

The spectra, structures and electrochemistry of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ complexes, and their reactions with $\text{Co}_2(\text{CO})_8$

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Abstract

A series of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ complexes, **1** are reported, where Ar = (a) C_6H_5 , (b) 4- PhC_6H_4 , (c) 1- C_{10}H_7 (1-naphthyl), (d) 2- C_{10}H_7 (2-naphthyl), (e) 9- C_{14}H_9 (9-phenanthryl), (f) 9- C_{14}H_9 (9-anthryl), (g) 1- C_{16}H_9 (1-pyrenyl), (h) 1- $\text{C}_{20}\text{H}_{11}$ (1-perylenyl), (i) 2- $\text{C}_4\text{H}_3\text{S}$ (2-thienyl), (j) $\text{C}_{10}\text{H}_9\text{Fe}$ (ferrocenyl), (k) SiMe_3 , and (l) H. **1a–1i** react with $\text{Co}_2(\text{CO})_8$ to give the $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}\}\{\text{Co}_2(\text{CO})_6\}$ derivatives **2**. All **1** and **2** have been characterised by elemental analysis and spectroscopy (IR, UV–Vis, ^1H NMR and ^{13}C NMR), X-ray diffraction for **1e** (Ar = 9-phenanthryl), **1j** (Ar = ferrocenyl) and **1l** (Ar = H), electrochemistry for all **1**, and spectroelectrochemistry for **1j**.
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1. Introduction

The acetylide linkage in $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-X}$ complexes, and related compounds such as $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-X}$, allows facile electronic communication between the electron-rich $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$ moiety and X which can affect the characteristic chemistry of both X and $\text{C}\equiv\text{C}$ [1]. However, if X is an electron-withdrawing group the molecule is a donor- π -acceptor (D- π -A) system which may have non-linear optical (NLO) properties [2], although

$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_5$, **1a**, does not appear to be particularly effective in this respect [3].

We have shown that polycyclic aromatic hydrocarbon residues containing 1–5 aromatic rings (e.g., 3-pyrenyl) can act as an electron-donor endgroup in D- π -A systems in the presence of suitable acceptors [4], and were interested to see if it is possible for them to act as acceptors in the presence of a $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$ donor. Although the results reported for **1a** were not encouraging [3], there was the possibility that more highly annelated PAH end-groups would prove to be better acceptors than Ph. Furthermore, our electrochemical/OTTLE studies on a series of $\text{Fc-C}\equiv\text{C-Ar}$ (Fc = ferrocenyl) derivatives showed they, or more particularly their $[\text{Fc-C}\equiv\text{C-Ar}]^+$ derivatives, have unusual spectroscopic properties [5], which might also be found in their $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ counterparts.

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Consequently we prepared a series of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ complexes **1**, where Ar = (a) C_6H_5 , (b) 4- PhC_6H_4 , (c) 1- C_{10}H_7 (1-naphthyl), (d) 2- C_{10}H_7 (2-naphthyl), (e) 9- C_{14}H_9 (9-phenanthryl), (f) 9- C_{14}H_9 (9-anthryl), (g) 3- C_{16}H_9 (3-pyrenyl), (h) 1- $\text{C}_{20}\text{H}_{11}$ (1-perylenyl), (i) 2- $\text{C}_4\text{H}_3\text{S}$ (2-thienyl), and (j) $\text{C}_{10}\text{H}_9\text{Fe}$ (ferrocenyl). They have been characterised by spectroscopic and electrochemical data, and the molecular structures of a number of them determined by X-ray diffraction. **1** have been reacted with $\text{Co}_2(\text{CO})_8$ to give $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}\}\{\text{Co}_2(\text{CO})_6\}$ derivatives **2**.

2. Experimental

Published procedures or extensions thereof were used to prepare $\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Br}$ [6] and $\text{ArC}\equiv\text{CH}$ [7] {Ar = 4- $\text{C}_6\text{H}_5\text{C}_6\text{H}_4$, 4- $\text{Me}_2\text{NC}_6\text{H}_4$, 1- C_{10}H_7 (1-naphthyl), 2- C_{10}H_7 (2-naphthyl), 9- C_{14}H_9 (9-phenanthryl), 9- C_{14}H_9 (9-anthryl), 3- C_{16}H_9 (3-pyrenyl), 1- $\text{C}_{20}\text{H}_{11}$ (1-perylenyl), 2- $\text{C}_4\text{H}_3\text{S}$ (2-thienyl), and $\text{C}_{10}\text{H}_9\text{Fe}$ (ferrocenyl)}. Other chemicals were purchased and used as received.

Unless it is stated otherwise, all reactions were carried out at room temperature in the dark under an atmosphere of nitrogen in dried and deoxygenated solvents. They were monitored by IR spectroscopy. Infrared spectra were recorded on a Perkin–Elmer Paragon 1000 FTIR spectrometer. UV–Vis spectra were recorded on a UNICAM UV2 spectrometer. NMR spectra were obtained on a Jeol JNM-GX270 FT-NMR spectrometer. ^1H (270 MHz) and ^{13}C (67.8 MHz) chemical shifts are reported downfield from tetramethylsilane as internal standard with coupling constants in Hertz. Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin.

Cyclic and square wave voltammetry in CH_2Cl_2 were performed using a three-electrode cell with a polished Pt 1 mm disk working electrode; solutions were $\sim 10^{-3}$ M in electroactive material and 0.10 M in supporting electrolyte (recrystallised TBAPF₆). Data was recorded on an EG & G PAR 273A or Powerlab/4sp computer-controlled potentiostat. Scan rates of 0.05–1 V s^{-1} were typically employed for cyclic voltammetry and for square-wave voltammetry, square-wave step heights of 5 mV, a square amplitude of 25 mV with a frequency of 15 Hz. All potentials are referenced to decamethylferrocene against which $E_{1/2}$ for sublimed ferrocene was 0.55 V. Infrared and UV–Vis OTTLE data were obtained from standard cells with platinum grid electrodes.

2.1. Preparation of $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ni-CC-Ar}$ [8]

A solution of equimolar amounts of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Br}$ (0.1 g, 0.22 mmol) and $\text{ArC}\equiv\text{C}$

(0.22 mmol) and a catalytic amount of CuI (5 mg) in triethylamine (50 ml) was stirred in the absence of light for 16 h. The solvent was then removed under reduced pressure, and the residue was dissolved in dichloromethane and chromatographed on basic alumina using dichloromethane/diethylether (1:1) to elute $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ni-C}\equiv\text{C-Ar}]$, **1**, where Ar = (a) C_6H_5 , (b) 4- PhC_6H_4 , (c) 1- C_{10}H_7 (1-naphthyl), (d) 2- C_{10}H_7 (2-naphthyl), (e) 9- C_{14}H_9 (9-phenanthryl), (f) 9- C_{14}H_9 (9-anthryl), (g) 3- C_{16}H_9 (3-pyrenyl), (h) 1- $\text{C}_{20}\text{H}_{11}$ (1-perylenyl), (i) 2- $\text{C}_4\text{H}_3\text{S}$ (2-thienyl), and (j) $\text{C}_{10}\text{H}_9\text{Fe}$ (ferrocenyl). These were recrystallised from CH_2Cl_2 –pentane mixtures.

$[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ni-C}\equiv\text{C-SiMe}_3]$, **1k**, was prepared similarly from $\text{Ni}(\eta\text{C}_5\text{H}_5)(\text{PPh}_3)\text{Br}$ and trimethylsilylacetylene. The terminal acetylide **1l**, was prepared by hydrolysis of a solution of **1k** (0.36 g, 0.072 mmol) in methanol (20 ml) with K_2CO_3 (2 mmol) for 5 h. The solvent was removed from the reaction mixture at reduced pressure, and the residue extracted with dichloromethane. The solution was filtered through a pad of anhydrous magnesium sulfate and the solvent removed at reduced pressure to give green $[(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ni-C}\equiv\text{C-H}]$, **1l**, previously prepared by a different route [9]. Any further attempts at purification of this compound gave a less pure product.

2.1.1. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_5$ (**1a**)

Yield = 80% (Found: C, 76.4; H, 5.1%; $\text{C}_{31}\text{H}_{25}\text{NiP}$ requires C, 76.4; H, 5.1%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2099 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2098 (KBr). ^1H NMR (CDCl_3): δ 6.64–7.72 [20H, m, C_6H_5 and PPh_3], 5.24 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 124.6–134.0 [m, C_6H_5 , PPh_3], 119.6 [s, Ni–C \equiv C], 92.5 [s, C_5H_5], 86.2 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 271 (19000), 290 (sh), 316 (sh, 17000), 422 (1210) in CH_2Cl_2 ; 420 (1200) in CH_3CN .

2.1.2. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4}$ (**1b**)

Yield = 80% (Found: C, 79.5; H, 5.3%; $\text{C}_{37}\text{H}_{29}\text{NiP}$ requires C, 79.2; H, 5.2%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2096 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2095 (KBr). ^1H NMR (CDCl_3): δ 6.67–7.79 [24H, m, C_6H_5 , C_6H_4 and PPh_3], 5.26 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 120.7–142.0 [m, C_6H_5 , PPh_3], 119.7 [s, Ni–C \equiv C], 92.7 [d, $J_{\text{CP}} = 2.1$ Hz, C_5H_5], 87.5 [d, $^2J_{\text{CP}} = 49.5$ Hz, Ni–C].

2.1.3. $\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_7$ (**1c**) ($\text{C}_{10}\text{H}_7 = 1\text{-naphthyl}$)

Yield = 70% (Found: C, 78.6; H, 5.1%; $\text{C}_{35}\text{H}_{27}\text{NiP}$ requires C, 78.2; H, 5.1%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2084 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2085 (KBr). ^1H NMR (CDCl_3): δ 4.58–7.79 [22H, m, C_{10}H_7 , and PPh_3], 5.21 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 124.7–134.8 [m, C_{10}H_7 , PPh_3], 118.0 [s, Ni–C \equiv C], 92.9 [d, $J_{\text{CP}} = 2.1$ Hz, C_5H_5], 91.1 [d, $^2J_{\text{CP}} = 48.5$ Hz, Ni–C]. $\lambda_{\text{max}}/\text{nm}$

($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 312 (21000), 330 (16000), 361 (11400), 425 nm (1670) in CH_2Cl_2 .

2.1.4. $\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_7$ (**Id**)

($\text{C}_{10}\text{H}_7 = 2\text{-naphthyl}$)

Yield = 80% (Found: C, 78.2; H, 5.1%; $\text{C}_{35}\text{H}_{27}\text{NiP}$ requires C, 78.2; H, 5.1%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2084 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2085 (KBr). ^1H NMR (CDCl_3): δ 6.70–7.80 [22H, m, C_{10}H_7 , and PPh_3], 5.28 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 125.6–135.2 [m, C_{10}H_7 , PPh_3], 118.7 [s, $\text{Ni-C}\equiv\text{C}$], 92.7 [d, $J_{\text{CP}} = 2.2$ Hz, C_5H_5], 87.8 [d, $^2J_{\text{CP}} = 49.5$ Hz, Ni-C]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 310 (22800), 331 (15700), 358 (11200), 429 nm (1540) in CH_2Cl_2 .

2.1.5. $\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (**Ie**)

($\text{C}_{14}\text{H}_9 = 9\text{-phenanthryl}$)

Yield = 80% (Found: C, 79.8; H, 5.0%; $\text{C}_{39}\text{H}_{29}\text{NiP}$ requires C, 79.8; H, 5.0%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2090 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2091 (KBr). ^1H NMR (CDCl_3): δ 7.21–8.69 [24H, m, C_{14}H_9 , and PPh_3], 5.32 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 117.5–135.0 [m, C_{14}H_9 , PPh_3], 118.0 [s, $\text{Ni-C}\equiv\text{C}$], 92.8 [d, $J_{\text{CP}} = 2.1$ Hz, C_5H_5], 91.4 [d, $^2J_{\text{CP}} = 48.5$ Hz, Ni-C]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 334 (11000), 368 (8600), 420 nm (sh, 1340) in CH_2Cl_2 .

2.1.6. $\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (**If**)

($\text{C}_{14}\text{H}_9 = 9\text{-anthryl}$)

Yield = 80% (Found: C, 80.4; H, 5.2%; $\text{C}_{39}\text{H}_{29}\text{NiP}$ requires C, 79.8; H, 5.0%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2075 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2075 (KBr). ^1H NMR (CDCl_3): δ 7.06–8.00 [24H, m, C_{14}H_9 , and PPh_3], 5.37 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 122.6–134.4 [m, C_{14}H_9 , PPh_3], 116.9 [s, $\text{Ni-C}\equiv\text{C}$], 92.9 [d, $J_{\text{CP}} = 2.2$ Hz, C_5H_5], 99.0 [d, $^2J_{\text{CP}} = 48.5$ Hz, Ni-C]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 258 (50000), 387 (sh, 5300), 411 (sh, 8700), 433 (sh, 12400) 449 nm (13700) in CH_2Cl_2 .

2.1.7. $\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{16}\text{H}_9$ (**Ig**)

($\text{C}_{16}\text{H}_9 = 3\text{-pyrenyl}$)

Yield = 80% (Found: C, 80.1; H, 4.9%; $\text{C}_{41}\text{H}_{29}\text{NiP}$ requires C, 80.5; H, 4.8%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2081 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2080 (KBr). ^1H NMR (CDCl_3): δ 7.30–8.20 [24H, m, C_{16}H_9 , and PPh_3], 5.35 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 124.4–135.1 [m, C_{16}H_9 , PPh_3], 119.9 [s, $\text{Ni-C}\equiv\text{C}$], 93.6 [d, $J_{\text{CP}} = 2.2$ Hz, C_5H_5], 94.3 [d, $^2J_{\text{CP}} = 47.5$ Hz, Ni-C]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 254, 280 (26000), 293 (24000), 350 (15900), 367 (17500), 388 (19600), 416 (19400) in CH_2Cl_2 .

2.1.8. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{20}\text{H}_{11}$ (**Ih**)

($\text{C}_{20}\text{H}_{11} = 3\text{-perylene}$)

Yield = 80% (Found: C, 81.4; H, 4.7%; $\text{C}_{45}\text{H}_{31}\text{NiP}$ requires C, 81.7; H, 4.7%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2081

(CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2081 (KBr). ^1H NMR (CDCl_3): δ 6.97–8.07 [26H, m, $\text{C}_{20}\text{H}_{11}$ and PPh_3], 5.31 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 119.6–135.1 [m, C_6H_5 , PPh_3], 119.5 [s, $\text{Ni-C}\equiv\text{C}$], 92.9 [s, C_5H_5], 95.2 [d, $^2J_{\text{CP}} = 47.5$ Hz, Ni-C]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 433 (sh, 11000), 458 (21300), 486 (28000) in CH_2Cl_2 .

2.1.9. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_4\text{H}_3\text{S}$ (**Ii**)

($\text{C}_4\text{H}_3\text{S} = 2\text{-thienyl}$)

Yield = 70% (Found: C, 70.0; H, 4.8%; $\text{C}_{29}\text{H}_{25}\text{NiPS}$ requires C, 70.0; H, 4.8%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2086 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2084 (KBr). ^1H NMR (CDCl_3): δ 6.36–7.76 [20H, m, $\text{C}_4\text{H}_3\text{S}$ and PPh_3], 5.24 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 122.1–134.3 [m, $\text{C}_4\text{H}_3\text{S}$, PPh_3], 92.7 [d, $J_{\text{CP}} = 2.1$ Hz, C_5H_5], 92.8 [d, $^2J_{\text{CP}} = 48$ Hz, Ni-C].

2.1.10. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_9\text{Fe}$ (**Ij**)

($\text{C}_{10}\text{H}_9 = \text{ferrocenyl}$)

Yield = 95% (Found: C, 70.2; H, 5.1%; $\text{C}_{35}\text{H}_{29}\text{FeNiP}$ requires C, 70.6; H, 5.2%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2102 (CH_2Cl_2); $\nu(\text{C}\equiv\text{C})$ 2099 (KBr). ^1H NMR (CDCl_3): δ 7.40–7.87 [15H, m, PPh_3], 5.19 [5H, s, $\text{C}_5\text{H}_5\text{Ni}$], 3.78 [4H, m, $\text{C}_5\text{H}_4\text{Fe}$], 3.61 [5H, s, $\text{C}_5\text{H}_5\text{Fe}$]. ^{13}C NMR (CDCl_3): δ 128.1–134.7 [m, PPh_3], 115.2 [s, $\text{Ni-C}\equiv\text{C}$], 92.6 [d, $J_{\text{CP}} = 2.2$ Hz, $\text{C}_5\text{H}_5\text{Ni}$], 66.5, 70.3, 73.6 [all s, $\text{C}_5\text{H}_4\text{Fe}$], 69.0 [s, $\text{C}_5\text{H}_5\text{Fe}$]. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 424 (1100) in CH_2Cl_2 .

2.1.11. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-SiMe}_3$ (**Ik**)

Yield = 75% (Found: C, 69.6; H, 6.1, P, 6.2%; $\text{C}_{28}\text{H}_{29}\text{NiPSi}$ requires C, 69.6; H, 6.1; P, 6.4%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 2026 (CH_2Cl_2). ^1H NMR (CDCl_3): δ 7.3–7.7 [15H, m, PPh_3], 5.17 [5H, s, C_5H_5], -0.37 [9H, s, SiMe_3]. ^{13}C NMR (CDCl_3): δ 128.1–134.1 [m, PPh_3], 110.6 [d, $^2J_{\text{CP}} = 46$ Hz, Ni-C], 92.5 [s, C_5H_5], 0.8 [s, SiMe_3]. ^{31}P NMR (CDCl_3): δ 41.9. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 416 nm (1060) in CH_2Cl_2 .

2.1.12. $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ (**Il**)

Yield = 82% (Found: C, 72.9; H, 5.4; P, 7.5%; $\text{C}_{25}\text{H}_{21}\text{NiP}$ requires C, 73.0; H, 5.2; P, 7.5%). IR ν/cm^{-1} : $\nu(\text{C}\equiv\text{C})$ 1959, $\nu(\text{CC-H})$ 3276 cm^{-1} (CH_2Cl_2). ^1H NMR (CDCl_3): δ 7.4–7.7 [15H, m, PPh_3], 5.18 [5H, s, C_5H_5], 1.47 [1H, d, $^4J_{\text{PH}} = 2$ Hz, CCH]. ^{13}C NMR (CDCl_3): δ 128.1–133.8 [m, C_6H_5 , PPh_3], 105.0 [s, $\text{Ni-C}\equiv\text{C}$], 92.6 [s, C_5H_5], 80.8 [d, $^2J_{\text{CP}} = 46$ Hz, Ni-C]. ^{31}P NMR (CDCl_3): δ 42.0. $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$) 417 nm (1060) in CH_2Cl_2 .

2.2. Reaction of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ (**I**), with $\text{Co}_2(\text{CO})_8$

Equimolar amounts of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ (0.02 mmol) and $\text{Co}_2(\text{CO})_8$ (0.07 g, 0.02 mmol) in dichloromethane (30 ml) were stirred for 1 h. The

solvent was removed under reduced pressure, and the residue chromatographed on alumina using hexane to elute any unreacted $\text{Co}_2(\text{CO})_8$ and dichloromethane to elute the product as a brown/red band. Removal of the solvent and recrystallisation of the residue from diethylether gave brown $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}\}\{\text{Co}_2(\text{CO})_6\}$ (**2**) where Ar = (a) C_6H_5 , (b) 4- PhC_6H_4 , (d) 1- C_{10}H_7 (1-naphthyl), (e) 2- C_{10}H_7 (2-naphthyl), (f) 9- C_{14}H_9 (9-phenanthryl), (g) 9- C_{14}H_9 (9-anthryl), (h) 3- C_{16}H_9 (3-pyrenyl), (i) 1- $\text{C}_{20}\text{H}_{11}$ (1-perylenyl) and (j) 2- $\text{C}_4\text{H}_3\text{S}$ (2-thienyl). $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}\}\{\text{Co}_2(\text{CO})_6\}$ (**2l**) could be prepared but as it was very unstable and decomposed rapidly, only its IR spectrum could be measured.

2.2.1. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_5\}\{\text{Co}_2(\text{CO})_6\}$ (**2a**)

Yield = 50% (Found: C, 57.3; H, 3.2%; $\text{C}_{37}\text{H}_{25}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 57.5; H, 3.2%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2065, 2030, 1998 in CH_2Cl_2 ; 2064, 2030, 1999 in KBr. ^1H NMR (CDCl_3): δ 6.95–7.62 [20H, m, C_6H_5 and PPh_3], 5.19 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 205.8 (s, CO), 124.3–138.6 [m, C_6H_5 , PPh_3], 94.9 [s, C_5H_5], 80.2 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C], 76.5 [s, Ni–C \equiv C].

2.2.2. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4}\}\{\text{Co}_2(\text{CO})_6\}$ (**2b**)

Yield = 60% (Found: C, 60.5; H, 3.4%; $\text{C}_{43}\text{H}_{29}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 60.8; H, 3.4%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2066, 2033, 1997 in CH_2Cl_2 ; 2065, 2032, 1997 in KBr. ^1H NMR (CDCl_3): δ 7.10–7.82 [24H, m, C_6H_5 , C_6H_4 and PPh_3], 5.21 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 203.6 (s, CO), 123.6–134.2 [m, C_6H_5 , C_6H_4 , PPh_3], 94.6 [s, C_5H_5], 81.5 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C], 76.5 [s, Ni–C \equiv C].

2.2.3. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_7\}\{\text{Co}_2(\text{CO})_6\}$ (**2c**) ($\text{C}_{10}\text{H}_7 = 1\text{-naphthyl}$)

Yield = 60% (Found: C, 59.6; H, 3.2%; $\text{C}_{41}\text{H}_{27}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 59.8; H, 3.3%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2067, 2033, 1996 in CH_2Cl_2 ; 2066, 2032, 1997 in KBr. ^1H NMR (CDCl_3): δ 6.65–7.71 [22H, m, C_{10}H_7 and PPh_3], 5.20 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 204.6 (s, CO), 122.6–135.6 [m, C_{10}H_7 , PPh_3], 94.5 [s, C_5H_5], 90.1 [s, Ni–C \equiv C], 82.4 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.4. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_7\}\{\text{Co}_2(\text{CO})_6\}$ (**2d**) ($\text{C}_{10}\text{H}_7 = 2\text{-naphthyl}$)

Yield = 60% (Found: C, 59.8; H, 3.4%; $\text{C}_{41}\text{H}_{27}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 59.8; H, 3.3%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2065, 2031, 1991 in CH_2Cl_2 ; 2065, 2030, 1992 in KBr. ^1H NMR (CDCl_3): δ 7.05–7.68 [22H, m, C_{10}H_7 and PPh_3], 5.22 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 204.1 (s, CO), 124.2–136.0 [m, C_{10}H_7 , PPh_3], 100.1 [s, Ni–C \equiv C], 94.2 [s, C_5H_5], 83.7 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.5. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9\}\{\text{Co}_2(\text{CO})_6\}$ (**2e**) ($\text{C}_{14}\text{H}_9 = 9\text{-phenanthryl}$)

Yield = 50% (Found: C, 61.9; H, 3.3%; $\text{C}_{45}\text{H}_{29}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 61.9; H, 3.3%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2061, 2032, 1995 in CH_2Cl_2 ; 2062, 2032, 1996 in KBr. ^1H NMR (CDCl_3): δ 7.00–8.24 [24H, m, C_{14}H_9 and PPh_3], 5.19 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 204.6 (s, CO), 121.9–133.9 [m, C_{14}H_9 , PPh_3], 112.1 [s, Ni–C \equiv C], 93.9 [s, C_5H_5], 80.5 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.6. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9\}\{\text{Co}_2(\text{CO})_6\}$ (**2f**) ($\text{C}_{14}\text{H}_9 = 9\text{-anthryl}$)

Yield = 55% (Found: C, 61.7; H, 3.3%; $\text{C}_{45}\text{H}_{29}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 61.9; H, 3.3%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2060, 2030, 1989 in CH_2Cl_2 ; 2062, 2031, 1990 in KBr. ^1H NMR (CDCl_3): δ 6.93–7.82 [24H, m, C_{14}H_9 and PPh_3], 5.20 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 204.1 (s, CO), 122.1–134.9 [m, C_{14}H_9 , PPh_3], 109.7 [s, Ni–C \equiv C], 94.7 [s, C_5H_5], 83.6 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.7. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{16}\text{H}_9\}\{\text{Co}_2(\text{CO})_6\}$ (**2g**) ($\text{C}_{16}\text{H}_9 = 3\text{-pyrenyl}$)

Yield = 55% (Found: C, 62.6; H, 3.3%; $\text{C}_{47}\text{H}_{29}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 62.9; H, 3.2%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2058, 2030, 1990 in CH_2Cl_2 ; 2060, 2030, 1991 in KBr. ^1H NMR (CDCl_3): δ 6.96–7.82 [24H, m, C_{16}H_9 and PPh_3], 5.22 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 205.3 (s, CO), 122.3–135.8 [m, C_{16}H_9 , PPh_3], 110.5 [s, Ni–C \equiv C], 94.4 [s, C_5H_5], 83.3 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.8. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{20}\text{H}_{11}\}\{\text{Co}_2(\text{CO})_6\}$ (**2h**) ($\text{C}_{20}\text{H}_{11} = 3\text{-perylenyl}$)

Yield = 45% (Found: C, 64.3; H, 3.4%; $\text{C}_{51}\text{H}_{31}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 64.7; H, 3.3%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2058, 2031, 1991 in CH_2Cl_2 ; 2059, 2030, 1992 in KBr. ^1H NMR (CDCl_3): δ 7.10–7.91 [26H, m, $\text{C}_{20}\text{H}_{11}$ and PPh_3], 5.21 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 203.9 (s, CO), 123.6–135.3 [m, $\text{C}_{20}\text{H}_{11}$, PPh_3], 109.6 [s, Ni–C \equiv C], 94.5 [s, C_5H_5], 85.1 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.9. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_4\text{H}_3\text{S}\}\{\text{Co}_2(\text{CO})_6\}$ (**2i**) ($\text{C}_4\text{H}_3\text{S} = 2\text{-thienyl}$)

Yield = 30% (Found: C, 53.8; H, 3.0%; $\text{C}_{35}\text{H}_{23}\text{Co}_2\text{-NiO}_6\text{P}$ requires C, 53.9; H, 3.0%). IR ν/cm^{-1} : $\nu(\text{CO})$ 2064, 2034, 2001 in CH_2Cl_2 ; 2064, 2035, 2001 in KBr. ^1H NMR (CDCl_3): δ 6.12–7.71 [18H, m, C_4H_3 and PPh_3], 5.21 [5H, s, C_5H_5]. ^{13}C NMR (CDCl_3): δ 202.6 (s, CO), 120.5–136.6 [m, C_4H_3 , PPh_3], 99.2 [s, Ni–C \equiv C], 93.9 [s, C_5H_5], 84.2 [d, $^2J_{\text{CP}} = 48$ Hz, Ni–C].

2.2.10. $\{\text{Ni}(\eta\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}\}\{\text{Co}_2(\text{CO})_6\}$ (**2l**)

IR ν/cm^{-1} : $\nu(\text{CO})$ 2061, 2022, 1991 in CH_2Cl_2 .

2.3. Structure determinations for **1e**, **1j** and **1l**

Green crystals of **1e** and **1j** were grown from dichloro-methane–hexane mixtures by diffusion, and of **1l** from chloroform–hexane mixtures. Crystal data for **1e**, **1j** and **1l** are given in Table 1.

A block of **1e**, a plate of **1j**, and a block of **1l**, were used for data collection. Data were collected on a Bruker SMART CCD at 183(2) K for **1e**, an Enraf-Nonius CAD-4 at 294(2) K for **1j** [10] and a Bruker SMART APEX CCD at 100(2) K for **1l**. Data for **1e** and **1l** were processed using SMART [11] with empirical absorption corrections applied using SADABS [12]. For **1j** data were processed using the NCRVAX suite of programs and the ABSORP routine to apply absorption corrections [13].

All three structures were solved using SHELXS-97 [14] and refined by full-matrix least-squares using SHELXL-97 [15]. All non-hydrogen atoms were assigned anisotropic temperature factors with hydrogen atoms included in calculated positions using a riding model. There are two independent molecules in the unit cell of **1j**, designated A and B. Disorder is present in the cyclo-

pentadienyl ligand coordinated to the Ni atom of molecule A and the two sites (occupancy 0.52:0.48) were treated using soft DELU/ISOR/FLAT restraints in the final stages of refinement. For this structure, graphics were obtained using ORTEP [16] and PLATON [17].

Molecular structures of **1e**, **1j** and **1l** with atom labelling are shown in Figs. 1–3, and selected bond lengths and angles in Table 2.

3. Results and discussion

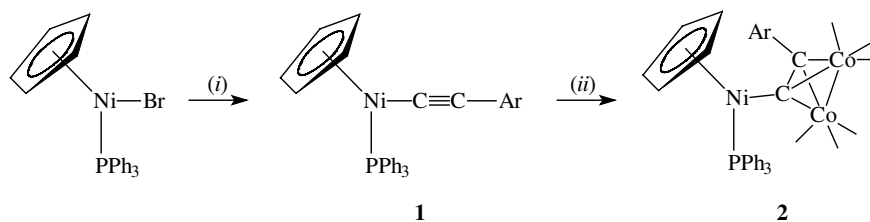
The reactions carried out in this work are shown in the Scheme 1. The alkynyl–nickel complexes **1**, are air-stable solids which are insoluble in water but soluble in common organic solvents with their solubility decreasing with increasing size of the Ar group. All are green with the exception of **1i**, which is orange.

The alkynes **1** react with $\text{Co}_2(\text{CO})_8$ in the usual fashion [18] to give $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}\}\{\text{Co}_2(\text{CO})_6\}$, **2**, which have structures similar to that of $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-CHO}\}\{\text{Co}_2(\text{CO})_6\}$ [1]. Ni

Table 1

Crystal data for $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (**1e**), $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{C}\equiv\text{C-Fc}$ (**1j**) and $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ (**1l**)

	$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (1e)	$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{C}\equiv\text{C-Fc}$ (1j)	$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ (1l)
Empirical formula	$\text{C}_{35}\text{H}_{29}\text{NiP}$	$\text{C}_{35}\text{H}_{29}\text{FeNiP}$	$\text{C}_{25}\text{H}_{21}\text{NiP}$
Formula weight	587.30	595.11	411.10
Temperature (K)	183(2)	293(2)	100(2)
Wavelength (Å)	0.71073	0.71093	0.71073
Crystal system	Monoclinic	Monoclinic,	Orthorhombic
Space group	$P2_1/c$	$P2_1/n$	$Pbca$
Unit cell dimensions			
<i>a</i> (Å)	11.056(3)	9.7458(10)	9.4694(9)
<i>b</i> (Å)	24.614(6)	29.928(3)	16.4972(16)
<i>c</i> (Å)	11.422(3)	19.620(2)	25.313(3)
α (°)			90
β (°)	107.875(4)	103.796(8)	90
γ (°)			90
<i>V</i> (Å ³)	2958.2(12)	5557.7(10)	3954.4(7)
<i>Z</i>	4	8	8
Calculated density (Mg/m ³)	1.319	1.422	1.381
Absorption coefficient (mm ⁻¹)	0.736	1.280	1.068
<i>F</i> (000)	1224	2464	1712
Crystal size (mm)	0.70 × 0.36 × 0.32	0.24 × 0.22 × 0.05	0.70 × 0.40 × 0.20
θ Range for data collection (°)	2.05–26.48	2.5–25.1	1.61–28.26
Index ranges (<i>hkl</i>)	–12 → 13, –30 → 30, –14 → 14	–11 → 11, 0 → 35, 0 → 25	–12 → 12, –21 → 21, –33 → 32
Reflections collected	36417	10176	30439
Independent reflections [<i>R</i> _{int}]	6032 [0.0577]	9953 [0.023]	4688 [0.0642]
Data completeness	$2\theta = 52.96^\circ$, 98.6%	$2\theta = 56^\circ$, 99%	$2\theta = 56.52^\circ$, 95.6%
Absorption correction	Multiscan	Numerical	Semi-empirical from equivalents
Maximum and minimum transmission	1.000 and 0.829	0.933 and 0.749	0.8147 and 0.4666
Refinement method	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	6032/0/370	9953/84/731	4688/0/244
Goodness-of-fit on <i>F</i> ²	1.025	0.90	1.296
Final <i>R</i> indices [<i>I</i> > 2 (<i>I</i>)]	$R_1 = 0.0387$, $wR_2 = 0.0754$	$R_1 = 0.0537$, $wR_2 = 0.0851$	$R_1 = 0.0791$, $wR_2 = 0.1556$
<i>R</i> indices (all data)	$R_1 = 0.0696$, $wR_2 = 0.0852$	$R_1 = 0.1955$, $wR_2 = 0.1053$	$R_1 = 0.0974$, $wR_2 = 0.1608$
Largest difference in peak and hole (e Å ⁻³)	0.29 and –0.35	0.44 and –0.43	1.015 and –1.478
Largest shift/error max.	<0.001	0.001	



Scheme 1. (i) $\text{ArCCH/Et}_3\text{N/CuI}$; (ii) $\text{Co}_2(\text{CO})_8/\text{CH}_2\text{Cl}_2$ (CO ligands have been omitted for clarity).

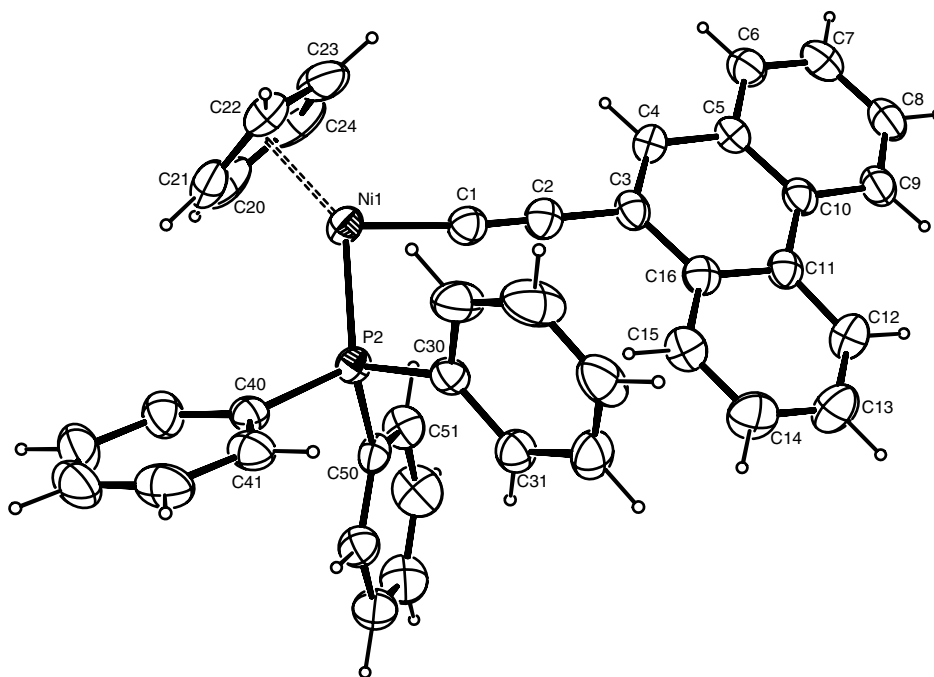


Fig. 1. The structure and atom labelling of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (**1e**).

and Ar are attached to the C atoms of the dicobalttetrahedrane core of the molecule. All are dark brown solids soluble in the usual organic solvents. They are somewhat air-sensitive in the solid state and much more so in solution.

3.1. Molecular structures of the alkynyl–Ni complexes **1e**, **1j** and **11**

The molecular structures of **1e**, **1j** and their parent **11** are illustrated in Figs. 1–3. Selected bond lengths and angles are given in Table 2.

All three compounds have the expected two-legged piano-stool structure with a planar η^5 -cyclopentadienyl ligand coordinated to a planar $\text{P-Ni-C}\equiv\text{C}$ moiety such that the two planes are approximately orthogonal. $\text{Ni-C}\equiv\text{C}$ are virtually linear, $174.0(3)^\circ$ – $176.9(5)^\circ$, and P-Ni-C close to 90° . The $\text{Ni-C}(1)$ and $\text{C}(1)\equiv\text{C}(2)$ distances each lie within a very narrow range and are equal within experimental error at $1.830(6)$ – $1.865(6)$ and $1.204(4)$ – $1.213(3)$ Å, respectively. They are comparable to those found for other compounds of this type

[19–22]. In particular, the dimensions of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$, **11**, are very similar to those of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}\equiv\text{C-H}$ [20].

In $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$, **11**, the C_5H_5 and $\text{Ph}_3\text{P-Ni-C}\equiv\text{CH}$ planes have an angle of 85.6° between them and are oriented so that the P-Ni-C plane is at right-angles to the α_v plane of the $\eta^5\text{-C}_5\text{H}_5$, i.e., a β isomer [1]. As a consequence the cyclopentadienyl ring is distorted towards an ene-enyl moiety. The reasons for this are discussed elsewhere, [23 and references therein].

In $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$, **1e**, the angle between the $\text{P-Ni-C}(1)\equiv\text{C}(2)$ and cyclopentadienyl planes is 89.8° . The phenanthryl fragment is also planar and its plane is close to that of the $\text{P-Ni-C}(1)\text{-C}(2)$ moiety with an angle of 12.1° between them. This is similar to the situation in **1a** [22] and contrasts with that in $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-CH}(\text{CN})_2$ [1], where the $\text{P-Ni-C}(1)\equiv\text{C}(2)$ and $\text{CH}(\text{CN})_2$ planes are close to orthogonal. The $\text{P-Ni-C}(1)$ plane is oriented such that it is coincident with the α_v plane of the C_5 ring and is an α_b isomer [1] with the Ni-P bond eclipsing $\text{C}(21)$. The C_5 ring is distorted towards a diene with two short

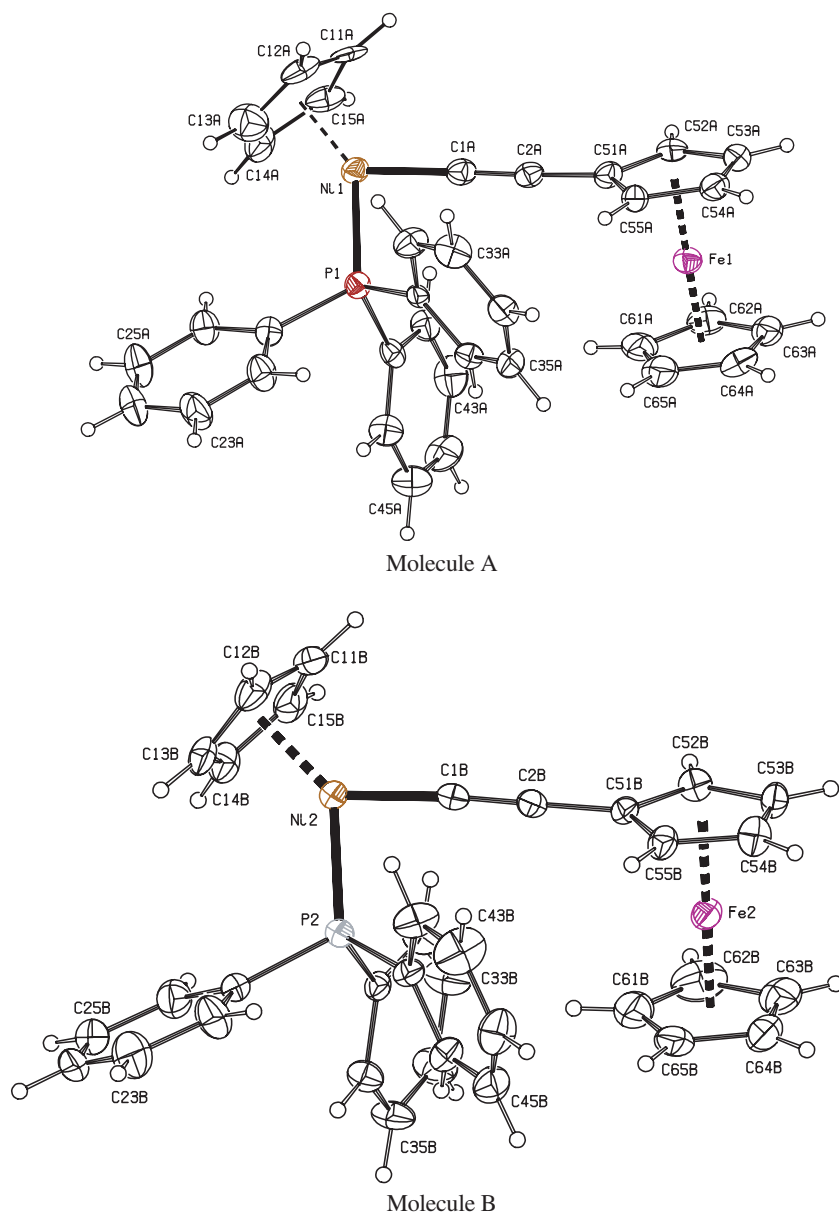


Fig. 2. The structure and atom labelling of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Fc}$ (**1j**).

C–C bonds, C(20)–C(24)/C(22)–C(23), and one particularly short Ni–C_{ring} bond to C(21). The bond distances and angles within the phenanthryl group are normal.

There are two molecules (A and B) in the asymmetric unit of $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_5\text{H}_4\}\text{Fe}(\eta^5\text{-C}_5\text{H}_5)$, **1j**, which differ slightly in geometry. Molecule A, has its Ni-bound cyclopentadienyl ligand disordered over two sites. In the non-disordered molecule B the Ni-coordinated cyclopentadienyl ligand adopts the same orientation with respect to the P–Ni–C plane as it does in the phenanthryl derivative **1e**, but there is no marked distortion of the C₅H₅. However, although the structures of **1e** and **1j** are similar, in the phenanthryl derivative the angle between the planar endgroup and the P–Ni–C(1) plane is 12.1°, in the ferrocenyl derivative it

is 50.1° and 60.1° for isomers A and B, respectively. Furthermore the P–Ni–C(1) angles of 86.77(17)° and 85.97(17)° in **1j** are very low compared with those of other $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-X}$ complexes. In **1j** the Fe–C(C₅H₄), 2.031(6)–2.047(6) Å, show much greater variation than the Fe–C(C₅H₅), 2.021(7)–2.025(7) Å, but both are shorter than the Ni–C(C₅H₅) distances, 2.083–2.134(6) Å (values quoted are for molecule B) which are normal.

3.2. Spectra of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-CC-Ar}$ (**1**)

The $\nu(\text{C}\equiv\text{C})$ vibrations of **1** give rise to weak but readily identifiable IR absorption bands. Their frequencies are a function of Ar, and decrease along the series

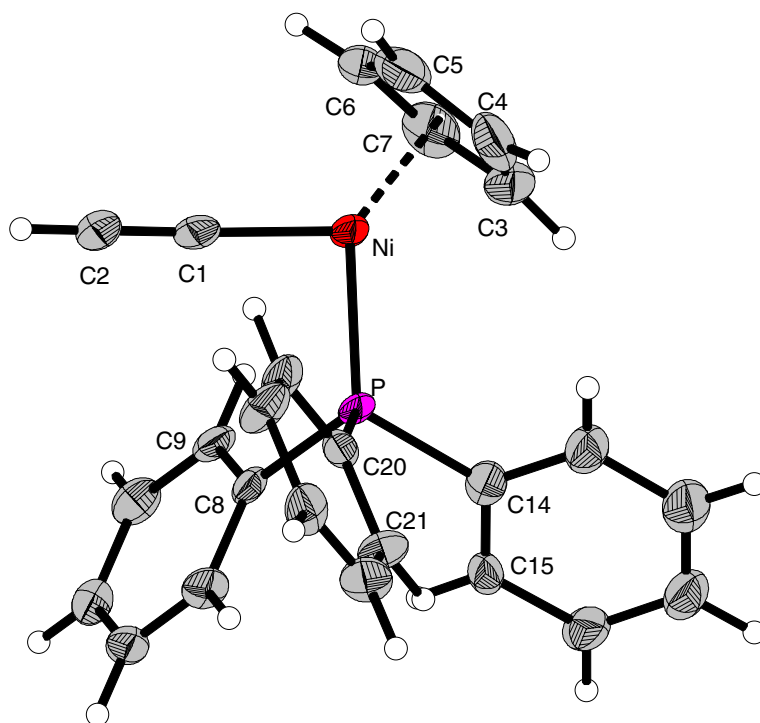


Fig. 3. The structure and atom labelling of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ (**II**).

Ar = ferrocenyl (2102 cm^{-1}) > C_6H_5 > $4\text{-PhC}_6\text{H}_4$ > 2-naphthyl \sim 9-phenanthryl > 2-thienyl > 1-naphthyl > 3-pyrenyl \sim 1-perylenyl > 9-anthryl (2075 cm^{-1}). As the $\nu(\text{C}\equiv\text{C})$ frequencies are $2110\text{--}2115\text{ cm}^{-1}$ for all $\text{ArC}\equiv\text{CH}$, and 1959 cm^{-1} for $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$, **II**, it appears that the $\text{C}\equiv\text{C}$ in **1a–j** are more like those in $\text{ArC}\equiv\text{CH}$ than that in $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$. The IR spectrum of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ shows an absorption band at 3276 cm^{-1} which is absent from the spectra of other **1** and is attributed to $\nu(\text{CC-H})$.

The ^1H NMR spectra of **1** show a singlet due to the $\eta^5\text{-C}_5\text{H}_5$ group and numerous resonances due to the Ph_3P ligand and Ar groups which could not always be separated and assigned individually. Unlike the other compounds, the spectrum of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ shows a doublet at $\delta\ 1.47$ ($J = 2.4\text{ Hz}$) due to the ^{31}P coupled acetylenic proton, and that of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-SiMe}_3$ shows a singlet at $\delta\ -0.39$ due to the SiMe_3 group. In the ^{13}C NMR spectra the resonances due to Ph_3P and Ar groups also overlap whilst the $\eta^5\text{-C}_5\text{H}_5$ ligand gives rise to a singlet or a doublet due to limited coupling to ^{31}P ($J = 2.2\text{ Hz}$). The resonances due to C(1) and C(2) of the alkynyl group are weak; the former is a readily identified doublet ($J = \text{ca. } 49\text{ Hz}$) due to coupling to ^{31}P , but the latter is usually a singlet and cannot always be found. The chemical shifts for C(1) are found in the range $86.2\text{--}99.3\ \delta$ and are increasingly deshielded for Ar = C_6H_5 > $4\text{-PhC}_6\text{H}_4$ > 2-naphthyl > 1-naphthyl > 9-phenanthryl > 2-thienyl > 3-pyrenyl \sim 1-perylenyl > 9-anthryl, a series

which is similar to that for $\nu(\text{C}\equiv\text{C})$. The chemical shifts for $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ and $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-SiMe}_3$ occur at extremes of 80.8 and $110.6\ \delta$, respectively. The resonances for C(2) are all found downfield from those due to C(1) ($110.7\text{--}120.2\ \delta$) and become increasingly deshielded for Ar = 2-naphthyl > 3-pyrenyl > C_6H_5 \sim $4\text{-PhC}_6\text{H}_4$ > 1-perylenyl > 1-naphthyl \sim 9-phenanthryl > 9-anthryl, compared with $105.5\ \delta$ for $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$.

The UV–Vis spectrum of **1a** shows an intense absorption band at 271 nm ($\epsilon = 19000\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) which tails into the visible region. Embedded in this tail is a much weaker band ($\epsilon = 1210\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) at 422 nm . As a comparable band is also present in the spectrum of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ (417 nm , $\epsilon = 1060\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), we attribute this weak band to an electronic transition within the $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C}$ moiety. It can be seen in the spectra of other derivatives of **1**, but not when Ar = 9-anthryl, 3-pyrenyl and 3-perylenyl. As the annellation of the Ar end-group increases, absorption bands due to electronic transitions of the aryl group move to lower energies, become more intense and swamp the ca. 420 nm band. Consequently **1i** is red-orange in colour whilst the other **1** are varying shades of green. Previous experience [5] suggests that the “aromatic” bands correspond to the substituent-sensitive p bands of the parent hydrocarbon, ArH. These shift to longer wavelengths in going from ArH to $\text{ArC}\equiv\text{C-H}$, and lose their vibrational fine structure if there is significant conjugation into the substituents [24]. In **1f–h** these “aromatic” bands are found at longer

Table 2
Selected bond lengths (Å) and bond angles (°) for **1f**, **1j** (molecule A and molecule B) and **11**

Ni(η^5 -C ₅ H ₅)(PPh ₃)-C≡C-C ₁₄ H ₉ (1f) (C ₁₀ H ₇ = 9-phenanthryl)		Ni(η^5 -C ₅ H ₅)(PPh ₃)-C≡C-C ₅ H ₄ Fe(η^5 -C ₅ H ₅), 1j		Ni(η^5 -C ₅ H ₅)(PPh ₃)-C≡C-H, 11			
		Molecule A	Molecule B				
Coordination about Ni							
Ni(1)–P(2)	2.1453(8)	Ni(1)–P(1)	2.1303(17)	Ni(2)–P(2)	2.1272(16)	Ni–P	2.1494(13)
Ni(1)–C(1)	1.858(8)	Ni(1A)–C(1)	1.865(6)	Ni(2)–C(1B)	1.830(6)	Ni–C(1)	1.850(5)
Ni(1)–C(20)	2.131(3)	Ni(1)–C(11A)	2.112(16)	Ni(2)–C(11B)	2.093(6)	Ni(1)–C(3)	2.088(5)
Ni(1)–C(21)	2.072(3)	Ni(1)–C(12A)	2.08(2)	Ni(2)–C(12B)	2.134(6)	Ni(1)–C(4)	2.141(5)
Ni(1)–C(22)	2.165(3)	Ni(1)–C(13A)	2.05(3)	Ni(2)–C(13B)	2.083(6)	Ni(1)–C(5)	2.128(5)
Ni(1)–C(23)	2.110(3)	Ni(1)–C(14A)	2.15(3)	Ni(2)–C(14B)	2.122(6)	Ni(1)–C(6)	2.086(5)
Ni(1)–C(24)	2.107(3)	Ni(1)–C(15A)	2.15(2)	Ni(2)–C(15B)	2.132(6)	Ni(1)–C(7)	2.152(5)
C(20)–C(21)	1.438(4)	C(11A)–C(12A)	1.42(3)	C(11B)–C(12B)	1.386(8)	C(3)–C(4)	1.438(8)
C(21)–C(22)	1.385(4)	C(12A)–C(13A)	1.36(2)	C(12B)–C(13B)	1.393(8)	C(4)–C(5)	1.385(8)
C(22)–C(23)	1.418(4)	C(13A)–C(14A)	1.43(5)	C(13B)–C(14B)	1.399(8)	C(5)–C(6)	1.427(8)
C(23)–C(24)	1.425(4)	C(14A)–C(15A)	1.44(3)	C(14B)–C(15B)	1.385(8)	C(6)–C(7)	1.412(8)
C(20)–C(24)	1.384(5)	C(11A)–C(15A)	1.42(2)	C(11B)–C(15B)	1.413(8)	C(3)–C(7)	1.420(7)
P(2)–Ni(1)–C(1)	92.44(8)	P(1)–Ni(1)–C(1A)	86.77(17)	P(2)–Ni(2)–C(1B)	85.97(17)	P–Ni–C(1)	90.29(15)
Within the Ni–C≡C moiety							
Ni(1)–C(1)	1.858(3)	Ni(2)–C(1A)	1.865(6)	Ni(2)–C(1B)	1.830(6)	Ni–C(1)	1.850(5)
C(1)–C(2)	1.213(3)	C(1B)–C(2A)	1.206(7)	C(1B)–C(2B)	1.210(7)	C(1)–C(2)	1.203(7)
C(2)–C(3)	1.449(3)	C(2B)–C(51A)	1.435(8)	C(2B)–C(51B)	1.442(7)		
Ni(1)–C(1)–C(2)	174.0(2)	Ni(2)–C(1A)–C(2A)	175.2(5)	Ni(2)–C(1B)–C(2B)	175.8(6)	Ni–C(1)–C(2)	176.9(5)
C(1)–C(2)–C(3)	179.0(3)	C(1B)–C(2A)–C(51A)	172.9(6)	C(1B)–C(2B)–C(51B)	175.7(6)		
Within the Ar moiety							
C(3)–C(4)	1.365(3)	Fe(1)–C(51A)	2.053(6)	Fe(2)–C(51B)	2.047(6)		
C(3)–C(4)	1.448(3)	Fe(1)–C(52A)	2.030(5)	Fe(2)–C(52B)	2.031(6)		
C(4)–C(5)	1.435(3)	Fe(1)–C(53A)	2.018(6)	Fe(2)–C(53B)	2.083(6)		
C(5)–C(6)	1.414(3)	Fe(1)–C(54A)	2.031(6)	Fe(2)–C(54B)	2.034(6)		
C(6)–C(7)	1.369(4)	Fe(1)–C(55A)	2.031(6)	Fe(2)–C(55B)	2.034(6)		
C(7)–C(8)	1.399(4)	C(51A)–C(52A)	1.404(7)	C(51B)–C(52B)	1.418(7)		
C(8)–C(9)	1.377(4)	C(52A)–C(53A)	1.405(7)	C(52B)–C(53B)	1.406(7)		
C(9)–C(10)	1.420(3)	C(53A)–C(54A)	1.396(7)	C(53B)–C(54B)	1.415(8)		
C(5)–C(10)	1.424(3)	C(54A)–C(55A)	1.411(7)	C(54B)–C(55B)	1.403(7)		
C(10)–C(11)	1.456(3)	C(51A)–C(55A)	1.419(7)	C(51B)–C(55B)	1.422(7)		
C(11)–C(16)	1.428(3)	Fe(1)–C(61A)	2.047(6)	Fe(2)–C(61B)	2.047(6)		
C(11)–C(12)	1.410(3)	Fe(1)–C(62A)	2.024(7)	Fe(2)–C(62B)	2.024(7)		
C(12)–C(13)	1.368(4)	Fe(1)–C(63A)	2.042(6)	Fe(2)–C(63B)	2.021(7)		
C(13)–C(14)	1.399(4)	Fe(1)–C(64A)	2.031(6)	Fe(2)–C(64B)	2.021(7)		
C(14)–C(15)	1.379(4)	Fe(1)–C(65A)	2.019(7)	Fe(2)–C(65B)	2.024(6)		
C(15)–C(16)	1.417(3)	C(61A)–C(62A)	1.412(9)	C(61B)–C(62B)	1.398(10)		
		C(62A)–C(63A)	1.386(9)	C(62B)–C(63B)	1.404(9)		
		C(63A)–C(64A)	1.390(9)	C(63B)–C(64B)	1.386(9)		
		C(64A)–C(65A)	1.394(8)	C(64B)–C(65B)	1.386(8)		
		C(61A)–C(65A)	1.408(9)	C(61B)–C(65B)	1.388(9)		

wavelengths than for ArH [25]. They also have vibrational structures which are similar those observed for ArH though not as well-defined nor identical in appearance, particularly when Ar = 9-anthryl. This suggests that resonance interaction between Ar and Ni is limited. The typical absorption bands for a ferrocenyl group expected for **1j**, are swamped by the Ni(η^5 -C₅H₅)(PPh₃)-C≡C absorptions. It should be noted that the UV–Vis spectra of **1** are independent of solvent.

3.3. Electrochemistry of Ni(η^5 -C₅H₅)(PPh₃)-C≡C-Ar (**1**)

1 undergo a primary one electron oxidation process **A** (Fig. 4). For Ni(η^5 -C₅H₅)(PPh₃)-C≡C-H, $E_p^a = 0.83$ V,

but for the acene or phenyl complexes **1a–1i** E_p^a lie in the range 0.76–0.81 V (Table 3). We note that in Ni(η^5 -C₅H₅)(PPh₃)-C≡C-X derivatives the oxidation potential increases with increasing acceptor capability of X; for example, $E_p^a = 0.98$ V when X = CHO. This suggests that the aromatic end-groups Ar are acting as donors and, as the potential E_p^a decreases slightly for **1g** < **1f** < **1h**, that the larger polycyclic aromatic groups pyrenyl, anthryl and perylenyl are better donors than the smaller ones. Consequently, the HOMO for the primary oxidation must have a contribution from the acetylide and Ni(η^5 -C₅H₅) moieties, a conclusion also reached by Humphries et al. [3]. In the electrochemistry of **1j** the reversible ferrocenyl couple precedes **A** and the equal currents for these two couple confirms that the

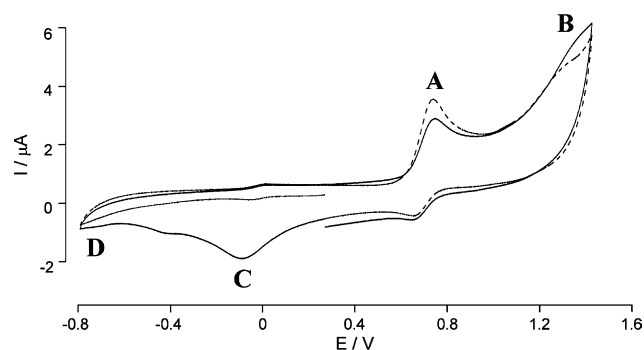


Fig. 4. Full CV of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_5$ ($\text{CH}_2\text{Cl}_2/\text{TBAPF}_6$) 500 mV s^{-1} .

Table 3

Cyclic voltammetry for $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ (**1**)

Compound	E_p^a (A)	i_c/i_a
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_5$ (1a)	0.81	0.7
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_6\text{H}_4\text{Ph-4}$ (1b)	0.81	0.5
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_7$ (1-naphthyl) (1c)	0.81	1.0
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_7$ (2-naphthyl) (1d)	0.81	1.0
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (9-phenanthryl) (1e)	0.81	0.3
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{14}\text{H}_9$ (9-anthryl) (1f)	0.77	1.0
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{16}\text{H}_9$ (3-pyrenyl) (1g)	0.79	1.0
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{20}\text{H}_{11}$ (3-perylenyl) (1h)	0.76	1.0
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_4\text{H}_3\text{S-2}$ (2-thienyl) (1i)	0.80	1.0
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_9\text{Fe}^+$ (ferricenium) (1j ⁺)	1.03 ^b	0.8
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-H}$ (1l)	0.83	<0.1
$\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-CHO}$ [1]	1.04	<0.1

^a E_p^a (A) (200 mV s^{-1}); i_c/i_a (1500 mV s^{-1}); (CH_2Cl_2 , TBAPF_6 , 0.1 M, Pt electrode, internal Fc^* reference).

^b E^0 [$\text{Ferrocenyl}^{+/0}$] for this compound is 0.41 V.

primary process **A** is a one-electron transfer. $E^0[\text{Fc}^{+/0}] = 0.41\text{ V}$ for this couple, compared to $E^0[\text{Fc}^{+/0}] = 0.72\text{ V}$ for $\text{FcC}\equiv\text{CH}$, shows that the $(\eta\text{-C}_5\text{H}_5)\text{Ni}$ entity is acting as a strong *donor* with respect to the ferricenium acetylide substituent. The positive charge on **1j**⁺ increases E_p^a to 1.03 V.

A striking feature of the electrochemistry of **1** is the variation in the chemical reversibility of **A** as a function of scan rate and solvent, as well as alkyne substituent. For **1a** in CH_2Cl_2 for example: at scan rates $<100\text{ mV s}^{-1}$, $i_c/i_a = 0.1$; at $100\text{--}400\text{ mV s}^{-1}$, $i_c/i_a = 0.5$; at 2 V s^{-1} , $i_c/i_a = 1$, that is, chemically reversible. The companion cathodic feature occurs at $E_p^c = 0.68\text{ V}$. In CH_3CN , however, no companion cathodic feature is observed up to 5 V s^{-1} , and in the temperature range 295–193 K. Similar behaviour is observed for the ferrocenyl complex **1j**⁺ and the complexes with polycyclic aromatic acetylide substituents **1b–1i** (Fig. 5). These data are consistent with a primary oxidation of **1** to give a Ni(III) species at E_p^a (**A**) followed by a rapid chemical reaction which is influenced by the donor ability of the

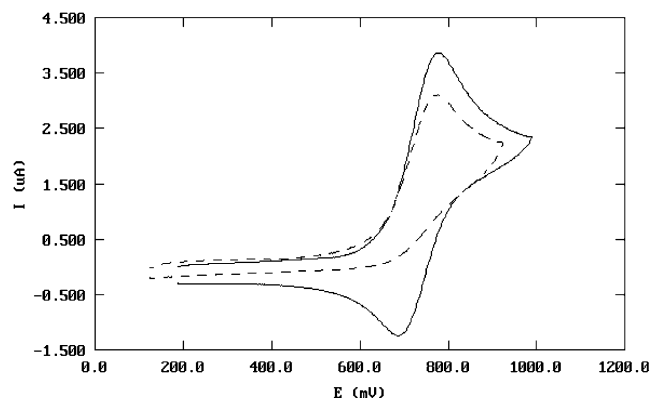


Fig. 5. CV of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{16}\text{H}_9$, 200 mV s^{-1} : (-----) CH_2Cl_2 ; (—) MeCN .

solvent. There are no reduction waves in the cyclic voltammetry of **1a–1h**, other than that associated with **A**, providing the anodic potential does not exceed 0.95 V.

If the anodic scan range in CH_2Cl_2 is extended, another oxidation process **B** appears at E_p^a 1.2–1.5 V. On cathodic scans after **B** two new reduction processes are seen; **C** at $E_p^c \sim -0.08\text{ V}$ and **D** at -0.80 V (Fig. 4). **B** and **C** are identical to the redox parameters of free Ph_3P [26]. In agreement with this assignment, the electrochemical parameters of **B** and **D** are independent of solvent and of the acetylide substituent. Thus, at least in part, the current of **B** is due to uncoordinated Ph_3P . Our caution here is because the oxidation potentials for $\text{ArC}\equiv\text{CH}$ and the irreversible oxidation of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2]^+$, a known reaction product of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{X}$ derivatives, both occur in the region of 1.25–1.5 V [27]. **D** has a current ratio of $i(\text{D})/i(\text{A})$ between <0.1 and 0.9 depending on the solvent and acetylide substituent. Its current has no relationship to that of **B** or the chemical reversibility of **A**. Electrochemical profiles are similar on repeat scans. To further investigate whether ligand loss from the Ni(III) species was a component of the chemical irreversibility, the electrochemistry was repeated in the presence of CO and PPh_3 . CO had no effect. Unexpectedly, the addition of PPh_3 caused **A** to be completely irreversible in both CH_2Cl_2 and CH_3CN between 50 mV s^{-1} and 2 V s^{-1} for all complexes (Fig. 6). Features **B** and **C** are reinforced and **D** unaffected, as expected if the assignments are correct.

It is clear that stability of the 17e Ni(III) species depends on the type of acetylide substituents with the most stable being those with π -donor substituents, and that the formation of this species leads to the rapid loss of PPh_3 and a decomposition reaction. A seemingly contradictory observation is that the addition of PPh_3 or a donor solvent assists this instability. Unfortunately, IR and UV–Vis OTTLT studies, or chemical oxidation with the aminium salt ‘Magic Blue’, did not give further

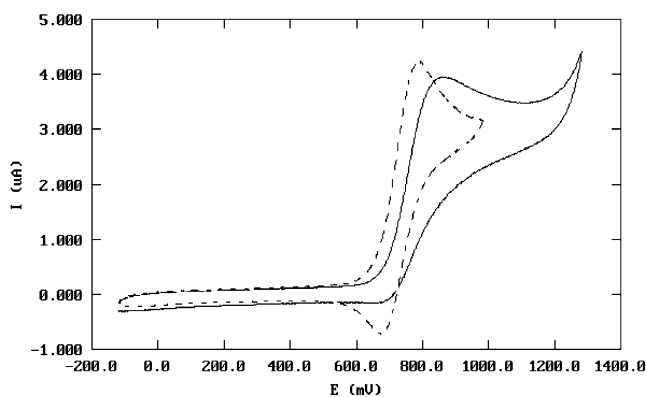


Fig. 6. CV of $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-C}_{10}\text{H}_6$: (-----) $200\text{ mV s}^{-1}/-45\text{ }^\circ\text{C}$; (—) after addition of PPh_3 .

insight into the EC mechanism. There is no electrochemical evidence for a disproportionation of Ni(III) to Ni(IV) and Ni(II) (a common route for decomposition of Ni(I) complexes) [28]. Furthermore, $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)_2$ is not produced and there is no other electroactive species linked to **A** apart from PPh_3 . Explanations which satisfy the data are that dimerisation or a $\eta^5 \rightarrow \eta^1$ (or η^3) transformation takes place upon formation of the 17e species.

The UV spectrum of $\mathbf{1j}^+$ generated in the OTTLE cell was recorded and is illustrated in Fig. 7. The significant feature is the low energy transition at 1550 nm. Bands such as this are found in the spectra of most $\text{Fc}^\oplus\text{-C}\equiv\text{CR}$ species and are assigned to an LMCT from a donor orbital on R to the ferrocenium LUMO [5]. The energy of this transition for $\mathbf{1j}^+$ is lower than those for most $\text{Fc}^\oplus\text{-C}\equiv\text{CAr}$ [5] and is similar to the IVCT band recorded for $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{-C}\equiv\text{C-Fc}^\oplus$ at 1590 nm [29]. Clearly, $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$ is functioning as a strong donor to the ferrocenium end-group through the π linkage.

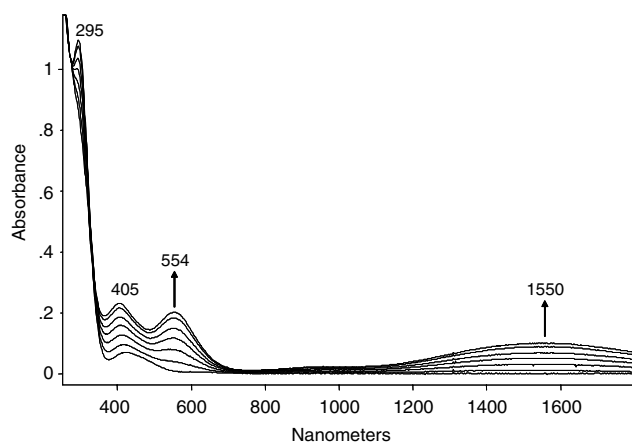


Fig. 7. The electronic spectrum of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Fc}]^+$, $[\mathbf{1j}]^+$, generated in the OTTLE cell on electrochemical oxidation of $[\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Fc}]$ ($[\mathbf{1j}]$).

3.4. Spectra of $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}\}\text{Co}_2(\text{CO})_6$ (**2**)

The IR spectra of **2** in dichloromethane solution show three absorption bands due to the $\nu(\text{CO})$ vibrations of the $\text{Co}_2(\text{CO})_6$ moiety with the broad band at lowest frequency having more than one component (cf. [30]). Their relative intensities are comparable to those of other (alkyne) $\text{Co}_2(\text{CO})_6$ compounds, but their frequencies are much lower {cf. (3-pyrenyl- $\text{C}\equiv\text{C-H})\text{Co}_2(\text{CO})_6$, $\nu(\text{CO}) = 2090, 2054, 2025\text{ cm}^{-1}$; (2-thienyl- $\text{C}\equiv\text{C-H})\text{Co}_2(\text{CO})_6$, $\nu(\text{CO}) = 2094, 2058, 2028\text{ cm}^{-1}$; $(\text{Ph-C}\equiv\text{C-Ph})\text{Co}_2(\text{CO})_6$, $\nu(\text{CO}) = 2091, 2055, 2026\text{ cm}^{-1}$ }. This is attributed to the strong donor capabilities of the $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Ni}$ substituents which leads to a considerable increase in the electron-richness of the C_2Co_2 moiety and a decrease of ca. 30 cm^{-1} of the $\nu(\text{CO})$ frequencies as has been discussed elsewhere [1]. In a second, less marked, effect the $\nu(\text{CO})$ frequencies of **2** are lower for the larger Ar groups than for the smaller, which further suggests that the former are better donors to the dicobaltatetrahedrane moiety than are the latter. The donor capabilities of acetylene substituents in $(\text{RCCR}')\text{Co}_2(\text{CO})_6$ complexes is evident in the decrease of their $\nu(\text{CO})$ frequencies along the series $\text{R,R}' = \text{H,H} > \text{Ph,H} > \text{Ph,Ph} > \text{Ph,Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$.

4. Conclusions

Spectroscopic and electrochemical evidence suggests that in $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}$ complexes **1** communication between the $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$ group and the Ar groups is limited, at least in the ground state, and is not sufficient to bring about any significant changes in the dimensions of the $\text{Ni-C}\equiv\text{C-Ar}$ moiety as determined by X-ray diffraction. However, there is a lowering of the $\nu(\text{C}\equiv\text{C})$ frequencies of **1**, as compared with $\text{Ar-C}\equiv\text{C-H}$, and changes in the $\delta(^{13}\text{C})$ chemical shifts for $\text{Ni-C}\equiv\text{C}$, which increase in importance as the annelation of Ar increases but are always limited. These and other spectroscopic data suggest that it is unlikely that any **1** would exhibit significant second order NLO activity, as has been confirmed by others [3].

The frequencies of the $\nu(\text{CO})$ bands of the $\{\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-Ar}\}\{\text{Co}_2(\text{CO})_6\}$ complexes **2**, derived from **1**, confirm that the $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$ moiety is a powerful electron-donor but also indicate that the aryl group Ar are weaker donors. This is consistent with the electrochemical data.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data

Centre, CCDC Nos. CCDC 269736 (**1e**), CCDC 271151 (**1j**) and CCDC 270147 (**1l**). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>)

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