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Synthesis and electrochemical study of cobalt carbonyl complexes of trimethylsilyl-substituted 1,3,5-triethynylbenzene

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Abstract

Treatment of 1,3,5-tris(trimethylsilylethynyl)benzene or 1,3,5-triethynylbenzene with $Co_2(CO)_8$ or $Co_2(CO)_6(dppm)$ produced the formation of substituted ethynylcobalt complexes with one, two or three $Co_2(CO)_6$ or $Co_2(CO)_4(dppm)$ units, $[\{X_3(Co_2(CO)_6)C_2\}_n(XC{\equiv}C)_m(1,3,5\text{-}C_6H_3)]$ ($X = H$ or $SiMe_3$) ($n = 1$, 2 or 3; $m = 3 - n$) and $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}_n(SiMe_3C{\equiv}C)_m(1,3,5\text{-}C_6H_3)]$ ($n = 1$ or 2; $m = 3 - n$), in a high yield. Desilylation of the non-metallated alkynes in $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}(SiMe_3C{\equiv}C)_2(1,3,5\text{-}C_6H_3)]$ occurred on treatment with KOH. Electrochemical results provide evidence for communication between the C_2Co_2 centres. Crystals of $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}_2(SiMe_3C{\equiv}C)(1,3,5\text{-}C_6H_3)]$ suitable for single-crystal X-ray diffraction were grown and the molecular structure of this compound is discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Carbonyl complexes; π-Acetylene complexes; Electrochemistry

1. Introduction

Organometallic compounds whose metal centres are joined by organic ligands with delocalised π-systems and rigid molecular architectures may be suitable as precursors for solid state materials of technological interest [1,2] as non-linear optical [3,4] or quasi-one-dimensional conductors [5]. The properties of such materials can be tuned by varying the organic link or by adjusting the metal environment. Polyyne segments are recognised to allow long-distance electronic interactions through π delocalisation [6–10], and the degree of electronic interaction between the redox centres can be determined by electrochemical methods [11–14].

Complexes where the redox centres are either '$Co_2(CO)_6$' or '$Co_2(CO)_4$dppm' moieties and the bidentate ligand is a μ-diyne are well known [15]. As a continuation on the preparation of redox-active clusters linked by unsaturated spacers [16], we report in this work the synthesis and the redox properties of the π-acetylene organometallic complexes containing the 1,3,5-tris(trimethylsilylethynyl)benzene and the 1,3,5-triethynylbenzene units in order to study the mutual influence between metal centres spanned with these ligands. The triethynylbenzene core as a π-delocalised organic spacer is of particular interest because it allows a precisely controlled geometry and has several active coordination sites.

2. Experimental

2.1. Reagents and general techniques

All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an

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atmosphere of oxygen-free Ar. All solvents for synthetic use were reagent grade, dried as appropriate and distilled 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 three freeze–pump–thaw cycles after distillation and before use. $Me_3Si–C≡CH$ (TMSA), 1,3,5-tribromobenzene, $Co_2(CO)_8$, Py (Fluka), 1,2-bis(diphenylphosphino)methane (dppm), tetrabutylammonium fluoride (TBAF) and decamethylferrocene (Aldrich) were used as received. Trimethylamine *N*-oxide (Aldrich) was sublimed prior to use and stored under Ar. The compounds $Co_2(CO)_6$dppm [17] and 1,3,5-tris(trimethylsilyl)ethynylbenzene [18] were prepared according to literature procedures. The ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AMX-300 or 500 instrument. ^{1}H-NMR spectra were referenced to tetramethylsilane, whereas ^{31}P-NMR were referenced to external 85% H_3PO_4. Infrared spectra were measured on a Perkin–Elmer 1650 infrared spectrometer. Elemental analyses were 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 by the Mass Laboratory of the University Autónoma of Madrid.

Electrochemical measurements were carried out with a computer driven PAR Mo. 273 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 ($TBAPF_6$) as supporting electrolyte. Cyclic and square wave voltammetry (CV and SWV, respectively) studies were made on a polycrystalline Pt working electrode (0.05 cm^2); the counterelectrode was a Pt gauze and the reference electrode was a silver wire quasi-reference electrode. Decamethylferrocene (Fc*) and/or ferrocene (Fc) were used as internal standards, and all potentials in this work are referred to the Fc^{*+}/Fc^* couple. Under the actual conditions of the experiments, $E_{1/2}$ (Fc^+/Fc) was $+0.44$ V vs Fc^{*+}/Fc^* in THF, and $+0.55$ V vs Fc^{*+}/Fc^* in CH_2Cl_2.

2.2. Preparation of [{SiMe$_3$(Co$_2$(CO)$_6$)C$_2$}(SiMe$_3$C≡C)$_2$(1,3,5-C$_6$H$_3$)] (**1**), [{SiMe$_3$(Co$_2$(CO)$_6$)C$_2$}$_2$(SiMe$_3$C≡C)(1,3,5-C$_6$H$_3$)] (**2**) and [{SiMe$_3$(Co$_2$(CO)$_6$)C$_2$}$_3$(1,3,5-C$_6$H$_3$)] (**3**)

To a solution of 1,3,5-tris(trimethylsilylethynyl)benzene (0.3 g, 0.82 mmol) in hexane (50 ml) was added 0.25 equivalents (**1**), one equivalent (**2**) or three equivalents (**3**) of $Co_2(CO)_8$, respectively. The reactions were monitored by FTIR. After the mixture was stirred for 5 h at room temperature (r.t.), the solvent was removed under vacuum. The compounds were isolated and purified by thin-layer chromatography (TLC) using hexane as eluent, as bands 1, 2 and 3, respectively.

(**1**) Yield: 85%. IR (hexane, cm^{-1}): $\nu_{C≡C}$ 2164 (w); ν_{CO} 2089 (s), 2054 (vs), 2026 (s). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.51 (t, 1H, Ph); 7.46 (t, 2H, Ph); 0.40 (s, 9H, –CSiMe$_3$); 0.25 (s, 18H, ≡CSiMe$_3$). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 199.5 (s, CO); 140.0 (s, C_3); 134.8 (s, C_6); 132.6 (s, C_4); 123.6 (s, C_5); 104.1 (s, C_2); 103.1 (s, C_7); 95.5 (s, C_8); 80.3 (s, C_1); 0.8 (s, –CSiMe$_3$); -0.2 (s, ≡CSiMe$_3$). MS (FAB$^+$) *m/z*: 624.1 [$M^+ - CO$]. Anal. Found: C, 49.62; H, 4.58. Calc. for $C_{27}H_{30}Co_2O_6Si_3$: C, 49.64; H, 4.60%.

(**2**) Yield: 70%. IR (hexane, cm^{-1}): $\nu_{C≡C}$ 2164 (w); ν_{CO} 2088 (s), 2055 (vs), 2027 (s). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.59 (t, 1H, Ph); 7.46 (t, 2H, Ph); 0.40 (s, 18H, –CSiMe$_3$); 0.27 (s, 9H, ≡CSiMe$_3$). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 199.5 (s, CO); 139.8 (s, C_3); 131.5 (s, C_5); 130.3 (s, C_4); 123.6 (s, C_6); 104.1 (s, C_2); 103.3 (s, C_7); 95.6 (s, C_8); 80.8 (s, C_1); 1.0 (s, –CSiMe$_3$); -0.2 (s, ≡CSiMe$_3$). MS (FAB$^+$) *m/z*: 854.0 [$M^+ - 3CO$]. Anal. Found: C, 42.02; H, 3.11. Calc. for $C_{33}H_{30}Co_4O_{12}Si_3$: C, 42.19; H, 3.20%.

(**3**) Yield: 98%. IR (hexane, cm^{-1}): ν_{CO} 2088 (s), 2057 (vs), 2022 (s). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.52 (s, 3H, Ph); 0.40 (s, 27H, SiMe$_3$). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 199.6 (s, CO); 139.9 (s, C_3); 130.9 (s, C_4); 104.1 (s, C_2); 80.6 (s, C_1); 0.9 (s, –SiMe$_3$). MS (FAB$^+$) *m/z*: 1195.6 [$M^+ - CO$]. Anal. Found: C, 38.18; H, 2.40. Calc. for $C_{39}H_{30}Co_6O_{18}Si_3$: C, 38.22; H, 2.45%.

2.3. Preparation of [{SiMe$_3$(Co$_2$(CO)$_4$dppm)C$_2$}(SiMe$_3$C≡C)$_2$(1,3,5-C$_6$H$_3$)] (**4**) and [{SiMe$_3$(Co$_2$(CO)$_4$dppm)C$_2$}$_2$(SiMe$_3$C≡C)(1,3,5-C$_6$H$_3$)] (**5**)

To a solution of 1,3,5-tris(trimethylsilylethynyl)benzene (0.19 g, 0.51 mmol) in hexane (40 ml) was added 3.4 g (5.1 mmol) of $Co_2(CO)_6$dppm. After the mixture was stirred for 5 days at r.t., it was filtered through a hexane-packed alumina column (200 g). The column was washed with hexane and the total eluent was removed under vacuum. The residue was purified by TLC using hexane as eluent, and **4** and **5** were isolated as red bands.

(**4**) Yield: 70%. IR (hexane, cm^{-1}): $\nu_{C≡C}$ 2160 (w); ν_{CO} 2020 (s), 1992 (vs), 1966 (s). ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.60–6.95 (m, 23H, Ph); 3.20 (t, 2H, $J_{PH} =$ 10.3 Hz, CH$_2$); 0.32 (s, 9H, –CSiMe$_3$); 0.25 (s, 18H, ≡CSiMe$_3$). ^{31}P-NMR ($CDCl_3$): δ 35.8 (s, br). ^{13}C-NMR (500 MHz, $CDCl_3$): δ 203.1 (s, CO); 144.1 (s, C_3); 138.5 (t, $J_{CP} = 24.6$ Hz, *i*-Ph); 134.4 (t, $J_{CP} = 16.4$ Hz, *i*-Ph); 132.8 (s, C_4); 132.5 (t, $J_{CP} = 6.5$ Hz, *o*-Ph); 130.1 (t, $J_{CP} = 6.0$ Hz, *o*-Ph); 129.6 (s, *p*-Ph); 129.0 (s, *p*-Ph); 128.5 (t, $J_{CP} = 4.7$ Hz, *m*-Ph); 127.8 (t, $J_{CP} = 4.8$ Hz, *m*-Ph); 123.3 (s, C_5); 104.1 (s, C_2,C_7); 94.4 (s, C_8); 88.7 (s, C_1); 29.6 (s, CH$_2$); 1.4 (s, –CSiMe$_3$); 0.9 (s, ≡CSiMe$_3$). MS (FAB$^+$) *m/z*: 952.0 [$M^+ - CO$]. Anal. Found: C, 61.14; H, 5.28. Calc. for $C_{50}H_{52}Co_2O_4P_2Si_3$: C, 61.16; H, 5.30%.

(**5**) Yield: 20%. IR (hexane, cm^{-1}): $\nu_{C\equiv C}$ 2152 (w); ν_{CO} 2018 (s), 1995 (vs), 1962 (s). ^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.10–6.95 (m, 43H, Ph); 3.47 (t, 4H, $J_{PH} =$ 10.1 Hz, CH$_2$); 0.35 (s, 9H, ≡CSiMe$_3$); 0.23 (s, 18H, –CSiMe$_3$). ^{31}P-NMR (CDCl$_3$): δ 34.5 (s, br). ^{13}C-NMR (500 MHz, CDCl$_3$) δ: 203.1 (s, CO); 144.7 (s, C$_3$); 139.0 (t, $J_{CP} = 23.9$ Hz, *i*-Ph); 135.3 (t, $J_{CP} = 17.1$ Hz, *i*-Ph); 133.0 (t, $J_{CP} = 6.1$ Hz, *o*-Ph); 132.0 (s, C$_5$); 130.8 (t, $J_{CP} = 5.8$ Hz, *o*-Ph); 130.5 (s, C$_4$); 129.9 (s, *p*-Ph); 129.6 (s, *p*-Ph); 129.0 (t, $J_{CP} = 4.3$ Hz, *m*-Ph); 128.2 (t, $J_{CP} =$ 4.6 Hz, *m*-Ph); 124.3 (s, C$_6$); 105.4 (s, C$_2$); 104.1 (s, C$_7$); 93.8 (s, C$_8$); 88.3 (s, C$_1$); 30.1 (s, CH$_2$); 1.8 (s, –CSiMe$_3$); 0.9 (s, ≡CSiMe$_3$). MS (FAB$^+$) *m*/*z*: 1567.4 [M$^+$ − CO]. Anal. Found: C, 64.88; H, 5.62. Calc. for $C_{79}H_{74}Co_4O_8P_4Si_3$: C, 65.07; H, 5.65%.

Both compounds can also be prepared by reaction of **3** and dppm (ratio 1:1) in presence of two equivalents of Me$_3$NO in hexane as solvent. After similar working, **4** and **5** were separated.

2.4. Preparation of [{SiMe$_3$(Co$_2$(CO)$_4$dppm)C$_2$}(HC≡C)$_2$(1,3,5-C$_6$H$_3$)] (**6**)

0.03 g (0.03 mmol) of [{SiMe$_3$(Co$_2$(CO)$_4$dppm)C$_2$}-(SiMe$_3$C≡C)$_2$(1,3,5-C$_6$H$_3$)] (**4**) was dissolved in a MeOH solution saturated with KOH. After the mixture was stirred for 24 h, the solvent was removed under vacuum and compound **6** was extracted with several portions of Et$_2$O. Yield: 90%. IR (hexane, cm^{-1}): $\nu_{\equiv CH}$ 3304 (w); $\nu_{C\equiv C}$ 2080 (w); ν_{CO} 2021 (s), 1995 (vs), 1967 (s). ^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.80–6.90 (m, 23H, Ph); 3.26 (t, 2H, $J_{PH} = 24.7$ Hz, CH$_2$); 3.02 (s, 2H, ≡CH); 0.33 (s, 9H, SiMe$_3$). ^{31}P-NMR (CDCl$_3$): δ 30.0 (s, br). ^{13}C-NMR (500 MHz, CDCl$_3$): δ 203.1 (s, CO); 134.4 (s, C$_6$); 133.0 (t, $J_{CP} = 5.9$ Hz, *i*-Ph); 132.7 (t, $J_{CP} = 13.0$ Hz, *i*-Ph); 131.7 (t, $J_{CP} = 3.0$ Hz, *o*-Ph); 131.0 (t, $J_{CP} =$ 5.1 Hz, *o*-Ph); 130.5 (s, *p*-Ph); 130.4 (s, *p*-Ph); 128.5 (t, $J_{CP} = 4.5$ Hz, *m*-Ph); 127.8 (t, $J_{CP} = 4.5$ Hz, *m*-Ph); 122.4 (s, C$_5$); 77.1 (s, C$_8$); 29.6 (s, CH$_2$); 1.7 (s, –SiMe$_3$). MS (FAB$^+$) *m*/*z*: 808.2 [M$^+$ − CO]. Anal. Found: C, 58.15; H, 3.95. Calc. for $C_{44}H_{36}Co_2O_4P_2Si$: C, 58.17; H, 3.97%.

Table 1
Crystal data and structure refinement for compound **5**

Empirical formula	$C_{79}H_{74}Co_4O_8P_4Si_3$
Formula weight	1595.25
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	16.2945(2)
b (Å)	26.4671(4)
c (Å)	18.5025(2)
α (°)	90
β (°)	94.525(7)
γ (°)	90
V (Å^3)	7954.67(18)
Z	4
D_{calc} (Mg m^{-3})	1.332
Absorption coefficient (mm^{-1})	0.997
F(000)	3288
Crystal size (mm)	0.35 × 0.30 × 0.20
Theta range for data collection (°)	2.56–27.48
Index ranges	$0 \leq h \leq 21$, $0 \leq k \leq 34$, $-23 \leq l \leq 23$
Reflections collected	62 008
Independent reflections	18 080 [R(int) = 0.029]
Absorption correction	Multi-scan (DENZO-SMN)
Refinement method	Full-matrix least-squares on *F*2
Data/restraints/parameters	18 080/0/883
Goodness-of-fit on *F*2	1.026
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0397$, $wR_2 = 0.0792$
R indices (all data)	$R_1 = 0.0636$, $wR_2 = 0.0875$
Largest difference peak and hole (e Å^{-3})	0.362 and −0.389

2.5. Preparation of [{H(Co$_2$(CO)$_6$)C$_2$}$_2$(HC≡C)(1,3,5-C$_6$H$_3$)] (**7**) and [{H(Co$_2$(CO)$_6$)C$_2$}$_3$(1,3,5-C$_6$H$_3$)] (**8**)

To a solution of 0.28 g (1.86 mmol) of 1,3,5-triethynylbenzene in hexane (50 ml) was added 0.63 g (1.86 mmol) of Co$_2$(CO)$_8$. The reaction was monitored by FTIR and ^{1}H-NMR. After 1 h, the solvent was extracted by vacuum and the residue was purified by TLC using hexane as eluent.

(**7**) Yield: 30%. IR (hexane, cm^{-1}): $\nu_{\equiv CH}$ 3303 (w); ν_{CO} 2094 (s), 2062 (vs), 2032 (s). ^{1}H-NMR (500 MHz, CDCl$_3$): δ 7.62 (d, 1H, *o*-Ph); 7.55 (d, 2H, *i*-Ph); 6.36 (s, 2H, –CH); 3.12 (s, 1H, ≡CH). ^{13}C-NMR (500 MHz, CDCl$_3$): δ 199.0 (s, CO); 139.3 (s, C$_3$); 132.3 (s, C$_5$); 130.7 (s, C$_4$); 123.3 (s, C$_6$); 88.4 (s, C$_2$); 82.4 (s, C$_7$); 78.5 (s, C$_8$); 72.6 (s, C$_1$). MS (FAB$^+$) *m*/*z*: 693.7 [M$^+$ − CO]. Anal. Found: C, 39.75; H, 0.78. Calc. for $C_{24}H_6Co_4O_{12}$: C, 39.89; H, 0.83%.

(**8**) Yield: 60%. MS (FAB$^+$) *m*/*z*: 951.5 [M$^+$ − 2CO]. The spectroscopic data are already reported in and are consistent with [15m].

2.6. X-ray crystallography

Dark red crystals of [{SiMe$_3$(Co$_2$(CO)$_4$dppm)C$_2$}$_2$-(SiMe$_3$C≡C)(1,3,5-C$_6$H$_3$)] (**5**) are obtained by recrystallisation of the complex from CH$_2$Cl$_2$–hexane mixtures. A summary of selected crystallographic data for **5** is given in Table 1. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). A combination of 1° phi and omega (with kappa offsets) scans was used to collect sufficient data. The data frames were integrated and scaled using the DENZO-SMN package [19]. The structure was solved and refined using the SHELXTL/PC V5.1 package [20]. The structure was

Table 2
Bond lengths (Å) and angles (°) for **5**

Bond lengths			
Co(1)–C(2)	1.773(3)	P(1)–C(121)	1.841(2)
Co(1)–C(1)	1.792(3)	P(3)–C(151)	1.831(2)
Co(1)–C(10)	1.973(2)	P(3)–C(161)	1.839(2)
Co(1)–C(11)	1.980(2)	P(3)–C(32)	1.849(2)
Co(1)–P(1)	2.2225(6)	P(2)–C(141)	1.836(2)
Co(1)–Co(2)	2.4892(4)	P(2)–C(131)	1.838(2)
Co(2)–C(4)	1.775(3)	P(2)–C(31)	1.844(2)
Co(2)–C(3)	1.790(2)	P(4)–C(181)	1.834(2)
Co(2)–C(11)	1.963(2)	P(4)–C(171)	1.838(2)
Co(2)–C(10)	1.993(2)	P(4)–C(32)	1.843(2)
Co(2)–P(2)	2.2281(6)	Si(1)–C(19)	1.851(2)
Co(3)–C(6)	1.771(3)	Si(3)–C(21)	1.852(2)
Co(3)–C(5)	1.786(3)	C(10)–C(11)	1.355(3)
Co(3)–C(20)	1.980(2)	C(11)–C(12)	1.477(3)
Co(3)–C(21)	1.986(2)	C(12)–C(17)	1.399(3)
Co(3)–P(3)	2.2396(7)	C(12)–C(13)	1.400(3)
Co(3)–Co(4)	2.4906(4)	C(13)–C(14)	1.401(3)
Co(4)–C(8)	1.771(3)	C(14)–C(15)	1.395(3)
Co(4)–C(7)	1.786(3)	C(14)–C(18)	1.448(3)
Co(4)–C(20)	1.966(2)	C(15)–C(16)	1.397(3)
Co(4)–C(21)	1.990(2)	C(16)–C(17)	1.408(3)
Co(4)–P(4)	2.2107(7)	C(16)–C(20)	1.470(3)
P(1)–C(111)	1.827(2)	C(18)–C(19)	1.205(3)
P(1)–C(31)	1.840(2)	C(20)–C(21)	1.347(3)
Bond angles			
C(10)–Co(1)–C(11)	40.09(8)	C(17)–C(12)–C(13)	118.52(18)
C(10)–Co(1)–Co(2)	51.48(6)	C(17)–C(12)–C(11)	120.07(18)
C(11)–Co(1)–Co(2)	50.56(6)	C(13)–C(12)–C(11)	121.35(19)
P(1)–Co(1)–Co(2)	99.38(2)	C(12)–C(13)–C(14)	120.41(19)
C(11)–Co(2)–C(10)	40.05(8)	C(15)–C(14)–C(13)	119.79(18)
C(11)–Co(2)–Co(1)	51.17(6)	C(15)–C(14)–C(18)	118.16(18)
C(10)–Co(2)–Co(1)	50.76(6)	C(13)–C(14)–C(18)	122.03(19)
P(2)–Co(2)–Co(1)	94.681(19)	C(14)–C(15)–C(16)	121.29(19)
C(20)–Co(3)–C(21)	39.71(9)	C(15)–C(16)–C(17)	117.74(19)
C(20)–Co(3)–Co(4)	50.61(6)	C(15)–C(16)–C(20)	120.90(19)
C(21)–Co(3)–Co(4)	51.27(6)	C(17)–C(16)–C(20)	121.27(18)
P(3)–Co(3)–Co(4)	98.65(2)	C(12)–C(17)–C(16)	122.16(19)
C(20)–Co(4)–C(21)	39.82(9)	C(19)–C(18)–C(14)	176.4(2)
C(20)–Co(4)–Co(3)	51.11(6)	C(18)–C(19)–Si(1)	178.3(2)
C(21)–Co(4)–Co(3)	51.15(7)	C(21)–C(20)–C(16)	139.5(2)
P(4)–Co(4)–Co(3)	93.14(2)	C(21)–C(20)–Co(4)	71.03(13)
C(11)–C(10)–Si(2)	150.81(18)	C(16)–C(20)–Co(4)	137.42(15)
C(11)–C(10)–Co(1)	70.26(13)	C(21)–C(20)–Co(3)	70.39(14)
Si(2)–C(10)–Co(1)	130.76(12)	C(16)–C(20)–Co(3)	132.43(15)
C(11)–C(10)–Co(2)	68.80(13)	Co(4)–C(20)–Co(3)	78.27(8)
Si(2)–C(10)–Co(2)	129.42(12)	C(20)–C(21)–Si(3)	146.82(19)
Co(1)–C(10)–Co(2)	77.76(8)	C(20)–C(21)–Co(3)	69.90(14)
C(10)–C(11)–C(12)	139.4(2)	Si(3)–C(21)–Co(3)	132.11(13)
C(10)–C(11)–Co(2)	71.15(13)	C(20)–C(21)–Co(4)	69.14(13)
C(12)–C(11)–Co(2)	138.20(15)	Si(3)–C(21)–Co(4)	132.65(13)
C(10)–C(11)–Co(1)	69.65(13)	Co(3)–C(21)–Co(4)	77.58(8)
C(12)–C(11)–Co(1)	131.96(15)	P(1)–C(31)–P(2)	111.57(11)
Co(2)–C(11)–Co(1)	78.27(8)	P(4)–C(32)–P(3)	107.11(11)

solved by direct methods and refinement was by full-matrix least-squares on F^2 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 the corresponding C-atoms for the phenyl H-atoms and 50% larger for the methyl H-atoms. Final positional parameters for **5** are given in Table 2. Anisotropic thermal parameters, hydrogen atom parameters and structure amplitudes are available as supplementary material. Table 2 contains bond distances and angles. Fig. 1 presents a molecular diagram of **5**. The final positional parameters are available as supplementary material.

3. Results and discussion

3.1. Synthesis and spectroscopic properties

1,3,5-Tris(trimethylsilylethynyl)benzene reacts with 0.25, one or three equivalents of $Co_2(CO)_8$ in hexane at room temperature to give after workup cobalt complexes $[\{SiMe_3(Co_2(CO)_6)C_2\}(SiMe_3C\equiv C)_2(1,3,5\text{-}C_6H_3)]$ (**1**), $[\{SiMe_3(Co_2(CO)_6)C_2\}_2(SiMe_3C\equiv C)(1,3,5\text{-}C_6H_3)]$ (**2**), $[\{SiMe_3(Co_2(CO)_6)C_2\}_3(1,3,5\text{-}C_6H_3)]$ (**3**) in 85, 70 and 98% yield, respectively (Scheme 1). Complex **1** was purified and **2** was separated from **3** by TLC with hexane.

Complexes containing bis(diphenylphosphino)methane were prepared in order to stabilise the dicobalt fragment by the bridging effect between the two metal atoms. The compounds can readily be prepared by direct reaction of $Co_2(CO)_6(dppm)$ with 1,3,5-tris(trimethylsilylethynyl)benzene, or by substitution reaction of two carbonyl ligands at the $Co_2(CO)_6$ moieties by dppm in complex **3**. Both reactions gave rise to a mixture of complexes, $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}(SiMe_3C\equiv C)_2(1,3,5\text{-}C_6H_3)]$ (**4**) and $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}_2(SiMe_3C\equiv C)(1,3,5\text{-}C_6H_3)]$ (**5**), and were separated by TLC with hexane. The substitution reaction appears to proceed via loss of $Co_2(CO)_6$ units because of the steric effect of the dppm ligand.

All these compounds have been characterised by analytical and spectroscopic data (IR, ^1H-, ^{13}C-, ^{31}P-

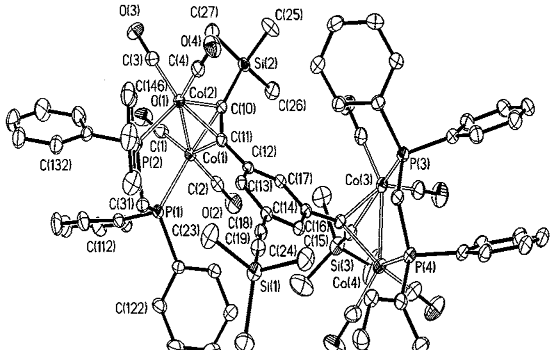
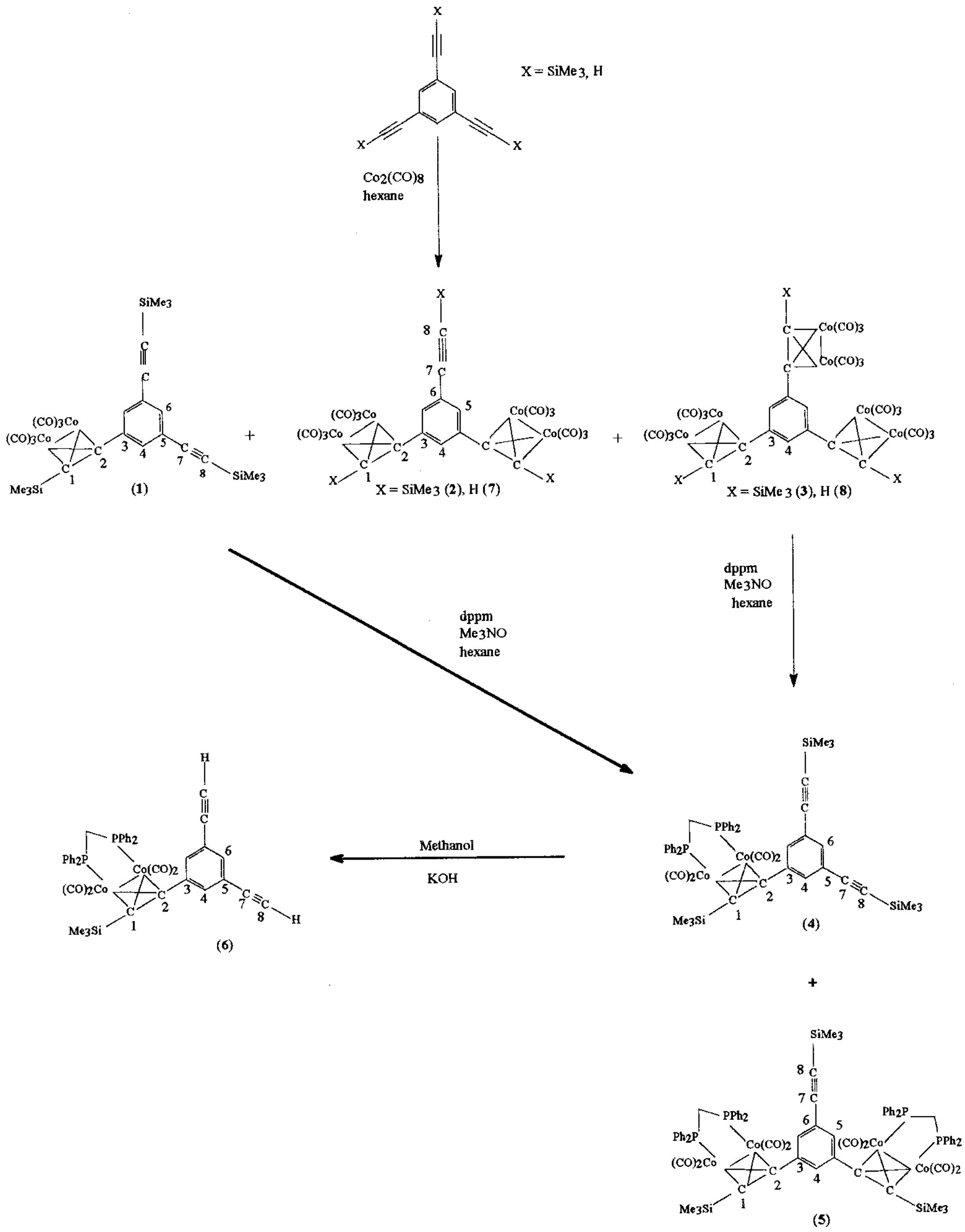


Fig. 1. ORTEP diagram of $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}_2(SiMe_3C\equiv C)(1,3,5\text{-}C_6H_3)]$ (**5**), with 30% ellipsoids. H atoms have been removed for clarity.



Scheme 1.

NMR, MS). The IR spectra of **1**–**3** exhibit three strong absorptions in the carbonyl stretching region at 2089–2000 cm^{-1}; in the dppm-substituted complexes **4**–**5** these absorptions lie at lower frequencies. In addition, compounds **1**, **2**, **4** and **5** contain uncomplexed C≡C triple bonds which give a $\nu_{C\equiv C}$ weak absorption at ca. 2160 cm^{-1}. The NMR data are consistent with the proposed structures (Scheme 1). In the ^{1}H-NMR spectra, the change in the chemical shifts of the SiMe$_3$ proton signals were consistent with the incorporation of 1, 2 and 3 Co$_2$(CO)$_6$ units in complexes **1**, **2** and **3**, respectively. In the ^{1}H-NMR spectra of **4**, **5** and **6** the –CH$_2$– protons of the dppm units are coupled with the two chemically equivalent P-atoms and they appear as triplets broadened by the adjacent Co-atoms, with ^{1}H–^{31}P coupling constants of $J \approx 10$ Hz. The ^{13}C-NMR chemical shifts of the carbonyls in the [{Co$_2$(CO)$_6$}(μ-RC$_2$R′)] complexes appear as one signal at around δ 199 ppm, suggesting that they are rapidly interchanging on the NMR scale. The ^{13}C-NMR resonances of the free and coordinated acetylene unit (C$_2$ and Co$_2$(CO)$_6$C$_2$) were easily observed, and the chemical shifts of the carbon atoms are in the range 104–80 ppm, and we have assigned the carbons of the –C$_6$H$_3$– rings by using Heteronuclear Multiple Quantum Coherence experiment (HMQC).

Deprotection of the two acetylene groups of **4** could be accomplished by treatment with saturated KOH in degassed methanol. $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}(HC\equiv C)_2(1,3,5\text{-}C_6H_3)]$ (**6**) was isolated in high yield (90%) after rapid chromatography on silica with hexane. As expected, the IR spectrum exhibits one $\nu_{C\equiv C}$ absorption at 2070 cm^{-1}, at lower frequency than those of the corresponding terminal $SiMe_3$ groups, and a medium $\nu_{\equiv CH}$ band at 3304 cm^{-1}. The ^{1}H-NMR spectrum shows one signal for the ≡CH protons at δ 3.02 ppm.

Similarly 1,3,5-triethynylbenzene reacts with $Co_2(CO)_8$ to afford a mixture of the complexes $[\{H(Co_2(CO)_6)C_2\}_2(HC\equiv C)(1,3,5\text{-}C_6H_3)]$ (**7**), $[\{H(Co_2(CO)_6)C_2\}_3(1,3,5\text{-}C_6H_3)]$ (**8**). The IR spectra show the expected absorptions in the carbonyl and C–H regions. In the ^{1}H-NMR spectrum, the change in the chemical shifts of the alkyne proton from δ 3.10 ppm in 1,3,5-triethynylbenzene to ca. δ 6.39 ppm in **7** and **8**, were consistent with the incorporation of $Co_2(CO)_6$ units. ^{13}C data are in agreement with the proposed structures (Scheme 1).

3.2. Description of the crystal and molecular structures of 5

The single-crystal X-ray structure determination of $[\{SiMe_3(Co_2(CO)_4dppm)C_2\}_2(SiMe_3C\equiv C)(1,3,5\text{-}C_6H_3)]$ (**5**) confirms the structure presented in Scheme 1. Compound **5** consists of a trisubstituted central benzene ring with a trimethylsilylethyne and two bimetallic Co complex moieties at the 1,3,5 positions. Each bimetallic Co complex has two terminal CO ligands on the Co atoms, bridging dppm ligands and bridging trimethylsilylethynyl ligands. The geometric parameters for **5** have been summarised in Table 2, and Fig. 1 presents a view of the molecule with the atom-labelling scheme.

The molecule has approximate C_2 symmetry but contains no crystallographic symmetry. The ligands around the Co centres can be considered to adopt a highly distorted tetrahedral geometry, if the second Co atom and the two ethynyl C atoms are considered as a 'cyclopropene-type' ligand occupying the fourth coordination site. Thus, the angles subtended at Co(1) between the centroid of the Co(2), C(10) and C(11) ring, and C(1), C(2) and P(1) are 116.0, 124.0 and 115.1°, respectively. The other three angles subtended at Co(1) are 100.07 (12), 101.05 (8), and 96.65 (8)°. Angles observed at the other Co centres are comparable. The Co–Co distances in the two complexes, 2.4892(4) and 2.4906(4) Å, are equivalent. Comparable Co–Co distances of 2.4628(8) and 2.4658(8) Å are reported for the related compound $Co_2(CO)_4(dppa)_2(\mu\text{-}\eta^2\text{-}Me_3SiC_2C\equiv CSiMe_3)$ [16] (also references therein).

The C(10)–C(11) distance in the bridging ethynyl ligand, 1.355(3) Å, is much longer than the C(18)–C(19) triple bond of 1.205(3) Å. The same effect is noted for C(20)–C(21), 1.347(3) Å, with both distances lying in the range 1.33–1.36 Å reported for the alkylenic C–C bond in related dicobalt complexes [15o]. The change in hybridisation at C(10)–C(11) also is reflected in the C(10)–C(11)–C(12) angle of 139.4(2)° and C(11)–C(10)–Si(2) angle of 150.8(2)°. The bridging ethynyl ligands are highly twisted out of the plane of the linking aryl group. The relevant torsion angles are: C(10)–C(11)–C(12)–C(17), −39.0°; C(10)–C(11)–C(12)–C(13), 144.0°; C(21)–C(20)–C(16)–C(17), −45.4°; and C(21)–C(20)–C(16)–C(15), 138.0°. This twisting is significantly larger than in the related molecule $[\{Co_2(CO)_6(HC\equiv C)\}_2(C_6H_4)]$ which may result from greater steric congestion in **5** [15o]. The Co–C distances in the 'Co_2C_2' core of **5** range from 1.963(2) to 1.993(2) Å and these distances do not show an asymmetry pattern as observed in $[\{Co_2(CO)_6(HC\equiv C)\}_2(C_6H_4)]$ [15o].

The average P–C distance of the bridging dppm ligands, 1.838(2) Å, is normal [21]; the P–C bond lengths are statistically equivalent. All other bond lengths and angles are comparable to those reported for similar structures [16] (and references therein).

3.3. Electrochemical study of 1–5

3.3.1. Electrochemistry of 1–3

The CV of **1** at 25 °C (Fig. 2a) shows a reduction wave at $E_{pc} = -1.15$ V vs Fc^{*+}/Fc^* in THF and −1.18 V in CH_2Cl_2 (at a sweep rate $v = 0.1$ V s^{-1}) with no coupled anodic peak (even for v as high as 5 V s^{-1}). An irreversible peak at 0.12 V is observed upon scan reversal, absent when the run starts at −0.16 V in the positive direction. This behaviour resembles other $Co_2(CO)_6$ alkyne derivatives [22–25], i.e. a one-electron reduction process is followed by the fast decomposition of the $\mathbf{1}^-$ radical anion (EC mechanism). Several fragments are produced; one of them is $Co(CO)_4^-$, which is oxidised at 0.12 V. In the presence of excess CO, the radical $RC_2R'Co(CO)_3$ is the other main product of the fragmentation of related compounds [23], its ready reduction to $RC_2R'Co(CO)_3^-$ originating an ECE overall mechanism. However, under the present actual conditions (no excess CO) the EC route is preferred. At −30 °C, the fragmentation of $\mathbf{1}^-$ is nearly quenched, as the CV shows a coupled anodic peak for the reduction process ($i_{pa}/i_{pc} \approx 0.85$ at 0.1 V s^{-1}) and the disappearance of the $Co(CO)_4^-$ oxidation peak (see Fig. 3a and Table 3 for $E_{1/2}$).

The oxidation of **1** in CH_2Cl_2 at 25 °C is completely irreversible at 0.1 V s^{-1} ($E_{pa} = 1.37$ V), but a coupled cathodic peak gradually appears as v increases, as indicative of an EC process. Accordingly, experiments performed at −30 °C show a partially chemically reversible wave with $E_{1/2} = 1.26$ V at 0.1 V s^{-1} (Fig. 3b).

Complexes **2** and **3** contain two and three, respectively, equivalent $C_2Co_2(CO)_6$ redox centres and are irreversibly reduced at 25 °C but, in contrast to **1**, the CV peaks are complex (Fig. 2b–c). Upon scan reversal, an anodic peak due to $Co(CO)_4^-$ oxidation is observed in both cases. SWV clearly shows that the reduction of **2** and **3** in THF gives rise to two and three distinct peaks, respectively. As temperature decreases to − 30 °C, the reduction processes gradually achieve chemical reversibility, with the appearance of coupled anodic peaks and diminution of the $Co(CO)_4^-$ oxidation peak (Fig. 4, Table 3). A comparison of the room and low temperature data in **2**–**3** indicates that the different peak components appearing at 25 °C correspond to the same processes that yield chemically reversible waves at − 30 °C. Therefore, the decomposition reaction following $\mathbf{2}^-$ and $\mathbf{3}^-$ formation is slower than that reported for related $[Co_2(CO)_6]_2[RC{\equiv}C–L–C{\equiv}C]$ complexes with different L [15h,25,26], in which an overall two-electron single irreversible peak is observed at 25 °C. The latter is assigned to the formation of a radical anion that readily decomposes to $Co(CO)_4^-$ and $[Co_2(CO)_6]$-$(RC{\equiv}C–L–C{\equiv}C)$, which gains one more electron at the same potential and further decomposes [26].

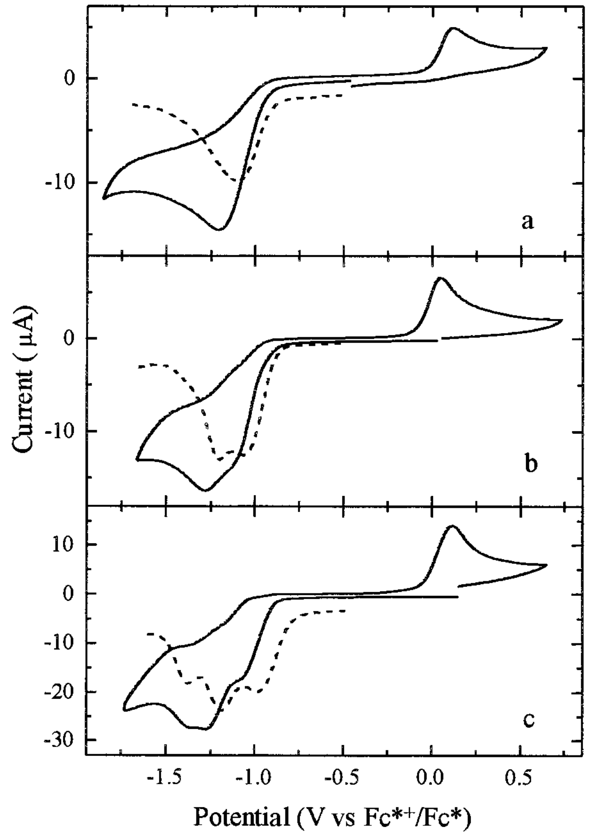


Fig. 2. Cyclic (solid) and square wave (dashed) voltammograms for the reduction of solutions of **1** (2.6 mM) (a), **2** (CV: 2.5 mM, SWV: 2.9 mM) (b) and **3** (CV: 3.1 mM, SWV: 4.0 mM) (c) in THF containing 0.2 M $TBAPF_6$ at 25 °C. CV: $v = 0.1$ V s^{-1}. SWV: scan increment = 2 mV; SW amplitude = 25 mV; frequency = 60 Hz (a–b) and 600 Hz (c).

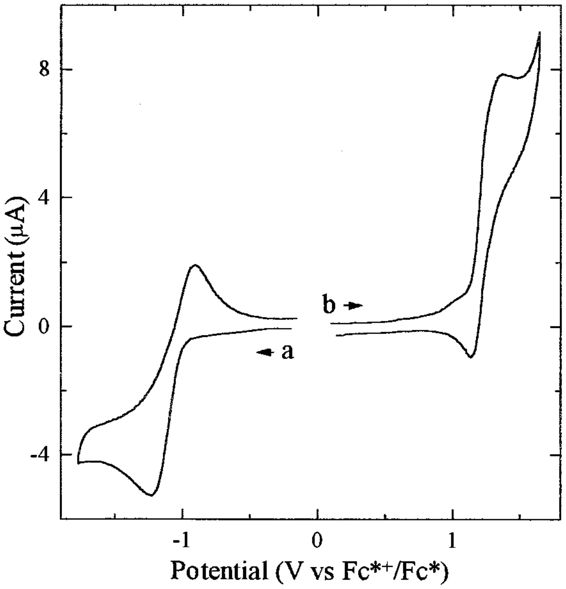


Fig. 3. Cyclic voltammograms for the reduction (a) and oxidation (b) of a solution of **1** in CH_2Cl_2 containing 0.2 M $TBAPF_6$ at 0.1 V s^{-1} and − 30 °C.

Table 3
Electrochemical data for **1**–**5** [a]

	$E_{1/2}$ for reduction	$\Delta E_{1/2}$ (red)	$E_{1/2}$ for oxidation	$\Delta E_{1/2}$ (ox)
1	−1.08 ^{b} (*−1.07* ^{b})		(*1.26* ^{b})	
2	−1.05 ^{b}; −1.19 ^{b}	0.14		
3	−1.00 ^{b}; −1.18 ^{b}; −1.36 ^{b} (*−1.02* ^{b}); (*−1.13* ^{b}); (*−1.22* ^{b})	0.18; 0.18 (*0.11*); (*0.09*)	(*1.41* ^{c})	
4	−1.70		0.69 (*0.72*)	
5	−1.72; −1.93	0.21	0.60; 0.76 (*0.62*); (*0.79*)	0.16 (*0.17*)

[a] In V vs. Fc*+/Fc* in THF solution (values in italics are in CH_2Cl_2 solution).

[b] From CV and SWV at −30 °C.

[c] E_p of irreversible wave at 25 °C.

The potential values listed in Table 3 correspond to $E°'(0,0/0,1-)$ and $E°'(0,1-/1-,1-)$ for **2**, and to $E°'(0,0,0/0,0,1-)$, $E°'(0,0,1-/0,1-,1-)$ and $E°'(0,1-,1-/1-,1-,1-)$ for **3**. The appearance of two and three different reduction peaks for **2** and **3**, respectively, and not of a single bi- or trielectronic wave, indicates the existence of charge delocalisation and electronic communication between the redox centres through the aromatic ligand. The separation between the different peaks ($\Delta E_{1/2}$, Table 3) is a measure of the magnitude of this effect and, for **2** and **3**, corresponds to class II systems in the Hush–Robin–Day classification of mixed-valence compounds [27], i.e. systems with low-moderate electronic delocalisation. The value of $\Delta E_{1/2}$ in **3** is consistent with those found for other trimetallic σ-acetylide complexes of 1,3,5-triethynylbenzene such as $[Fe(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}dppe)(C{\equiv}C\text{–})]_3(1,3,5\text{-}C_6H_3)$ [28] and $[Ru(\eta^5\text{-}C_5H_5)(PPh_3)_2(C{\equiv}C\text{–})]_3(1,3,5\text{-}C_6H_3)$ [29]. However, no electronic interaction was found in 1,3,5-tris(ferrocenylethynyl)benzene [30], evidencing that metal–metal communication strongly depends on the nature of the organometallic fragment.

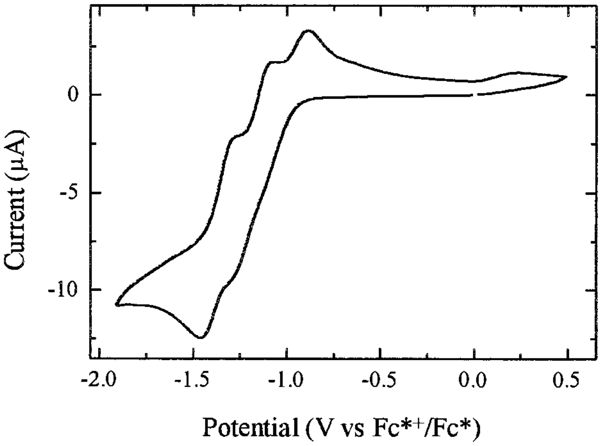


Fig. 4. Cyclic voltammogram for the reduction of a solution of **3** (3.8 mM) in THF containing 0.2 M $TBAPF_6$ at 0.05 V s^{-1} and − 30 °C.

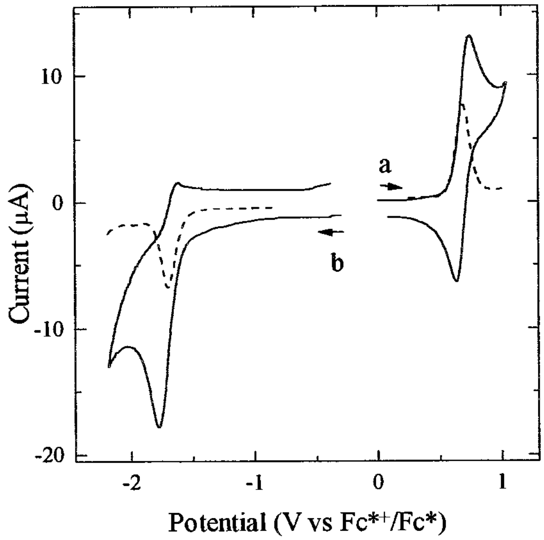


Fig. 5. CV (solid) and SWV (dashed) for the oxidation (a) and reduction (b) of a 1.5 mM solution of **4** in THF containing 0.2 M $TBAPF_6$ at 25 °C. CV: $v = 0.2$ V s^{-1} in (a) and 0.1 V s^{-1} in (b). SWV: scan increment = 2 mV; SW amplitude = 25 mV; frequency = 15 Hz.

Oxidation of **3** in CH_2Cl_2 at 25 °C yields an irreversible multielectronic wave at $E_p = 1.41$ V. No satisfactory low temperature results could be obtained in this case.

3.3.2. *Electrochemistry of* ***4–5***

In complexes **4** and **5**, the coordination of the dppm ligand to the C_2Co_2 centre increases its electron density and facilitates oxidation, whereas it is necessary to apply potentials ca. 600 mV more negative than in **1–2** to achieve reduction. In the room temperature CV and SWV oxidation of **4** (Fig. 5a), one chemically reversible wave is obtained with $i_{pc}/i_{pa} = 1$ in the 0.02–10 V s^{-1} range of CV sweep rates. Thus, $\mathbf{4}^+$ is chemically stable under the actual conditions of the experiment. $E_{1/2}$ in CH_2Cl_2 is 0.54 V less positive than for **1** (Table 3).

The CV and SWV reduction of **4** in THF at 25 °C takes place at a very negative potential, and a single, partially chemically reversible peak is obtained (Fig. 5b, Table 3). i_{pa}/i_{pc} is less than unity at 0.1 V s^{-1}, but increases with v, indicating that the stabilising effect of the chelating dppm makes the fragmentation of $\mathbf{4}^-$ much slower than for the parent $\mathbf{1}^-$. The shift in $E_{1/2}$ upon dppm coordination (0.62 V) and the increased lifetime of the radical anion are consistent with reported data [15h,15n,31]. The intensity of the cathodic peak seems to be appreciably higher than that obtained in the oxidation of the complex at the same v. This could indicate that one of the species resulting from the partial fragmentation of $\mathbf{4}^-$ might gain one more electron at the same potential.

The electrochemical oxidation of **5** shows two sequential reversible waves both in CV ($i_{pa}/i_{pc} = 1$ in the 0.02–10 V s^{-1} range) and SWV (Fig. 6). Correspondingly, the CV and SWV reduction of **5** displays two distinct waves, which are chemically reversible at room temperature for $v \geq 0.3$ V s^{-1}. $E_{1/2}$ values are assembled in Table 3.

From the oxidation waves in **5**, $\Delta E_{1/2}$ is 0.16 V in THF, a smaller value than that obtained from the reduction processes ($\Delta E_{1/2} = 0.21$ V). Differences in $\Delta E_{1/2}$ for oxidations and reductions are not unusual [15h,32], as different MOs are involved in each process and the through-bond electronic coupling dominates the through-space interaction in these systems. Both $\Delta E_{1/2}$ are in the range corresponding to class II mixed-valence compounds, and it can be concluded that there is low–moderate electronic interaction between the two equivalent organometallic redox centres in **5**. The presence of the phosphine ligand seems to enhance the electronic delocalisation, as $\Delta E_{1/2}$ (red) = 0.14 V in **2** and 0.21 V in **5**.

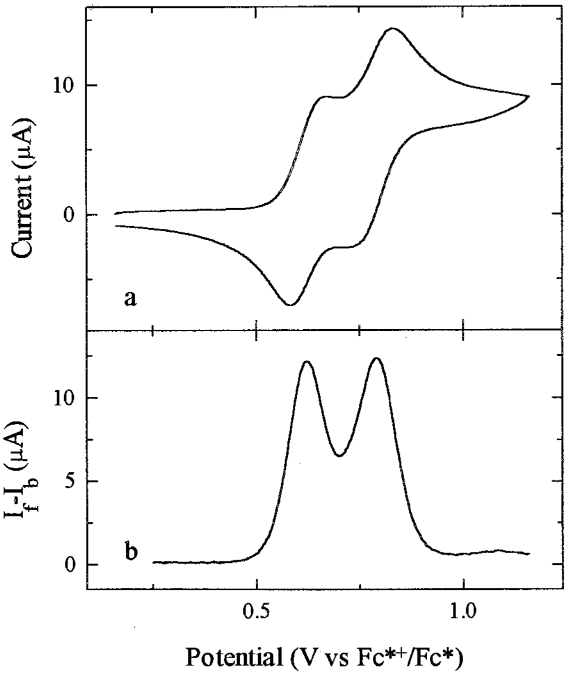


Fig. 6. CV (a) and SWV (b) for the oxidation of a solution of **5** in CH_2Cl_2 containing 0.2 M $TBAPF_6$ at 25 °C. (a) $v = 0.1$ V s^{-1}. (b) scan increment = 2 mV; SW amplitude = 25 mV; frequency = 10 Hz.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 167999 for compound **5**. Copies of this information may be obtained free of charge from The Director, CCDC, 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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