (s br, 2H,  $\text{C}\equiv\text{C-H}$ ); 2.52 (dt,  $J_{\text{HH}} = 12.4$  Hz,  $J_{\text{PH}} = 10.7$  Hz, 1H, P- $\text{CH}_2$ -P), 2.33 (dt,  $J_{\text{HH}} = 12.3$  Hz,  $J_{\text{PH}} = 11.2$  Hz, 1H, P- $\text{CH}_2$ -P); 1.62 (t,  $J_{\text{PH}} = 3.4$  Hz, 6H, -PMe), 1.55 (t,  $J_{\text{PH}} = 3.2$  Hz, 6H, -PMe).  $^{31}\text{P}$  NMR (121 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  16.1 (s br, 4P).  $^{13}\text{C}$  (125 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  206.8 (s, CO); 88.8 (s,  $\text{C}_3$ ,  $\text{C}_6$ ), 82.2 (s,  $\text{C}_4$ ,  $\text{C}_5$ ), 78.3 (s br,  $\text{C}_1$ ,  $\text{C}_8$  or  $\text{C}_2$ ,  $\text{C}_7$ ); 40.4 (t,  $J_{\text{CP}} = 21.5$  Hz, P- $\text{CH}_2$ -P); 20.4 (t,  $J_{\text{CP}} = 12.4$  Hz, Me), 18.6 (t,  $J_{\text{CP}} = 16.4$  Hz, Me). MS (FAB $^+$ ,  $m/z$ ): 828.1 ( $\text{M}^+$ ); 772.1 ( $\text{M}^+ - 2\text{CO}$ ); 744.1 ( $\text{M}^+ - 3\text{CO}$ ); 716.1 ( $\text{M}^+ - 4\text{CO}$ ); 688.1 ( $\text{M}^+ - 5\text{CO}$ ); 632.1 ( $\text{M}^+ - 7\text{CO}$ ); 604.1 ( $\text{M}^+ - 8\text{CO}$ ). Anal. Calc. for  $\text{C}_{26}\text{H}_{30}\text{O}_8\text{Co}_4\text{P}_4$ : C, 37.7; H, 3.6. Found: C, 37.4; H, 3.8%.

## 2.8. X-ray crystallography

Red crystals of **2** and **3** were obtained by recrystallization of the complexes from  $\text{CH}_2\text{Cl}_2$  to hexane mixtures. A summary of selected crystallographic data for **2** and **3** is given in Table 1. A red single crystal of

approximate dimensions  $0.14 \times 0.10 \times 0.04$  mm for **2** and  $0.20 \times 0.10 \times 0.02$  mm for **3** with prismatic shape was mounted on a glass fiber and transferred to a Bruker SMART 6K CCD area-detector three-circle diffractometer with a MAC Science Co., Ltd. Rotating Anode (Cu K $\alpha$  radiation,  $\lambda = 1.54178$  Å) generator equipped with Goebel mirrors at settings of 50 kV and 110 mA [8]. X-ray data were collected at 296 K for **2** and 295 K for **3**, with a combination of six runs at different  $\varphi$  and  $2\theta$  angles, 3600 frames. The data were collected using  $0.3^\circ$  wide  $\omega$  scans (15 s/frame at  $2\theta = 40^\circ$  and 30 s/frame at  $2\theta = 100^\circ$ ), crystal-to-detector distance of 4.0 cm.

The raw intensity data frames were integrated with the SAINT program [9], which also applied corrections for Lorentz and polarization effects.

The substantial redundancy in data allows empirical absorption corrections (SADABS) [10] to be applied using multiple measurements of symmetry-equivalent reflections (ratio of minimum to maximum apparent transmission: 0.590663 for **2** and 0.608741 for **3**). A total number of 21,992 reflections for **2** and 9655 for **3** were collected and 11,196 independent reflections for **2** and 5006 for **3** remained after merging  $R(\text{int}) = 0.0559$ ,

Table 1  
Crystal data and structure refinement for **2** and **3**

|  | <b>2</b>  | <b>3</b>  |
|--|---|---|
| Empirical formula                              | $\text{C}_{70}\text{H}_{56}\text{Cl}_2\text{Co}_4\text{O}_8\text{P}_4\text{Si}$ | $\text{C}_{66}\text{H}_{46}\text{Co}_4\text{O}_8\text{P}_4$           |
| Formula weight                                 | 1483.74   | 1326.63   |
| Temperature (K)                                | 296(2)  | 295(2)  |
| Wavelength (Å)                                 | 1.54178   | 1.54178   |
| Crystal system                                 | Triclinic   | Triclinic   |
| Space group                                    | $P\bar{1}$  | $P\bar{1}$  |
| Unit cell dimensions                           |   |   |
| $a$ (Å)  | 12.7914(4)  | 10.5807(2)  |
| $b$ (Å)  | 15.4032(5)  | 12.9680(2)  |
| $c$ (Å)  | 18.5139(6)  | 13.0490(2)  |
| $\alpha$ ( $^\circ$ )                          | 89.254(2)   | 101.5080(10)  |
| $\beta$ ( $^\circ$ )                           | 81.327(2)   | 107.5010(10)  |
| $\gamma$ ( $^\circ$ )                          | 83.438(2)   | 110.3340(10)  |
| Volume (Å $^3$ )                               | 3582.4(2)   | 1505.81(4)  |
| $Z$  | 2   | 1   |
| Density (calculated) (Mg/m $^3$ )              | 1.376   | 1.463   |
| Absorption coefficient (mm $^{-1}$ )           | 9.230   | 9.929   |
| $F(000)$                                       | 1512  | 674   |
| Crystal size                                   | $0.14 \times 0.10 \times 0.04$  | $0.20 \times 0.10 \times 0.02$  |
| Theta range for data collection ( $^\circ$ )   | 2.41–65.14  | 3.78–70.45  |
| Index ranges                                   | $-13 \leq h \leq 15$ , $-18 \leq k \leq 17$ ,<br>$-21 \leq l \leq 21$           | $-11 \leq h \leq 10$ , $-13 \leq k \leq 14$ ,<br>$-14 \leq l \leq 15$ |
| Reflections collected                          | 21,992  | 9655  |
| Independent reflections                        | 11,196 [ $R_{\text{int}} = 0.0559$ ]  | 5006 [ $R_{\text{int}} = 0.0397$ ]                                    |
| Completeness to theta = 65.14 $^\circ$         | 91.6%   | 86.9%   |
| Absorption correction                          | YES, SADABS v. 2.03   | YES, SADABS v. 2.03   |
| Refinement method                              | Full-matrix least-squares on $F^2$  | Full-matrix least-squares on $F^2$                                    |
| Data/restraints/parameters                     | 11,196/0/805  | 5006/0/462  |
| Goodness-of-fit on $F^2$                       | 0.963   | 1.030   |
| Final $R$ indices [ $I > 2\sigma(I)$ ]         | $R_1 = 0.0633$ , $wR_2 = 0.1413$  | $R_1 = 0.0354$ , $wR_2 = 0.0919$                                      |
| $R$ indices (all data)                         | $R_1 = 0.1553$ , $wR_2 = 0.1790$  | $R_1 = 0.0417$ , $wR_2 = 0.0966$                                      |
| Largest different peak and hole (e Å $^{-3}$ ) | 0.333 and $-0.244$  | 0.434 and $-0.211$  |

$R(\sigma) = 0.1028$  for **2** and  $R(\text{int}) = 0.0397$ ,  $R(\sigma) = 0.0508$  for **3**. The unit cell parameters were obtained by full-matrix least-squares refinements of 2501 and 3931 reflections for **2** and **3**, respectively.

The software package SHELXTL version 6.10 [11] was used for space group determination, structure solution and refinement. The structure was solved by direct methods (SHELXS-97) [12], completed with difference Fourier syntheses, and refined with full-matrix least-squares using SHELXL-97 [13] minimizing  $\omega(F_o^2 - F_c^2)^2$ . 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 dispersion factors are contained in the SHELXTL 6.10 program library. The hydrogen atom positions for the complex **2** were calculated geometrically and were allowed to ride on their parent carbon atoms with fixed isotropic  $U$ . For the complex **3** the hydrogens atoms were localized by its electronic densities and isotropically refined.

Final positional parameters, anisotropic thermal parameters, hydrogen atom parameters and structure amplitudes are available as supplementary material. Tables 2 and 3 contain selected bond distances and angles for **2** and **3**, respectively. Figs. 1 and 2 present a molecular diagram of **2** and **3**, respectively.

### 2.9. Electrochemical experiments

Electrochemical measurements were carried out with a computer driven AUTOLAB PGSTAT30 electrochemistry system in a three electrode cell under  $N_2$  atmosphere in anhydrous deoxygenated solvents (THF and  $CH_2Cl_2$ ) containing 0.2 M tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as supporting electrolyte. Cyclic and square-wave voltammetry (CV and SWV, respectively) were made. Polycrystalline Pt (0.05 cm<sup>2</sup>) and 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 an internal standard, and all potential values in this work are referred to the Fc\*<sup>+</sup>/Fc\* couple. Under the actual experimental conditions,  $E_{1/2}$  of the ferrocene couple (Fc<sup>+</sup>/Fc) was +0.44 V vs. Fc\*<sup>+</sup>/Fc\* in THF solution and +0.55 V vs. Fc\*<sup>+</sup>/Fc\* in  $CH_2Cl_2$  solution.

## 3. Results and discussion

### 3.1. Synthesis and spectroscopic characterization

The complexes  $[Co_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{-}(C\equiv C)_2C_2H)]$  (**2**) and  $[Co_2(CO)_4(\mu\text{-dppm})_2(\mu\text{-}\eta^2\text{-HC}_2\text{-}(C\equiv C)_2C_2H)]$  (**3**) were synthesized from **1**, following one of the standard methods of proteodesilylation.

Table 2  
Bond lengths (Å) and angles (°) for **2**

| Bond lengths (Å) |            |
|------------------|------------|
| C(1)–C(2)        | 1.349(9)   |
| C(1)–Si(1)       | 1.837(7)   |
| C(1)–Co(2)       | 1.966(7)   |
| C(1)–Co(1)       | 1.985(7)   |
| C(2)–C(3)        | 1.387(9)   |
| C(2)–Co(1)       | 1.958(6)   |
| C(2)–Co(2)       | 1.966(7)   |
| C(3)–C(4)        | 1.210(9)   |
| C(4)–C(5)        | 1.345(9)   |
| C(5)–C(6)        | 1.207(9)   |
| C(6)–C(7)        | 1.405(9)   |
| C(7)–C(8)        | 1.344(9)   |
| C(7)–Co(3)       | 1.954(6)   |
| C(7)–Co(4)       | 1.965(7)   |
| C(8)–Co(4)       | 1.944(7)   |
| C(8)–Co(3)       | 1.952(7)   |
| C(9)–P(2)        | 1.825(6)   |
| C(9)–P(1)        | 1.828(6)   |
| C(10)–P(3)       | 1.817(7)   |
| C(10)–P(4)       | 1.840(7)   |
| C(11)–Co(1)      | 1.776(8)   |
| C(12)–Co(1)      | 1.763(9)   |
| C(13)–Co(2)      | 1.780(9)   |
| C(14)–Co(2)      | 1.796(9)   |
| C(15)–Co(3)      | 1.796(9)   |
| C(16)–Co(3)      | 1.787(10)  |
| C(17)–Co(4)      | 1.773(8)   |
| C(18)–Co(4)      | 1.797(9)   |
| C(19)–P(1)       | 1.822(7)   |
| C(25)–P(1)       | 1.820(7)   |
| C(31)–P(2)       | 1.814(7)   |
| C(37)–P(2)       | 1.825(7)   |
| C(43)–P(3)       | 1.823(8)   |
| C(49)–P(3)       | 1.822(8)   |
| C(55)–P(4)       | 1.824(8)   |
| C(61)–P(4)       | 1.830(7)   |
| Co(1)–P(1)       | 2.232(2)   |
| Co(1)–Co(2)      | 2.4814(15) |
| Co(2)–P(2)       | 2.238(2)   |
| Co(3)–P(3)       | 2.222(2)   |
| Co(3)–Co(4)      | 2.4885(16) |
| Co(4)–P(4)       | 2.214(2)   |
| Bond angles (°)  |            |
| C(2)–C(1)–Si(1)  | 139.5(5)   |
| C(2)–C(1)–Co(2)  | 69.9(4)    |
| Si(1)–C(1)–Co(2) | 136.4(4)   |
| C(2)–C(1)–Co(1)  | 68.9(4)    |
| Si(1)–C(1)–Co(1) | 135.4(4)   |
| Co(2)–C(1)–Co(1) | 77.8(3)    |
| C(1)–C(2)–C(3)   | 143.2(7)   |
| C(1)–C(2)–Co(1)  | 71.1(4)    |
| C(3)–C(2)–Co(1)  | 133.8(5)   |
| C(1)–C(2)–Co(2)  | 70.0(4)    |
| C(3)–C(2)–Co(2)  | 132.8(5)   |
| Co(1)–C(2)–Co(2) | 78.5(2)    |
| C(4)–C(3)–C(2)   | 173.0(8)   |
| C(3)–C(4)–C(5)   | 178.7(8)   |
| C(6)–C(5)–C(4)   | 178.4(8)   |
| C(5)–C(6)–C(7)   | 171.2(8)   |
| C(8)–C(7)–C(6)   | 145.3(7)   |
| C(8)–C(7)–Co(3)  | 69.8(4)    |
| C(6)–C(7)–Co(3)  | 134.2(5)   |
| C(8)–C(7)–Co(4)  | 69.1(4)    |

Table 2 (continued)

| Bond angles (°)  |           |
|------------------|-----------|
| C(6)–C(7)–Co(4)  | 131.5(5)  |
| Co(3)–C(7)–Co(4) | 78.8(2)   |
| C(7)–C(8)–Co(4)  | 70.7(4)   |
| C(7)–C(8)–Co(3)  | 70.0(4)   |
| Co(4)–C(8)–Co(3) | 79.4(3)   |
| P(2)–C(9)–P(1)   | 110.9(3)  |
| P(3)–C(10)–P(4)  | 110.9(3)  |
| C(2)–Co(1)–C(1)  | 40.0(3)   |
| C(2)–Co(1)–Co(2) | 50.9(2)   |
| C(1)–Co(1)–Co(2) | 50.8(2)   |
| P(1)–Co(1)–Co(2) | 96.79(7)  |
| C(2)–Co(2)–C(1)  | 40.1(3)   |
| C(2)–Co(2)–Co(1) | 50.63(19) |
| C(1)–Co(2)–Co(1) | 51.4(2)   |
| P(2)–Co(2)–Co(1) | 96.72(7)  |
| C(8)–Co(3)–C(7)  | 40.2(3)   |
| C(8)–Co(3)–Co(4) | 50.2(2)   |
| C(7)–Co(3)–Co(4) | 50.76(19) |
| P(3)–Co(3)–Co(4) | 97.07(7)  |
| C(8)–Co(4)–C(7)  | 40.2(3)   |
| C(8)–Co(4)–Co(3) | 50.4(2)   |
| C(7)–Co(4)–Co(3) | 50.39(19) |
| P(4)–Co(4)–Co(3) | 96.47(7)  |

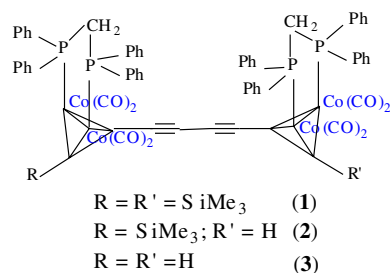
The reaction with  $\text{NBu}_4\text{F}$  in THF/MeOH (10:1) at room temperature leads to the monoprotionate and diprotionate derivatives, **2** and **3**, respectively. When wet THF is used only the compound **3** is obtained. The IR spectra of both compounds show two weak bands around 3300 and 2100  $\text{cm}^{-1}$  owing to  $\nu_{\text{C}=\text{H}}$  and  $\nu_{\text{C}\equiv\text{C}}$ , respectively. The  $\nu_{\text{CO}}$  of carbonyl ligands appear in the range 2030–1970  $\text{cm}^{-1}$ . In the  $^1\text{H}$  NMR spectrum of **2** two singlets at  $\delta = 0.44$  and 6.14 ppm owing to the trimethylsilyl group and acetylenic hydrogen respectively are observed. In this complex the two  $\text{Co}_2(\text{dppm})$  units are inequivalent and the  $\text{CH}_2$  of the phosphine ligands give rise to four multiplets, a double number than in **3** where the two  $\text{Co}_2(\text{dppm})$  units are equivalent. The two acetylenic hydrogens in **3** give a singlet signal at  $\delta = 6.13$  ppm. In the  $^{13}\text{C}$  NMR spectrum of **2** six resonances are observed in the 90–66 ppm range, owing to the carbon chain atoms, and the dppm ligands give four triplet signals for the *ipso*, *ortho* and *meta* carbon atoms and four singlets for the carbon atoms in *para* position. The  $\text{CH}_2$  of the phosphine ligands give rise to two triplets at 39.4 and 37.6 ppm, and a singlet at 0.44 ppm is assigned to  $\text{SiMe}_3$  group. The higher symmetry of complex **3** is manifested again in the  $^{13}\text{C}$  NMR spectrum, two resonances are observed for the chain carbon atoms in the 86–82 ppm range and the dppm ligands give two triplet signals for the *ipso*, *ortho* and *meta* carbon atoms and two singlets for those in *para* position. The  $\text{CH}_2$  is located at 37.5 ppm as a triplet. In the  $^{31}\text{P}$  spectra the dppm ligands of **3** give rise to a singlet resonance at  $\delta = 40.34$  ppm and the unequivalent ligands in **2** give two singlets at  $\delta = 40.55$  and 37.12 ppm. In addition,

Table 3

Bond lengths (Å) and angles (°) for **3**

| Bond lengths (Å) |            |
|------------------|------------|
| Co(1)–C(8)       | 1.784(3)   |
| Co(1)–C(7)       | 1.792(3)   |
| Co(1)–C(1)       | 1.950(3)   |
| Co(1)–C(2)       | 1.975(2)   |
| Co(1)–P(1)       | 2.2281(7)  |
| Co(1)–Co(2)      | 2.4742(6)  |
| Co(2)–C(5)       | 1.773(3)   |
| Co(2)–C(6)       | 1.786(3)   |
| Co(2)–C(1)       | 1.942(3)   |
| Co(2)–C(2)       | 1.970(2)   |
| Co(2)–P(2)       | 2.2352(7)  |
| P(1)–C(16)       | 1.828(3)   |
| P(1)–C(10)       | 1.832(3)   |
| P(1)–C(9)        | 1.842(3)   |
| P(2)–C(22)       | 1.825(3)   |
| P(2)–C(28)       | 1.835(3)   |
| P(2)–C(9)        | 1.837(3)   |
| C(1)–C(2)        | 1.354(4)   |
| C(2)–C(3)        | 1.380(3)   |
| C(3)–C(4)        | 1.217(4)   |
| C(4)–C(4)#1      | 1.348(5)   |
| Bond angles (°)  |            |
| C(1)–Co(1)–C(2)  | 40.37(10)  |
| C(1)–Co(1)–Co(2) | 50.37(8)   |
| C(2)–Co(1)–Co(2) | 51.06(7)   |
| P(1)–Co(1)–Co(2) | 95.16(2)   |
| C(1)–Co(2)–C(2)  | 40.51(10)  |
| C(1)–Co(2)–Co(1) | 50.67(8)   |
| C(2)–Co(2)–Co(1) | 51.24(7)   |
| P(2)–Co(2)–Co(1) | 98.86(2)   |
| C(2)–C(1)–Co(2)  | 70.86(16)  |
| C(2)–C(1)–Co(1)  | 70.80(16)  |
| Co(2)–C(1)–Co(1) | 78.96(10)  |
| C(1)–C(2)–C(3)   | 146.2(3)   |
| C(1)–C(2)–Co(2)  | 68.63(15)  |
| C(3)–C(2)–Co(2)  | 137.1(2)   |
| C(1)–C(2)–Co(1)  | 68.83(15)  |
| C(3)–C(2)–Co(1)  | 129.05(19) |
| Co(2)–C(2)–Co(1) | 77.70(9)   |
| C(4)–C(3)–C(2)   | 170.7(3)   |
| C(3)–C(4)–C(4)#1 | 179.2(4)   |
| P(2)–C(9)–P(1)   | 110.33(13) |

the molecular structure of both compounds were determined by single-crystal X-ray diffraction (Figs. 1 and 2).



In order to study the effect of a more basic and less bulky phosphine ligand, in the electrochemical response of this kind of complexes, we prepared the compound **4**,

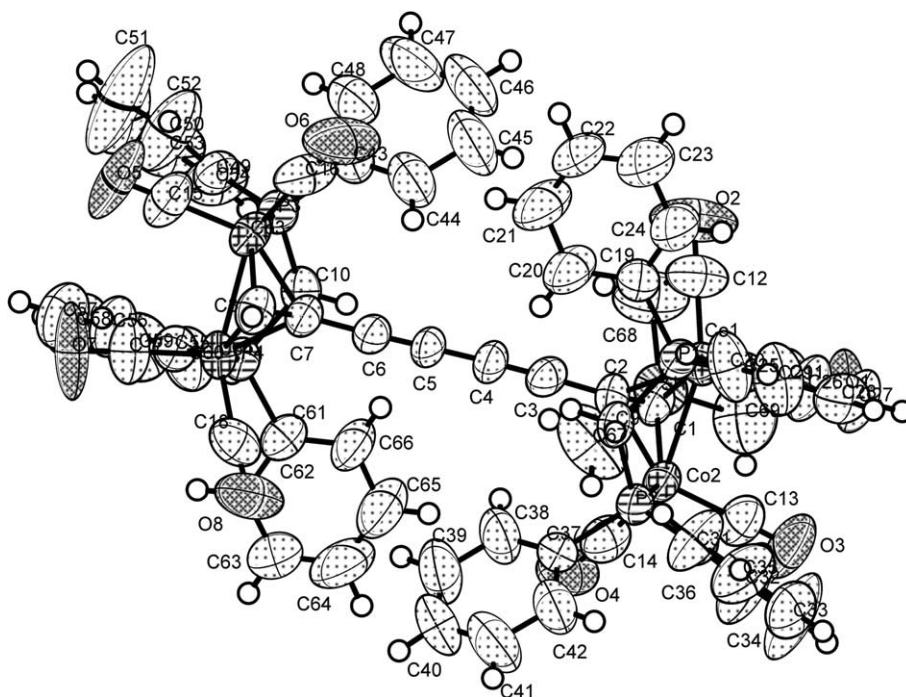


Fig. 1. ORTEP diagram of 2.

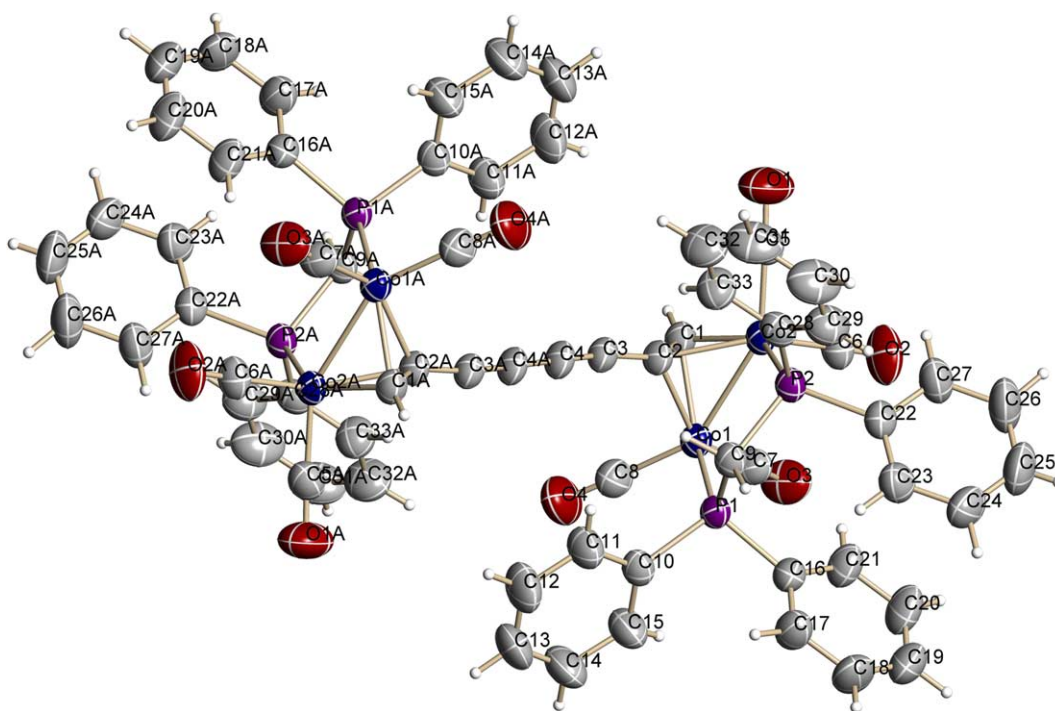
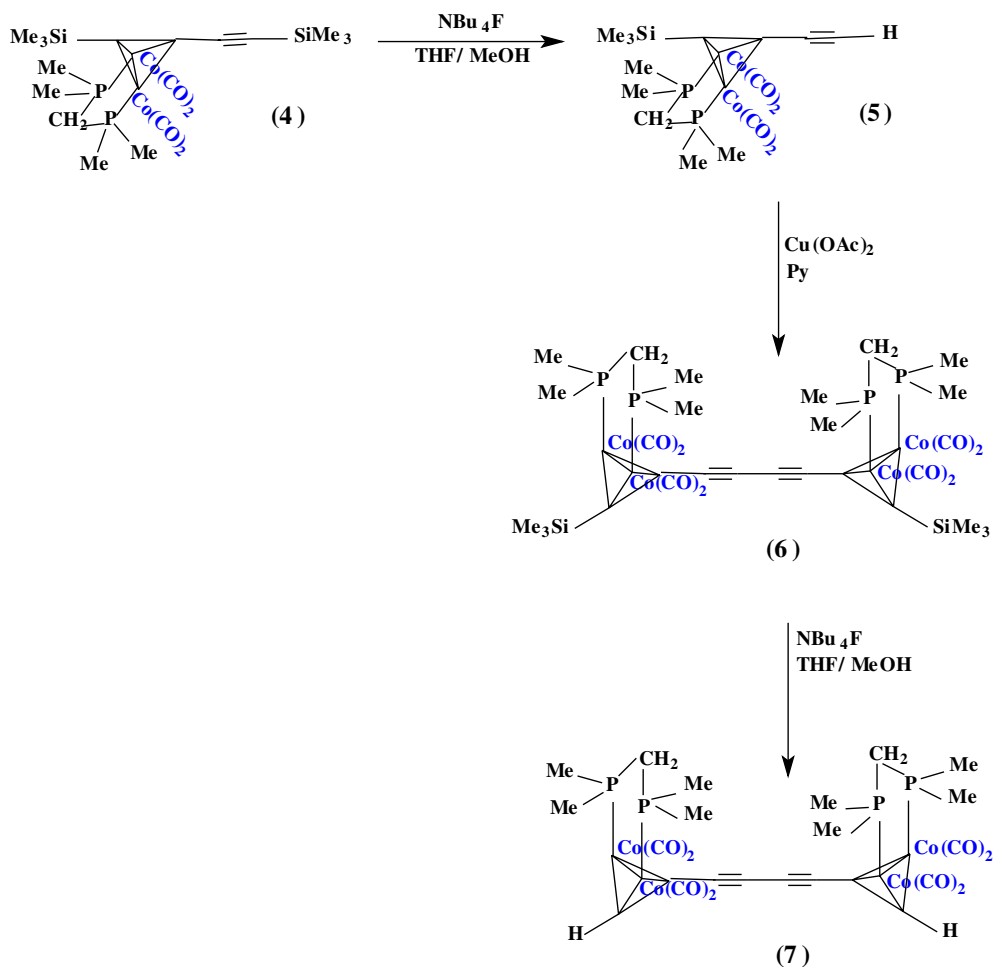


Fig. 2. ORTEP diagram of 3.

$[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)]$ , by substitution reaction of carbonyl ligands on  $\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$  by dmpm in presence of  $\text{Me}_3\text{NO}$ . The reaction of **4** with  $\text{NBu}_4\text{F}$  in THF/MeOH (10:1) at room temperature leads to the monoprotonate  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CH})$

(**5**), which by oxidative coupling under Eglington-Glaser conditions [14] leads to complex  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})]_2(\mu\text{-}\eta^2\text{-SiMe}_3\text{C}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{SiMe}_3)$  (**6**). The desilylation of **6** with  $\text{NBu}_4\text{F}$  in THF/MeOH (10:1) at room temperature leads to compound  $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})]_2(\mu\text{-}\eta^2\text{-HC}_2(\text{C}\equiv\text{C})_2\text{C}_2\text{H})$  (**7**) (see Scheme 1).



Scheme 1.

The four compounds have been characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR and mass spectroscopy. The IR and NMR spectra for **4** and **5** show the same pattern than those for the analogous dppm complexes synthesized by Diederich [5], with the expected signals shifts owing to the presence of the more basic dmpm ligand (see Section 2).

The IR spectrum of **6** shows three bands, in the 1960–2015 range, due to the terminal carbonyl ligands which are shifted to lower frequencies compared with those for compound **1** [5]. The  $^1\text{H}$  NMR spectrum shows a singlet at 0.28 owing to the  $\text{SiMe}_3$  groups. The  $\text{CH}_2$  protons of the dmpm ligands give rise to two double triplets at 2.72 and 2.09 ppm and the methyl groups are observed as triplets at 1.56 and 1.48 ppm. In the  $^{13}\text{C}$  NMR spectrum the  $-\text{C}_8-$  chain gives four resonances in the 87.3–76.4 ppm range which are assigned on basis of its multiplicity and intensity together with HMQC and HMBC experiments. The  $\text{CH}_2$  of the phosphine ligands give a triplet signal at 41.4 and the methyl groups are observed as two triplets at 20.8 and 18.1. The equivalent  $\text{SiMe}_3$  groups give a singlet at 0.6 ppm.

In the  $^1\text{H}$  NMR of **7** this singlet, obviously, is not observed but instead a broad singlet signal at 5.80 ppm,

owing to the acetylenic protons is shown. The rest of the spectral data are similar to those for compound **6** (see Section 2).

The electrochemical study of **2**, **3**, **4**, **5** and **6** is described below. That of **7** was not completed due to instability of intermediate species.

### 3.2. Description of the crystal and molecular structures of **2** and **3**

The compounds **2** and **3** crystallize (**2** with one  $\text{CH}_2\text{Cl}_2$  molecule) in the triclinic crystal system, space group  $P\bar{1}$ . The molecular structures consist of an octatetrayne chain capped by a H atom and a  $\text{SiMe}_3$  group (**2**) or two H atoms (**3**). The outermost acetylenic moieties are coordinated to  $\text{Co}_2(\text{CO})_4\text{dppm}$  fragments in each case, giving rise to two opposite  $\text{Co}_2\text{C}_2$  tetrahedrons with respect to the carbon chain. In the  $\text{Co}_2\text{C}_2$  tetrahedrons, both Co centres are connected to both carbon atoms. A phosphorus from the dppm ligand and two carbonyl ligands complete the coordination geometry around each Co centre. Treating the plane defined by the two cobalt atoms and the terminal carbon as the



base of the  $\text{Co}_2\text{C}_2$  tetrahedron, the bidentate dppm ligand occupies the two available pseudoequatorial positions. The geometric parameters for **2** and **3** have been summarized in Table 1 and Figs. 1 and 2 present a view of the molecules with the atom-labelling scheme.

In compound **2** the uncoordinated carbon atoms fragment is almost linear (angles  $\text{C}(6)\text{--C}(5)\text{--C}(4)$  and  $\text{C}(3)\text{--C}(4)\text{--C}(5)$  178.4(8) and 178.7(8), respectively) and show the typical short, long, short, long bond length alternation associated with a diyne moiety. The  $\text{Co}\text{--Co}$  distance 2.4814(5) and 2.4885(16) Å are comparable to those reported for the compounds  $[\{\text{SiMe}_3(\text{Co}_2(\text{CO})_4(\mu\text{-dppm}))\text{C}_2\}_2(\mu\text{-}\eta^2\text{-SiMe}_3\text{C}\equiv\text{C})(1,3,5\text{-C}_6\text{H}_3)]$  [1j],  $[\{\text{SiMe}_3(\text{Co}_2(\text{CO})_4(\mu\text{-dppm}))\text{C}_2\}_2(\mu\text{-}\eta^2\text{-HC}\equiv\text{C})(1,3,5\text{-C}_6\text{H}_3)]$  [1h],  $\text{Co}_2(\text{CO})_4(\mu\text{-dppa})(\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$  [15] (and references therein) and other similar clusters [16].

The  $\text{C}(1)\text{--C}(2)$  and  $\text{C}(7)\text{--C}(8)$  distances, 1.349(9) and 1.344(9) Å, respectively, are much longer than the  $\text{C}(3)\text{--C}(4)$  and  $\text{C}(5)\text{--C}(6)$  triple bonds, 1.210(9) and 1.207(9) Å, respectively. This reflects the loss of triple bond character as a result of coordination of the acetylenic moiety to the  $\text{Co}_2$  units. The  $\text{C}(2)\text{--C}(3)$  and  $\text{C}(7)\text{--C}(6)$  distances, 1.387(9) and 1.405(9) Å, respectively, are shorter than  $\text{C}\text{--C}$  single bonds as a result of conjugation. The change in hybridization at  $\text{C}(1)\text{--C}(2)$  and  $\text{C}(7)\text{--C}(8)$  is also reflected in the angles  $\text{C}(1)\text{--C}(2)\text{--C}(3)$ , 143.2(7)°,  $\text{C}(2)\text{--C}(1)\text{--Si}(1)$ , 139.5(5)°,  $\text{C}(8)\text{--C}(7)\text{--C}(6)$ , 145.3(7)° and  $\text{C}(7)\text{--C}(8)\text{--H}$ , 136.2(1)°. The  $\text{Co}\text{--C}$  distances in the  $\text{Co}_2\text{C}_2$  core of **2** range from 1.944(7) to 1.985(7) Å and these distances do not show an asymmetric pattern as observed in  $[\{\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HC}\equiv\text{C})\}_2(\text{C}_6\text{H}_4)]$  [17].

The average  $\text{P}\text{--C}$  distance of the bridging dppm ligands, 1.824(7) Å, is normal [18]. All other bond and angles are comparable to those reported for similar structures [1h,1j,15,16].

Fig. 2 shows that complex **3** is derived from **2** by substitution of the  $\text{Si}(1)\text{Me}_3$  group by a hydrogen atom. In general the structural parameters of the common fragments are similar, within experimental error. However in the  $\text{Co}_2\text{C}_2$  core the  $\text{Co}\text{--C}$  distances range from 1.942(3) to 1.975(2) Å and these distances show an asymmetric pattern as observed in  $[\{\text{Co}_2(\text{CO})_6(\mu\text{-}\eta^2\text{-HC}\equiv\text{C})\}_2(\text{C}_6\text{H}_4)]$  [17]. The  $\text{Co}_2\text{C}_2$  tetrahedron is distorted with the longer  $\text{Co}\text{--C}$  (alkyne) interactions being associated with the alkylenic carbon coordinated to the  $\text{C}(3)$  of the carbon chain.

### 3.3. Electrochemical studies

Complexes **4** and **5**, with only one dicobalt unit, show mono-electronic oxidation and reduction processes. Oxidations to  $4^+$  and  $5^+$  are chemically and electrochemically reversible in THF and  $\text{CH}_2\text{Cl}_2$  solution, even at room temperature and sweep rates as slow as  $20\text{ mV s}^{-1}$ . This behaviour is characteristic of bidentate-phosphine

substituted  $\text{Co}_2\text{C}_2$  redox centres [1h,1i,4a,4d,16b,19]. In **4** and **5**, the cluster bound  $\text{SiMe}_3$  group also contributes to this reversible chemistry [20]. However, to achieve complete chemical reversibility of the reduction processes in  $\text{CH}_2\text{Cl}_2$ , temperatures of ca.  $-30^\circ\text{C}$  at  $v = 0.1\text{ V s}^{-1}$ , or sweep rates as fast as  $1\text{ V s}^{-1}$  at  $25^\circ\text{C}$  have to be employed (see Fig. 3). This indicates that both anions  $4^-$  and  $5^-$  are involved in slow decomposition reactions in  $\text{CH}_2\text{Cl}_2$ . When the solvent employed is THF, the reduction process of **4** is chemically reversible at room temperature and  $0.1\text{ V s}^{-1}$ , showing the influence of the solvent on the stability of the anions formed.

Table 4 gathers  $E_{1/2}$  values for the oxidation and reduction of **4** and **5** together with those of closely related compounds measured in our laboratory under the same experimental conditions [1i]. It can be observed that both  $E_{1/2}(\text{ox})$  and  $E_{1/2}(\text{red})$  change with the basicity of the phosphine employed ( $\text{dmpm} > \text{dppa} > \text{dppm}$ ). Thus, for dmpm complexes **4** and **5**, the electron-donating character of the phosphine makes oxidation easier (less positive  $E_{1/2}$ ) and reduction more difficult (more negative  $E_{1/2}$ ). As observed, there is no significant influence on the  $E_{1/2}$  values due to the substitution of a terminal  $\text{SiMe}_3$  group in **4** by  $\text{--H}$  in **5**.

Complexes **2**, **3** and **6**, with two equivalent dicobalt redox centres, are closely related to **1**, which was previously studied by our group under the same experimental conditions [1h]. Table 5 summarizes the main electrochemical data concerning these compounds. When adequate conditions are set, all these complexes show two distinct oxidation and two distinct reduction processes, instead of single bielectronic ones. The value of  $\Delta E_{1/2}$ , the potential separation between the two waves, can be related to the thermodynamic stability of the mixed-valence species in each case, and depends on the extend

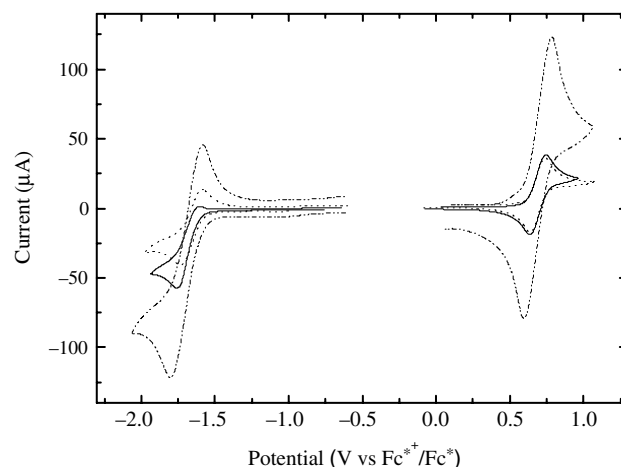


Fig. 3. Cyclic voltammograms for the reduction and oxidation of **5** in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M TBAPF<sub>6</sub>. (—) at  $25^\circ\text{C}$  and  $0.1\text{ V/s}$  on Pt. (---) at  $25^\circ\text{C}$  and  $1\text{ V/s}$  on Pt. (····) at  $-30^\circ\text{C}$  and  $0.1\text{ V/s}$  on C working electrode.

Table 4  
Electrochemical data for **4–5**<sup>a</sup> (and related compounds)

|   | $E_{1/2}$ (red)  | $E_{1/2}$ (ox)                            |
|---|------------------|---|
| $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$ ( <b>4</b> ) | –1.68<br>(–1.78) | 0.66 <sup>b</sup><br>(0.64)               |
| $[\text{Co}_2(\text{CO})_4(\mu\text{-dmpm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CH})$ ( <b>5</b> )      | –1.70<br>(–1.67) | 0.70 <sup>b</sup><br>(0.69)               |
| $[\text{Co}_2(\text{CO})_4(\mu\text{-dppa})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CSiMe}_3)$              | (–1.70)          | (0.75)                                    |
| $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CH})$                   | (–1.70)          | (0.75)                                    |
| $[\text{Co}_2(\text{CO})_4(\mu\text{-dppm})](\mu\text{-}\eta^2\text{-Me}_3\text{SiC}_2\text{C}\equiv\text{CH})$                   | –1.55<br>(–1.68) | 0.81 <sup>b</sup><br>(0.77 <sup>b</sup> ) |

<sup>a</sup> In V vs.  $\text{Fc}^{*+}/\text{Fc}^*$  in  $\text{CH}_2\text{Cl}_2$  solution (values in italics are in THF solution). Data are taken from CV and SWV at 25 °C unless otherwise stated.

<sup>b</sup> From CV and SWV at –30 °C.

Table 5  
Electrochemical data for **1–3** and **6**<sup>a</sup>(and related compounds)

|   | $E_{1/2}$ for reduction                 | $\Delta E_{1/2}$ (red) | $E_{1/2}$ for oxidation                               | $\Delta E_{1/2}$ (ox) |
|---|---|------------------------|---|-----------------------|
| 1 | –1.5; –1.68<br>(–1.57; 1.78)            | 0.18<br>(0.22)         | 0.71; 0.91 <sup>b</sup><br>(0.69; 0.83 <sup>b</sup> ) | 0.20<br>(0.14)        |
| 2 | –1.42 <sup>b</sup> ; –1.60 <sup>b</sup> | 0.18                   | 0.71 <sup>b</sup> ; 0.95 <sup>b</sup>                 | 0.24                  |
| 3 | –1.40 <sup>b</sup> ; –1.54 <sup>b</sup> | 0.14                   | 0.73 <sup>b</sup> ; 0.98 <sup>b</sup>                 | 0.25                  |
| 6 | –1.56 <sup>b</sup> ; –1.69 <sup>b</sup> | 0.13                   | 0.62 <sup>b</sup> ; 0.77 <sup>b</sup>                 | 0.15                  |

<sup>a</sup> In V vs.  $\text{Fc}^{*+}/\text{Fc}^*$  in  $\text{CH}_2\text{Cl}_2$  solution (values in italics are in THF solution). Data are taken from CV and SWV at 25 °C unless otherwise stated.

<sup>b</sup> From CV and SWV at –30 °C.

of electronic interactions between the redox centres through the bridging ligands [21]. As reflected in Table 5,  $\Delta E_{1/2}$  for the whole family of compounds indicates a moderate degree of electronic interactions; the substitution of dppm for the more basic and less steric demanding dmpm seems to decrease these interactions, hindering efficient mixing between filled metal fragment and polyene-based orbitals. However, other factors like coulombic repulsions or molecular rearrangements during the oxidation or reduction processes also influence  $\Delta E_{1/2}$  [1c]. Values of  $\Delta E_{1/2}$  for **1–3** and **6** are smaller than those observed when a shorter bridging carbon chain (4 C atoms) is employed [1h,4c], for which  $\Delta E_{1/2} \cong 0.4$  V, but comparable to values observed with longer bridging ligands, like in alkynylthiophene [16b] and alkynylbenzene [1h,1j] complexes.

The effect of the phosphine nature is more evident on the potential values for reduction and oxidation. As already observed for complexes with only one dicobalt redox centre, the more basic (i.e. electron-donating) dmpm makes removal of electrons easier ( $E_{1/2}$  (ox) less positive) and their addition more difficult ( $E_{1/2}$  (red) more negative). Another consequence of the change in phosphine substituent is the poorer stability of the oxidated and reduced species. Thus, the voltammetric reduction of **1** at room temperature showed two completely chemically reversible waves, whilst in the case of **6** both waves are only partially chemically reversible;

temperature has to be decreased to –30 °C and sweep rate increased to ca.  $1 \text{ V s}^{-1}$  to obtain an almost completely reversible reduction behaviour in **6** (Fig. 4). The effect is even greater on the oxidated species; complete chemical reversibility of the two waves could not be achieved for **6** even at –30 °C and fast sweep rates. The irreversible reduction of a decomposition product of the oxidated species can be observed at 0.06 V ( $v = 0.5 \text{ V s}^{-1}$ ) (Fig. 5).

When the end-groups  $\text{SiMe}_3$  in **1** are changed for the much smaller –H, in **2** and **3**, the major influence observed is on the chemical stability of the anions and cations formed (intermediate species included) in the reduction and oxidation processes. The oxidation of **1** in  $\text{CH}_2\text{Cl}_2$  yields a first completely reversible wave and a second partially chemically reversible one ( $i_{pc}/i_{pa} \approx 0.8$ ) at 25 °C and 0.1 V/s; the latter is completely reversible at –15 °C. Substitution of one end-group by

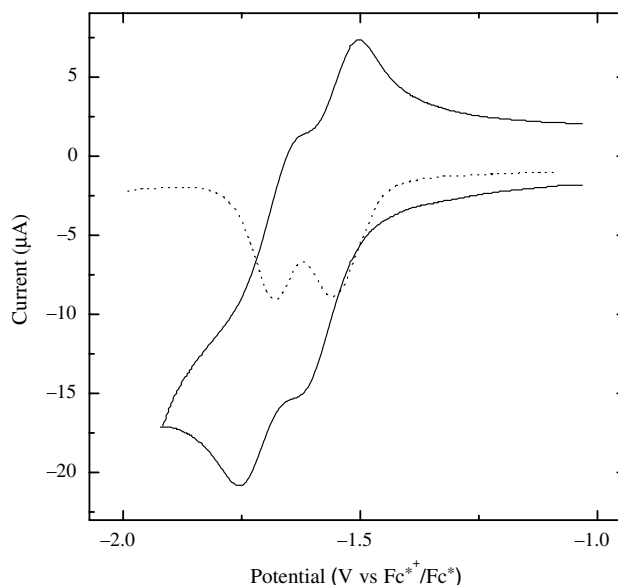


Fig. 4. Cyclic (—) and square-wave (---) voltammograms for the reduction of **6** in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M  $\text{TBAPF}_6$  at –30 °C. CV:  $v = 0.5 \text{ V/s}$ . SWV: scan increment = 2 mV; SW amplitude = 25 mV; frequency = 30 Hz. C working electrode.

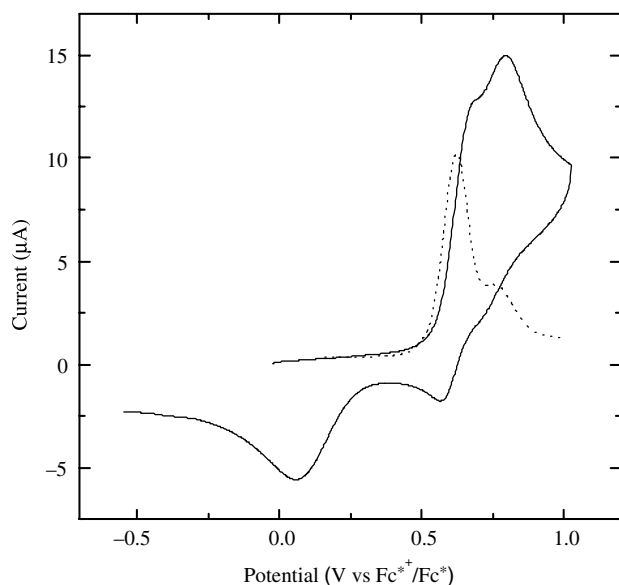


Fig. 5. Cyclic (—) and square-wave (- - -) voltammograms for the oxidation of **6** in  $\text{CH}_2\text{Cl}_2$  containing 0.2 M  $\text{TBAPF}_6$  at  $-30^\circ\text{C}$ . CV:  $v = 0.5$  V/s. SWV: scan increment = 2 mV; SW amplitude = 25 mV; frequency = 30 Hz. C working electrode.

–H in **2** results in  $i_{pc}/i_{pa} \approx 0.7$  at 1 V/s and  $-30^\circ\text{C}$  for the second wave. When both terminal groups are –H in **3**, only one irreversible oxidation wave is observed at  $25^\circ\text{C}$  and 0.1 V/s, indicating that the radical cation  $3^+$  is not stable in the time-scale of the experiment; increasing the sweep rate at to 5 V/s results in the appearance of a small cathodic wave upon sweep reversal, together with a second anodic wave. Reversibility of both waves is enhanced at  $-30^\circ\text{C}$ .

Similar results are observed when studying the reduction behaviour of **1**, **2** and **3**, although the stability of the anionic species seems to be somewhat greater as, for example, the reduction of **3** at room temperature yields two distinct quasi-reversible peaks.

All results on the stability of anions and cations derived from **1** as compared to those from **2–3** or **6**, seems to indicate that the bigger steric bulk of substituents (end-groups of the bridging ligand, or phosphine on the dicobalt unit) is an important factor which enhances the chemical stability of the radical and ionic species.

#### 4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 272712 and 272713 for compounds **6** and **7**. Copies of this information may be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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