

Experimental: All operations were performed either using cannula techniques on Schlenk lines under an atmosphere of dry nitrogen or in a Braun Labmaster 130 drybox under dry purified argon. Compound K(2-TBS-3,4-Me₂PC₄H₂) **1** was prepared as described previously^[13] and CoCl₂ was dehydrated for three hours at 250°C *in vacuo* prior to use. Solvents were distilled under dry nitrogen, THF from sodium-benzophenone ketyl and pentane from sodium-benzophenone ketyl- tetraglyme, and stored over activated 4Å molecular sieves. Electrochemical measurements, calibrated against internal ferrocene and expressed relative to SCE, were made on a Digital DEA-1 apparatus at platinum electrodes under dry argon in THF using a 3M Bu₄NBF₄ electrolyte. NMR measurements were made on a Bruker AVANCE 300 spectrometer and are referenced to internal capillary- contained TMS or external H₃PO₄ as appropriate. Mass spectra were obtained in methanol using a Bruker microTOF spectrometer.

Meso-2 An ice- cooled THF (150mL) solution of phospholide (10.0g, 37.8mmol) was treated with a single portion of CoCl₂ (1.96g, 15.1mmol) and stirred for 10 minutes. After warming to room temperature, the solvent was removed rapidly under reduced pressure, the deep red mixture was extracted with pentane (150 + 50mL) and the extract was filtered through celite. Crystallisation from *ca* 75mL of pentane at -40°C gave the 1,1'-diphosphacobaltocene as a 2 : 1 mixture of *meso*- and *rac*- diastereomers (8.2g, 85%). Further recrystallisation from pentane at -40°C gave essentially pure *meso-2* (34%). **Meso- 2.** ³¹P: not observable ¹H (Tol-d⁸) : δ 32.4 (3H, -CH₃), 1.8 (9H, -C(CH₃)₃), 1.6 (3H, -Si-CH₃), 0.0 (3H, Si-CH₃), -16.7 (3H, -CH₃), -46.1 (1H, -CH-). μ_{eff} = 1.70 BM (benzene- d⁶, 298K) **Rac- 2.** ³¹P: not observable ¹H (Tol-d⁸) : δ 20.6 (3H, -CH₃), 1.0 (9H, -C(CH₃)₃), 0.4 (3H, -Si-CH₃), -0.9 (3H, -Si-CH₃), -8.3 (3H, -CH₃), -80.4 (1H, -CH-).

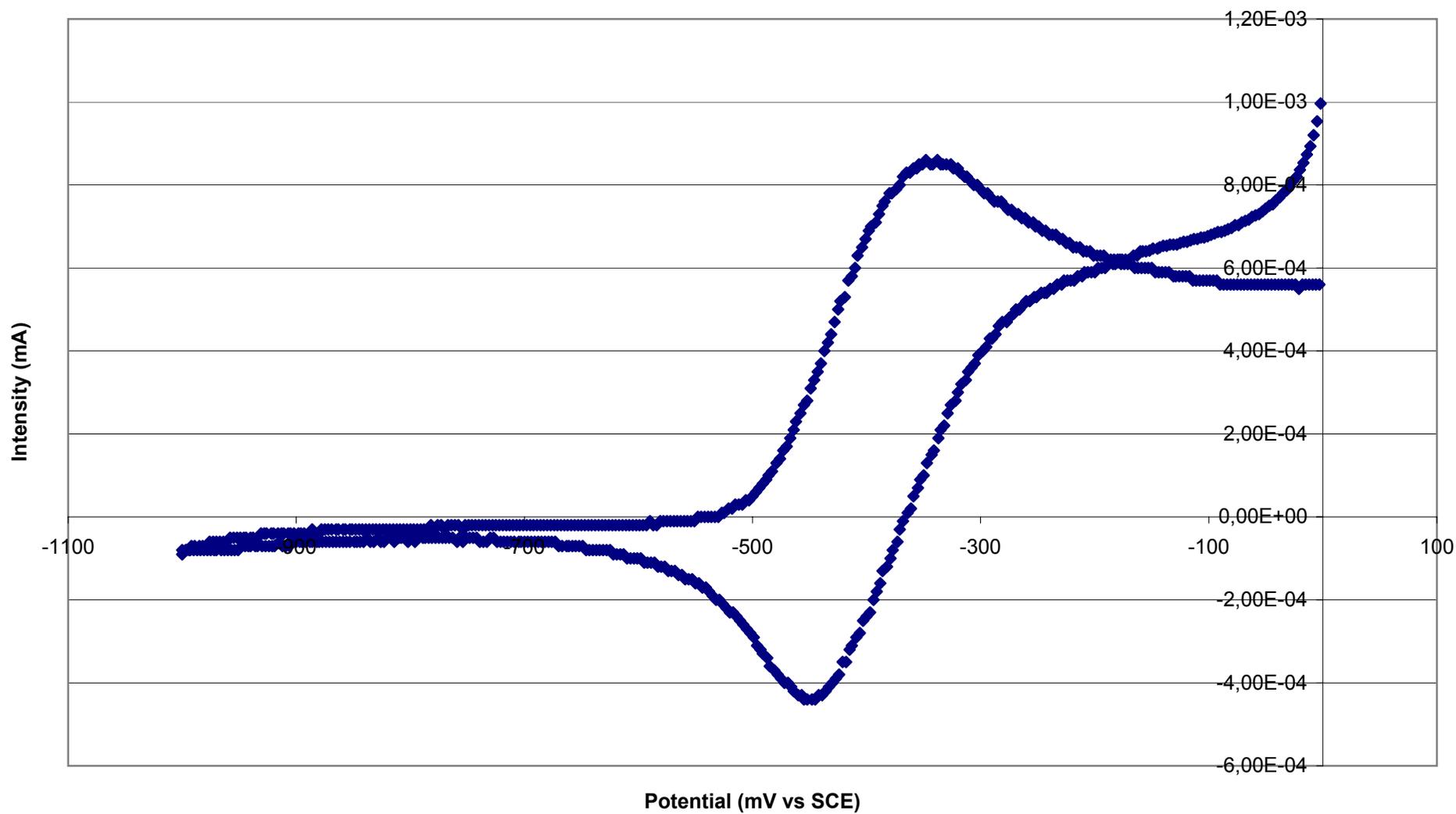
Rac-3 A room temperature solution of **1** (8.0g, 30.2mmol) in THF (150mL) was treated with solid CoCl₂ (1.96g, 15.1mmol). After three days of stirring, the THF was removed under reduced pressure and the oily product was extracted with pentane (150mL plus 50mL), filtered through celite, and evaporated to dryness. After redissolution in THF (100mL), ferricinium hexafluorophosphate (5.0g, 15.1mmol) was added at room temperature, the mixture was stirred for one hour and the solvents were removed under reduced pressure. The mixture was extracted with pentane (150mL), filtered and the crude solid residue (showing a *meso*- : *rac-3* ratio of 1: 9) was further washed with pentane (3x 30mL). The crude was recrystallised from methanol (100mL) at -40°C to give *rac-3* 35%. Alternatively the crude product was treated with water (0.5 mL) and triethylamine (1eq), stripped and extracted into dichloromethane (100mL), washed with degassed water (2x 50mL) and dried over MgSO₄. Chromatography (SiO₂, acetone) gave two bands from which *rac-3* (60%) and *meso-3* (8%) were obtained upon acidification with HBF₄. Fuller details of this methodology will be presented elsewhere. **Rac- 3** ³¹P (DCM-d²) : δ -2.2 (d, ²J_{P-H}=30.1Hz). ¹H (DCM-d²) : d 4.97 (d, 2H, CH, ²J_{H-P}=30.1Hz), 2.31 (s, 6H, C-Me), 2.14 (s, 6H, C-Me), 0.93 (s, 18H, tBu), 0.48 (s, 6H, Si-Me), 0.34 (s, 6H, Si-Me). ¹³C (DCM-d²): δ 125.9 (s, PC(TBDMS)-CMe), 121.8 (s, PCH-CMe), 101.3 (d, P-CH, ¹J_{C-P}=70.4Hz), 97.9 (d, P-C(TBDMS), ¹J_{C-P}=66.5Hz), 29.1 (s, C(CH₃)₃), 21.0 (s, -C(CH₃)₃), 18.4 (s, P-C(TBDMS)-CMe-), 16.6 (s,

-P-CH-CMe-), 0.0 (s, -SiMeMe t Bu), -1.4 (s, -SiMeMe t Bu) ppm. $E_{1/2}$ (50Vsec⁻¹) -0.39V (rev) (SCE). HRMS: (electrospray) 509.1792 calc for 509.1789. **Meso- 3:** ³¹P (DCM-d²): δ 10.1 (d, ²J_{P-H}=34.4Hz). ¹H (DCM-d²): d 5.70 (d, 2H, CH, ²J_{H-P}=34.4Hz), 2.33 (s, 6H, C-Me), 2.28 (s, 6H, C-Me), 0.89 (s, 18H, t Bu), 0.57 (s, 6H, Si-Me), 0.41 (s, 6H, Si-Me).

Crystal data: Meso-2: C₂₄H₄₄CoP₂Si₂, $M = 509.64$, monoclinic, space group P2₁/n₁, $a = 7.890(1)$, $b = 13.894(1)$, $c = 12.481(1)$ Å, $\beta = 95.674(1)$ °. $U = 1361.5(2)$ Å³. $Z = 2$, $D_c = 1.243$ gcm⁻³, $F(000) = 546$. Graphite monochromated X-ray Mo- K_α radiation, $\lambda = 0.71069$ Å. $\mu = 0.845$ cm⁻¹, $T = 150.0(10)$ K. Of 3964 independent reflections collected on a Kappa CCD diffractometer from a dark red plate of dimensions 0.22 x 0.20 x 0.15mm over $h = -9$ to 11, $k = -19$ to 15°, $l = -17$ to 17, 3299 having $I > 2\sigma(I)$ were refined on F^2 using direct methods in Shelxl. $wR_2 = 0.094$, $R_1 = 0.034$, GoF= 1.051, Final map: max diff 0.49(0.1) min-0.47(0.1)eÅ⁻³.

Rac-3: C₂₅H₄₈CoF₆OP₃Si₂, $M = 686.65$, monoclinic, space group C2/c, $a = 28.079(1)$, $b = 7.792(1)$, $c = 31.159(1)$ Å. $U = 6611.7(9)$ Å³. $Z = 8$, $D_c = 1.380$ gcm⁻³, $F(000) = 2880$. Graphite monochromated Mo- K_α radiation, $\lambda = 0.71069$ Å. $\mu = 0.789$ cm⁻¹, $T = 150.0(10)$ K. Of 6509 independent reflections from an orange needle of 0.22 x 0.12 x 0.08mm collected as above over $h = -35$ to 25 $k = -10$ to 9 $l = -39$ to 40°, 4801 having $I > 2\sigma(I)$ were refined on F^2 using direct methods in Shelxl. $wR_2 = 0.136$, $R_1 = 0.046$, GoF=1.020, Final map: max diff 0.92(0.1) min-0.50(0.1)e Å⁻³.

electrochemistry of rac-3 (4mmol/L, NBu₄BF₄ 3M, 50mV/s)



meso-2

	composition	symmetry	energy (eV)	
			alpha spin	beta spin
SOMO	piC - dxz	Ag	-4.71	
	piP + py	Au	-6.18	-5.99
	dx ² -y ²	Ag	-6.56	-5.71
	piC + px	Au	-6.56	-6.5
	dxy	Ag	-6.64	-5.85
	Pn	Ag	-6.69	-6.37
	Pn	Au	-7.13	-7.13
	piP + dyz	Ag	-7.51	-6.83

rac-2

	composition	symmetry	energy (eV)	
			alpha spin	beta spin
SOMO	piC - dxz	A	-4.63	
	piP + py	A	-6.26	-6.07
	piC + px	B	-6.53	-6.45
	dx ² -y ²	A	-6.56	-5.63
	dxy	A	-6.58	-5.74
	Pn + dyz	B	-6.61	-6.26
	Pn	A	-6.8	-6.5
	piP + dyz	B	-7.78	-7.4