

## The reactions of some $\sigma$ -alkynylnickel complexes with 7,7,8,8-tetracyanoquinodimethane

Peter Butler<sup>a</sup>, Anthony R. Manning<sup>a,\*</sup>, C. John McAdam<sup>b</sup>, Jim Simpson<sup>b</sup>

<sup>a</sup> Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

<sup>b</sup> Department of Chemistry, University of Otago, P.O. Box 56, Dunedin, New Zealand

Received 15 September 2007; received in revised form 30 October 2007; accepted 6 November 2007

Available online 22 November 2007

### Abstract

The  $\sigma$ -alkynyl complexes  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-R}$  (**1**),  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-X-C}\equiv\text{CH}$  (**2**) and  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\equiv\text{C-X-C}\equiv\text{C-Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$  (**3**), react with 7,7,8,8-tetracyanoquinodimethane, TCNQ, at 30 °C by insertion of the alkyne  $\text{C}\equiv\text{C}$  into a  $\text{C}=\text{C}(\text{CN})_2$  bond to give  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\{\text{C}_6\text{H}_4=\text{C}(\text{CN})_2\}\text{-C}\{\text{C}(\text{CN})_2\}\text{-R}$  (**4**), from **1**,  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\{\text{C}_6\text{H}_4=\text{C}(\text{CN})_2\}\text{-C}\{\text{C}(\text{CN})_2\}\text{-X-C}\equiv\text{CH}$  (**5**), from **2**, and  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\{\text{C}_6\text{H}_4=\text{C}(\text{CN})_2\}\text{-C}\{\text{C}(\text{CN})_2\}\text{-X-C}\equiv\text{C-Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$  (**6**), and  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}\{\text{C}_6\text{H}_4=\text{C}(\text{CN})_2\}\text{-C}\{\text{C}(\text{CN})_2\}\text{-X-C}\{\text{C}(\text{CN})_2\}\text{-C}\{\text{C}_6\text{H}_4=\text{C}(\text{CN})_2\}\text{-Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$  (**7**), from **3** {**R** = (a)  $\text{C}_6\text{H}_5$ , (b) 4- $\text{PhC}_6\text{H}_4$ , (c) 4- $\text{Me}_2\text{NC}_6\text{H}_4$ , (d) 1- $\text{C}_{10}\text{H}_7$  (1-naphthyl), (e) 2- $\text{C}_{10}\text{H}_7$  (2-naphthyl), (f) 9- $\text{C}_{14}\text{H}_9$  (9-phenanthryl), (g) 9- $\text{C}_{14}\text{H}_9$  (9-anthryl), (h) 3- $\text{C}_{16}\text{H}_9$  (3-pyrenyl), (i) 1- $\text{C}_{20}\text{H}_{11}$  (1-perylenyl), (j) 2- $\text{C}_4\text{H}_3\text{S}$  (2-thienyl), (k)  $\text{C}_{10}\text{H}_9\text{Fe}$  (ferrocenyl = Fc) and (l) H; **X** = (a) nothing, (b) 1,4- $\text{C}_6\text{H}_4$ , (c) 1,3- $\text{C}_6\text{H}_4$  and (d) 4,4'- $\text{C}_6\text{H}_4\text{-C}_6\text{H}_4$ }. The reaction is regio-specific and the other possible insertion product,  $\text{R-C}\{\text{C}_6\text{H}_4=\text{C}(\text{CN})_2\}\text{-C}\{\text{C}(\text{CN})_2\}\text{-Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)$  etc., is not formed. Under the same conditions, there is no evidence for the reaction of TCNQ with the  $\text{-C}\equiv\text{CH}$  of **2**,  $\text{PhC}\equiv\text{CH}$ , 1,4- $\text{C}_6\text{H}_4(\text{C}\equiv\text{CH})_2$  or  $\text{FcC}\equiv\text{CH}$ , or for the reaction of more than one  $\text{C}=\text{C}(\text{CN})_2$  of TCNQ with a Ni-alkynyl moiety. Complexes **4–7** are all air-stable, purple solids which have been characterised by elemental analysis and spectroscopy (IR, UV-Vis,  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR), and by X-ray diffraction for **4a**, **4b** and **4l**. The UV-Vis spectra of **4–7** are very similar. This implies that all contain the same active chromophore which, it is suggested, is  $\text{Ni-C}(5)=\text{C}_6\text{H}_4=\text{C}(\text{CN})_2$  and not  $\text{R-C}(4)=\text{C}(\text{CN})_2$ . This is inconsistent with the molecular structures of **4a**, **4b** and **4l** which show that the first of these potentially chromophoric fragments is planar or close to it with an in-built potential for delocalisation, whilst in the second the aryl group **R** is almost orthogonal to the  $\text{C}=\text{C}(\text{CN})_2$  plane. The molecular structures of **4a**, **4b** and **4l** also reveal a short  $\text{Ni}\cdots\text{C}(4)$  separation, indicative of a  $\text{Ni} \rightarrow \text{C}(4)$  donor-acceptor interaction. The electrochemistry of **4a** shows a quasi reversible oxidation at ca. 1 V and complicated reduction processes. It is typical of most **4**, but **4l** is different in that it shows the same quasi reversible oxidation at ca. 1 V but two reversible reductions at  $-0.26$  and  $-0.47$  V (vs.  $[\text{Fe}(\eta^5\text{-C}_5\text{Me}_5)_2]^{+/0}$  0.0 V).

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Ni; Alkyne; TCNQ; Insertion

### 1. Introduction

The reactions of  $\text{C}_2(\text{CN})_4$ , TCNE, with metalloalkynes  $\text{MC}\equiv\text{CR}$  have been extensively investigated. They give

cyclobutenyls which may subsequently isomerise to buta-1,3-dienyl complexes,  $(\text{NC})_2\text{C}=\text{C}(\text{M})\text{-C}(\text{R})=\text{C}(\text{CN})_2$  so the overall reaction is the insertion of the CC triple bond into the double bond of TCNE [1–11]. Other activated olefins react similarly [12]; in particular there has been a single report on the use of 7,7,8,8-tetracyanoquinodimethane, TCNQ, in this role. With *trans*- $\text{Pt}(\text{PMe}_3)_2(\text{C}\equiv\text{C-Me})_2$  it gives *trans*- $\text{Pt}(\text{PMe}_3)_2(\text{CCMe})\text{C}\{\text{C}_6\text{H}_4\text{C}(\text{CN})_2\}\text{C}\{\text{CC}(\text{CN})_2\}\text{Me}$  [13,14].

\* Corresponding author. Tel.: +353 1 7062495; fax: +353 1 7062127.

E-mail addresses: Anthony.Manning@ucd.ie (A.R. Manning), J.Simpson@alkali.otago.ac.nz (J. Simpson).

Herein we report on further reactions of TCNQ with metalloalkynes, particularly those containing a Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>) substituent. We had hoped that the reactions would give Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C-R/TCNQ charge transfer complexes similar to those obtained from ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>CH=CH-aryl) and TCNQ [15,16] and expected these to be more stable for the more highly annelated aryl groups. In the event, this did not happen and all reactions gave insertion products similar to those described above.

## 2. Experimental

### 2.1. General procedures

Published procedures or extensions thereof were used to prepare Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)Br [17], RC≡CH [18,19], HC≡C-C≡CH [20], 1,3-C<sub>6</sub>H<sub>4</sub>(C≡CH)<sub>2</sub> [21], 1,4-C<sub>6</sub>H<sub>4</sub>(C≡CH)<sub>2</sub> [21], and 4,4'-HC≡C-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>-C≡CH [20]. Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C-R (**1**), Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C-X-C≡CH (**2**) and Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C-X-C≡C-Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>) (**3**), {R = Ph, 4-PhC<sub>6</sub>H<sub>4</sub>, 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 1-C<sub>10</sub>H<sub>7</sub> (1-naphthyl), 2-C<sub>10</sub>H<sub>7</sub> (2-naphthyl), 9-C<sub>14</sub>H<sub>9</sub> (9-phenanthryl), 9-C<sub>14</sub>H<sub>9</sub> (9-anthryl), 3-C<sub>16</sub>H<sub>9</sub> (3-pyrenyl), 1-C<sub>20</sub>H<sub>11</sub> (1-perylenyl), 2-C<sub>4</sub>H<sub>3</sub>S (2-thienyl), C<sub>10</sub>H<sub>9</sub>Fe (ferrocenyl)} and H [22–24]. 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 when necessary.

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 measured on a Jeol JNM-GX270 FT-NMR spectrometer or a Varian Unity Inova 500 MHz NMR spectrometer for **4a** and **4l** only. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported downfield from tetramethylsilane as internal standard with coupling constants in Hertz. Cyclic and square-wave voltammetry in CH<sub>2</sub>Cl<sub>2</sub> were performed using a three-electrode cell with a polished Pt 1 mm disk working electrode; 10<sup>-3</sup> M in electroactive material and 0.10 M in supporting electrolyte (TEAP or TBAPF<sub>6</sub>). Data were recorded on a Powerlab/4sp computer-controlled potentiostat. Scan rates of 0.05–1 V s<sup>-1</sup> 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 decamethyl ferrocene; E<sub>1/2</sub> for sublimed ferrocene was 0.55 V. Elemental analyses were performed in the Microanalytical Laboratory, University College Dublin.

### 2.2. Reactions of Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C-R with tetracyanoquinodimethane (TCNQ)

TCNQ (0.2 g, 1.02 mmol) was added to a solution of Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C-R (1.02 mmol) in dichloro-

methane (30 mL). There was an immediate colour change from green or orange to red/purple. After 15 min the reaction mixture was chromatographed on silica using dichloromethane to elute the product in good yield. Removal of the solvent and recrystallisation of the residue from acetonitrile-ether mixtures gave dark crystals of Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}-C{=C(CN)<sub>2</sub>}-R (**4a-l**) where R = (a) C<sub>6</sub>H<sub>5</sub>, (b) 4-PhC<sub>6</sub>H<sub>4</sub>, (c) 4-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, (d) 1-C<sub>10</sub>H<sub>7</sub> (1-naphthyl), (e) 2-C<sub>10</sub>H<sub>7</sub> (2-naphthyl), (f) 9-C<sub>14</sub>H<sub>9</sub> (9-phenanthryl), (g) 9-C<sub>14</sub>H<sub>9</sub> (9-anthryl), (h) 3-C<sub>16</sub>H<sub>9</sub> (3-pyrenyl), (i) 1-C<sub>20</sub>H<sub>11</sub> (1-perylenyl), (j) 2-C<sub>4</sub>H<sub>3</sub>S (2-thienyl), (k) C<sub>10</sub>H<sub>9</sub>Fe (ferrocenyl) and (l) H.

There was no reaction between TCNQ and 1,4-diethynylbenzene, phenylacetylene or ferrocenyl acetylene even after 2 h at 30 °C.

#### 2.2.1. Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}-C{=C(CN)<sub>2</sub>}-C<sub>6</sub>H<sub>5</sub> (**4a**)

Anal. Calc. for C<sub>43</sub>H<sub>29</sub>N<sub>4</sub>NiP: C, 74.7; H, 4.2; N, 8.1. Found: C, 74.6; H, 4.2; N, 8.0%. IR  $\nu$ /cm<sup>-1</sup>:  $\nu$ (C≡N) 2212 (CH<sub>2</sub>Cl<sub>2</sub>);  $\nu$ (C≡N) 2213 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.19 [1H, br, C<sub>6</sub>H<sub>4</sub>], 6.7–7.7 [24H, m, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>5</sub> and PPh<sub>3</sub>], 5.34 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  203.1 (br), 184.5 (br), 156.2, 144.2, 143.2, 134.7, 133.6, 131.2, 130.9, 129.4, 128.8, 128.6, 127.6, 123.7, 120.3, 115.0, 114.8, 113.4, 113.3, 95.8, 73.6, 69.3.  $\lambda_{\max}$ /nm ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 478 (18,400), 571 (sh, 8,000) in CH<sub>2</sub>Cl<sub>2</sub>; 472 (17,100), 570 (sh, 8,100) in CH<sub>3</sub>CN.

#### 2.2.2. Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}-C{=C(CN)<sub>2</sub>}-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>5</sub>-4 (**4b**)

Anal. Calc. for C<sub>49</sub>H<sub>33</sub>N<sub>4</sub>NiP: C, 76.6; H, 4.3; N, 7.3. Found: C, 76.5; H, 4.3; N, 7.3%. IR  $\nu$ /cm<sup>-1</sup>:  $\nu$ (C≡N) 2223 (sh), 2212 (CH<sub>2</sub>Cl<sub>2</sub>);  $\nu$ (C≡N) 2223 (sh), 2213 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.61–8.49 [28H, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub> and PPh<sub>3</sub>], 5.35 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  182.5, 155.3, 142.7, 142.1, 120.4–135.0, 116.5, 116.2, 115.8, 95.9.  $\lambda_{\max}$ /nm ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 477 (19,400), 572 (sh, 10,500) in CH<sub>2</sub>Cl<sub>2</sub>; 475 (19,000), 573 (sh, 10,400) in CH<sub>3</sub>CN.

#### 2.2.3. Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}-C{=C(CN)<sub>2</sub>}-C<sub>6</sub>H<sub>4</sub>N(CH<sub>3</sub>)<sub>2-4</sub> (**4c**)

Anal. Calc. for C<sub>45</sub>H<sub>34</sub>N<sub>4</sub>NiP: C, 73.6; H, 4.7; N, 9.9. Found: C, 73.7; H, 4.7; N, 9.9%. IR  $\nu$ /cm<sup>-1</sup>:  $\nu$ (C≡N) 2212 (CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.69–7.43 [23H, m, C<sub>6</sub>H<sub>4</sub>, C<sub>6</sub>H<sub>4</sub>, PPh<sub>3</sub>], 5.33 [5H, s, C<sub>5</sub>H<sub>5</sub>], 2.90 [6H, s, NMe<sub>2</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  182.5, 155.3, 142.7, 142.1, 120.4–135.0, 116.5, 116.2, 115.8, 95.9.  $\lambda_{\max}$ /nm ( $\epsilon$ /dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 477 (19,400), 572 (sh, 10,500) in CH<sub>2</sub>Cl<sub>2</sub>; 475 (19,000), 573 (sh, 10,400) in CH<sub>3</sub>CN.

#### 2.2.4. Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}-C{=C(CN)<sub>2</sub>}-C<sub>10</sub>H<sub>7</sub> (**4d**) (C<sub>10</sub>H<sub>7</sub> = 1-naphthyl)

Anal. Calc. for C<sub>47</sub>H<sub>31</sub>N<sub>4</sub>NiP: C, 76.1; H, 4.2; N, 7.5. Found: C, 76.1; H, 4.2; N, 7.5%. IR  $\nu$ /cm<sup>-1</sup>:  $\nu$ (C≡N) 2223 (sh), 2122 (CH<sub>2</sub>Cl<sub>2</sub>);  $\nu$ (C≡N) 2223 (sh), 2113 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  6.22–7.92 [26H, C<sub>6</sub>H<sub>4</sub>, C<sub>10</sub>H<sub>7</sub>, PPh<sub>3</sub>], 5.37

[5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 201.8 [br], 182.0, 156.2, 144.2, 143.8, 122.4–134.9, 115.0, 114.8, 113.5, 112.9, 95.9, 76.5, 70.0. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 481 (20 600), 574 (sh, 10 000) in CH<sub>2</sub>Cl<sub>2</sub>; 475 (21 700), 574 (sh, 10 000) in CH<sub>3</sub>CN.

2.2.5. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>10</sub>H<sub>7</sub> (**4e**) (C<sub>10</sub>H<sub>7</sub> = 2-naphthyl)

Anal. Calc. for C<sub>47</sub>H<sub>31</sub>N<sub>4</sub>NiP: C, 76.1; H, 4.2; N, 7.5. Found: C, 76.1; H, 4.2; N, 7.5%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2223 (sh), 2122 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2223 (sh), 2113 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.27–8.50 [26H, m, C<sub>6</sub>H<sub>4</sub>, C<sub>10</sub>H<sub>7</sub>, PPh<sub>3</sub>] 5.41 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 183.1, 156.7, 144.1, 143.7, 121–135, 115.5, 115.4, 114.0, 113.9, 96.5, 77.3. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 478 (28 400), 571 (sh, 9400) in CH<sub>2</sub>Cl<sub>2</sub>; 472 (28 100), 570 (sh, 9300) in CH<sub>3</sub>CN.

2.2.6. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>14</sub>H<sub>9</sub> (**4f**) (C<sub>14</sub>H<sub>9</sub> = 9-phenanthryl)

Anal. Calc. for C<sub>51</sub>H<sub>33</sub>N<sub>4</sub>NiP: C, 77.4; H, 4.2; N, 7.1. Found: C, 77.4; H, 4.1; N, 7.0%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2122 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2113 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.24 [1H, dd, J = 9.5, 1.8 Hz, C<sub>6</sub>H<sub>4</sub>], 7.22 [1H, dd, J = 9.6, 1.8 Hz, C<sub>6</sub>H<sub>4</sub>], 7.04 [1H, dd, J = 9.8, 1.3 Hz, C<sub>6</sub>H<sub>4</sub>], 6.97 [1H, dd, J = 9.4, 2.1 Hz, C<sub>6</sub>H<sub>4</sub>], 7.0–8.9 [9H, m, C<sub>14</sub>H<sub>9</sub>], 6.6–7.0 [15H, m, PPh<sub>3</sub>], 5.39 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 202.1 [d, J = 23 Hz], 182.5, 155.0, 141.6, 141.1, 121–135, 115.5, 114.1, 113.5, 96.2, 70.3. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 475 (15 800), 576 (sh, 11 000) in CH<sub>2</sub>Cl<sub>2</sub>; 475 (15 700), 575 (sh, 11 100) in CH<sub>3</sub>CN.

2.2.7. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>14</sub>H<sub>9</sub> (**4g**) (C<sub>14</sub>H<sub>9</sub> = 9-anthryl)

Anal. Calc. for C<sub>51</sub>H<sub>33</sub>N<sub>4</sub>NiP: C, 77.4; H, 4.2; N, 7.1. Found: C, 77.3; H, 4.2; N, 7.1%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2223 (sh), 2122 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2223 (sh), 2113 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.1–9.0 [33H, C<sub>6</sub>H<sub>4</sub>, C<sub>14</sub>H<sub>9</sub>, PPh<sub>3</sub>] 5.36 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 181.7, 154.6, 140.9, 140.6, 122.4–134.3, 117.5, 117.2, 116.9, 96.1. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 484 (33 000), 578 (sh, 18 400) in CH<sub>2</sub>Cl<sub>2</sub>; 478 (29 000), 577 (sh, 18 400) in CH<sub>3</sub>CN.

2.2.8. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>16</sub>H<sub>9</sub> (**4h**) (C<sub>16</sub>H<sub>9</sub> = 3-pyrenyl)

Anal. Calc. for C<sub>53</sub>H<sub>33</sub>N<sub>4</sub>NiP: C, 78.1; H, 4.1; N, 6.9. Found: C, 78.0; H, 4.1; N, 6.9%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2122 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2113 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 6.97–7.98 [35H, m, C<sub>6</sub>H<sub>4</sub>, C<sub>16</sub>H<sub>9</sub>, PPh<sub>3</sub>] 5.40 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 183.5, 156.8, 144.4, 121.5–134.8, 115.6, 115.5, 114.2, 95.9 [s, C<sub>5</sub>H<sub>5</sub>]. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 475 (23 000), 576 (sh, 10 300) in CH<sub>2</sub>Cl<sub>2</sub>; 472 (22 500), 577 (sh, 10 200) in CH<sub>3</sub>CN.

2.2.9. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>20</sub>H<sub>11</sub> (**4i**) (C<sub>20</sub>H<sub>11</sub> = 3-perylenyl)

Anal. Calc. for C<sub>57</sub>H<sub>35</sub>N<sub>4</sub>NiP: C, 79.1; H, 4.1; N, 6.5. Found: C, 79.0; H, 4.0; N, 6.4%. IR ν/cm<sup>-1</sup>: ν(C≡N)

2222 (sh), 2122 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2223 (sh), 2113 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.34 [1H, dd, J = 9.4, 1.8 Hz, C<sub>6</sub>H<sub>4</sub>], 6.1–8.51 [28H, C<sub>6</sub>H<sub>4</sub>, C<sub>20</sub>H<sub>11</sub>, PPh<sub>3</sub>], 5.38 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 181.7, 153.6, 143.9, 122.3–134.9, 116.9, 115.8, 115.2, 96.1. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 470 (30 900), 578 (sh, 9500) in CH<sub>2</sub>Cl<sub>2</sub>; 460 (30 000), 578 (sh, 9400) in CH<sub>3</sub>CN.

2.2.10. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>4</sub>H<sub>3</sub>S (**4j**) (C<sub>4</sub>H<sub>3</sub>S = 2-thiophenyl)

Anal. Calc. for C<sub>41</sub>H<sub>27</sub>N<sub>4</sub>NiPS: C, 70.6; H, 3.9; N, 8.0. Found: C, 70.6; H, 3.8; N, 8.1%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2212 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2213 (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 5.81–8.43 [22H, m, C<sub>6</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>3</sub>S, PPh<sub>3</sub>], 5.35 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 180.6, 151.2, 141.6, 116.3–136.4 [m, C<sub>6</sub>H<sub>4</sub>, C<sub>4</sub>H<sub>3</sub>S, PPh<sub>3</sub>], 116.5, 116.2, 115.8, 95.9 [s, C<sub>5</sub>H<sub>5</sub>]. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 477 (23 400), 573 (sh, 18 400) in CH<sub>2</sub>Cl<sub>2</sub>; 475 (23 400), 573 (sh, 18 400) in CH<sub>3</sub>CN.

2.2.11. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–C<sub>5</sub>H<sub>4</sub>Fe(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>) (**4k**)

Anal. Calc. for C<sub>47</sub>H<sub>33</sub>FeN<sub>4</sub>NiP: C, 70.6; H, 4.1; N, 7.0. Found: C, 71.0; H, 4.1; N, 6.9%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2210 (CH<sub>2</sub>Cl<sub>2</sub>). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.24 [1H, d, J = 9.4 Hz, C<sub>6</sub>H<sub>4</sub>], 7.21 [1H, d, J = 9.6 Hz, C<sub>6</sub>H<sub>4</sub>], 7.03 [1H, d, J = 9.0 Hz, C<sub>6</sub>H<sub>4</sub>], 6.93 [1H, d, J = 9.1 Hz, C<sub>6</sub>H<sub>4</sub>], 7.3–7.8 [15H, m, PPh<sub>3</sub>], 5.21 [5H, s, C<sub>5</sub>H<sub>5</sub>(Ni)], 4.92 [5H, s, C<sub>5</sub>H<sub>5</sub>(Fe)], 4.7 and 5.2 [4H, both broad, C<sub>5</sub>H<sub>4</sub>(Fe)]. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 475 (25 500), 573 (sh, 18 400), 630 (10 000) in CH<sub>2</sub>Cl<sub>2</sub>.

2.2.12. Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–H (**4l**)

Anal. Calc. for C<sub>37</sub>H<sub>25</sub>N<sub>4</sub>NiP: C, 72.2; H, 4.1; N, 9.1. Found: C, 71.9; H, 4.2; N, 9.3%. IR ν/cm<sup>-1</sup>: ν(C≡N) 2224 (sh), 2211 (CH<sub>2</sub>Cl<sub>2</sub>); ν(C≡N) 2226 (sh), 2209, (KBr). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.78 [1, dd, J = 9.4, 1.8 Hz, C<sub>6</sub>H<sub>4</sub>], 7.2–7.77 [15H, m, PPh<sub>3</sub>], 7.07 [1H, s, CHC(CN)<sub>2</sub>], 7.06 [1, dd, J = 9.4, 1.8 Hz, C<sub>6</sub>H<sub>4</sub>], 6.79 [1, dd, J = 9.4, 1.3 Hz, C<sub>6</sub>H<sub>4</sub>], 6.58 [1, dd, J = 9.4, 1.3 Hz, C<sub>6</sub>H<sub>4</sub>], 5.34 [5H, s, C<sub>5</sub>H<sub>5</sub>]. <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 201.3 [C(5), d, J = 26 Hz], 161.3 [C(4)], 156.2 [C(9)], 143.0 [C(6)], 141.7 [C(11)], 129.6 [C(7)], 124.5 [C(10)], 120.1 [C(8)], 133.4 [d, J = 11 Hz, *o* Ph<sub>3</sub>P], 131.6 [s, *p* Ph<sub>3</sub>P], 130.1 [d, J = 49 Hz, *ipso* Ph<sub>3</sub>P], 128.9 [d, J = 10.8 Hz, *m* Ph<sub>3</sub>P], 114.8, 114.7, 114.4, 112.7, 94.9 [s, C<sub>5</sub>H<sub>5</sub>], 70.7, 69.6 [both s, C(3)/C(12)]. λ<sub>max</sub>/nm (ε/dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) 462 (28 000), 533 (sh, 17 000) in CH<sub>2</sub>Cl<sub>2</sub>; 462 (27 000), 525 (sh, 19 000) in CH<sub>3</sub>CN.

2.3. Reactions of Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C≡C–X–C≡CH with TCNQ

These were carried out as above using equimolar amounts of TCNQ (0.04 g, 0.19 mmol) and [Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C≡C–X–C≡CH] (0.19 mmol). Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)–C{≡C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}–C{≡C(CN)<sub>2</sub>}–X–

$C\equiv CH$  (**5a–d**) {X = (a) nothing, (b) 1,4- $C_6H_4$ , (c) 1,3- $C_6H_4$  and (d) 4,4'- $C_6H_4-C_6H_4$ }, were obtained in good yield. They did not react further with a large excess of TCNQ.

2.3.1.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C\equiv C-H$  (**5a**)

Anal. Calc. for  $C_{39}H_{25}NiN_4P$ : C, 73.2; H, 3.9; N, 8.8. Found: C, 73.1; H, 3.9; N, 8.6%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2096,  $\nu(C\equiv N)$  2212,  $\nu(CC-H)$  3300 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2095,  $\nu(C\equiv N)$  2213,  $\nu(CC-H)$  3300 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.89–7.81 [19H, m,  $C_6H_4$  and  $PPh_3$ ], 5.24 [5H, s,  $C_5H_5$ ], 1.70 [1H, s,  $CC-H$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 475 (27200), 571 (sh, 8000) in  $CH_2Cl_2$ ; 472 (30500), 570 (sh, 8100) in  $CH_3CN$ .

2.3.2.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(1,4-C_6H_4)-C\equiv C-H$  (**5b**)

Anal. Calc. for  $C_{45}H_{29}N_4NiP$ : C, 75.5; H, 4.1; N, 7.8. Found: C, 75.4; H, 4.0; N, 7.8%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2095,  $\nu(C\equiv N)$  2222 (sh), 2212,  $\nu(CC-H)$  3300 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2096,  $\nu(C\equiv N)$  2223 (sh), 2213,  $\nu(CC-H)$  3300 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  7.12–7.81 [23H, m,  $C_6H_4$ ,  $C_6H_4$  and  $PPh_3$ ], 5.23 [5H, s,  $C_5H_5$ ], 1.62 [1H, s,  $C\equiv C-H$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 470 (32400), 562 (sh, 9800) in  $CH_2Cl_2$ ; 471 (31700), 560 (sh, 10100) in  $CH_3CN$ .

2.3.3.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(1,3-C_6H_4)-C\equiv C-H$  (**5c**)

Anal. Calc. for  $C_{45}H_{29}N_4NiP$ : C, 75.5; H, 4.1; N, 7.8. Found: C, 75.6; H, 4.1; N, 7.9%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2096,  $\nu(C\equiv N)$  2222 (sh), 2212,  $\nu(CC-H)$  3300 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2223 (sh), 2095,  $\nu(C\equiv N)$  2213,  $\nu(CC-H)$  3300 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.8–8.8 [23H, m,  $C_6H_4$ ,  $C_6H_4$  and  $PPh_3$ ], 5.22 [5H, s,  $C_5H_5$ ], 1.61 [1H, s,  $CC-H$ ].  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  201.1 [br], 156.1, 144.2, 143.0, 120–135, 114.9, 114.8, 113.2, 112.9, 95.9, 82.3, 79.7, 77.3.  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 473 (18900), 560 (sh, 10000) in  $CH_2Cl_2$ ; 480 (17800), 562 (sh, 9000) in  $CH_3CN$ .

2.3.4.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(4,4'-C_6H_4-C_6H_4)-C\equiv C-H$  (**5d**)

Anal. Calc. for  $C_{51}H_{33}N_4NiP$ : C, 77.6; H, 4.2; N, 7.1. Found: C, 77.3; H, 4.2; N, 7.0%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2096,  $\nu(C\equiv N)$  2212,  $\nu(CC-H)$  3300 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2095,  $\nu(C\equiv N)$  2213,  $\nu(CC-H)$  3300 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.86–7.93 [27H, m,  $C_6H_4$ ,  $C_6H_4C_6H_4$ , and  $PPh_3$ ], 5.26 [5H, s,  $C_5H_5$ ], 1.53 [1H, s,  $C\equiv C-H$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 472 (29800) in  $CH_2Cl_2$ ; 470 (30300) in  $CH_3CN$ .

2.4. The reactions of  $Ni(\eta^5-C_5H_5)(PPh_3)-C\equiv C-X-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  with TCNQ

When these were carried out as above with equimolar amounts of TCNQ (0.04 g, 0.19 mmol) and  $Ni(\eta^5-$

$C_5H_5)(PPh_3)-C\equiv C-X-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (0.19 mmol),  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-X-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (**6a–d**), were obtained.

With a 2:1 molar ratio of TCNQ (0.02 g, 0.11 mmol) and  $Ni(\eta^5-C_5H_5)(PPh_3)-C\equiv C-X-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (0.055 mmol), the products were  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-X-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-Ni(\eta^5-C_5H_5)(PPh_3)$  (**7a–d**).

2.4.1.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (**6a**)

Anal. Calc. for  $C_{62}H_{44}N_4Ni_2P_2$ : C, 72.7; H, 4.3; N, 5.5. Found: C, 72.5; H, 4.3; N, 5.4%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2095,  $\nu(C\equiv N)$  2212 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2095,  $\nu(C\equiv N)$  2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.91–7.87 [34H, m,  $C_6H_4$ , and  $PPh_3$ ], 5.23 [5H, s,  $C_5H_5$ ], 5.22 [5H, s,  $C_5H_5$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 476 (32100) in  $CH_2Cl_2$ ; 473 (34900), in  $CH_3CN$ .

2.4.2.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(1,4-C_6H_4)-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (**6b**)

Anal. Calc. for  $C_{68}H_{48}N_4Ni_2P_2$ : C, 74.2; H, 4.4; N, 5.1. Found: C, 74.2; H, 4.3; N, 5.0%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2092,  $\nu(C\equiv N)$  2212 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2093,  $\nu(C\equiv N)$  2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.85–8.05 [38H, m,  $C_6H_4$ ,  $C_6H_4$  and  $PPh_3$ ], 5.26 [5H, s,  $C_5H_5$ ], 5.24 [5H, s,  $C_5H_5$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 472 (28200), 556 (sh, 9500) in  $CH_2Cl_2$ ; 472 (26500), 554 (sh, 9000) in  $CH_3CN$ .

2.4.3.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(1,3-C_6H_4)-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (**6c**)

Anal. Calc. for  $C_{68}H_{48}N_4Ni_2P_2$ : C, 74.2; H, 4.4; N, 5.1. Found: C, 74.2; H, 4.3; N, 5.0%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2094,  $\nu(C\equiv N)$  2222 (sh), 2212 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2094,  $\nu(C\equiv N)$  2223 (sh), 2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.64–7.85 [38H, m,  $C_6H_4$ ,  $C_6H_4$  and  $PPh_3$ ], 5.26 [5H, s,  $C_5H_5$ ], 5.25 [5H, s,  $C_5H_5$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 476 (45000), 563 (sh, 20000) in  $CH_2Cl_2$ ; 473 (45000), 557 (sh, 21000) in  $CH_3CN$ .

2.4.4.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(4,4'-C_6H_4-C_6H_4)-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  (**6d**)

Anal. Calc. for  $C_{74}H_{52}N_4Ni_2P_2$ : C, 75.5; H, 4.4; N, 4.7. Found: C, 75.6; H, 4.5; N, 4.7%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv C)$  2094,  $\nu(C\equiv N)$  2223 (sh), 2212 ( $CH_2Cl_2$ );  $\nu(C\equiv C)$  2094,  $\nu(C\equiv N)$  2223 (sh), 2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.92–8.13 [42H, m,  $C_6H_4$ ,  $C_6H_4C_6H_4$ , and  $PPh_3$ ], 5.24 [5H, s,  $C_5H_5$ ], 5.21 [5H, s,  $C_5H_5$ ].  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  155.6, 144.8, 142.3, 120–135, 115.0, 113.6, 95.9, 92.8.  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 474 (40200) 555 (sh, 17900) in  $CH_2Cl_2$ ; 471 (35900), 556 (sh, 16000) in  $CH_3CN$ .

2.4.5.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C\{=C(CN)_2\}-C\{=C_6H_4=C(CN)_2\}-Ni(\eta^5-C_5H_5)(PPh_3)$  (**7a**)

Anal. Calc. for  $C_{74}H_{48}N_8Ni_2P_2$ : C, 72.3; H, 3.9; N, 9.1. Found: C, 72.3; H, 3.9; N, 9.0%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv N)$  2222 (sh), 2212 ( $CH_2Cl_2$ );  $\nu(C\equiv N)$  2223 (sh), 2212 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.95–8.02 [38H, m,  $C_6H_4$ , and  $PPh_3$ ], 5.20 [10H, s,  $C_5H_5$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 472 (36,500) 551 (sh, 16900) in  $CH_2Cl_2$ ; 472 (34400), 550 (sh, 15100) in  $CH_3CN$ .

2.4.6.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(1,4-C_6H_4)-C\{=C(CN)_2\}-C\{=C_6H_4=C(CN)_2\}-Ni(\eta^5-C_5H_5)(PPh_3)$  (**7b**)

Anal. Calc. for  $C_{80}H_{52}N_8Ni_2P_2$ : C, 73.6; H, 4.0; N, 8.6. Found: C, 73.5; H, 4.1; N, 8.6%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv N)$  2222 (sh), 2212 ( $CH_2Cl_2$ );  $\nu(C\equiv N)$  2223 (sh), 2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.91–7.90 [42H, m,  $C_6H_4$ ,  $C_6H_4$ , and  $PPh_3$ ], 5.25 [10H, s,  $C_5H_5$ ].  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  140.6, 144.3, 162.1, 121–135, 115.4, 115.3, 114.0, 96.5.  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 475 (25200) 562 (sh, 11000) in  $CH_2Cl_2$ ; 478 (25900), 553 (sh, 10600) in  $CH_3CN$ .

2.4.7.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(1,3-C_6H_4)-C\{=C(CN)_2\}-C\{=C_6H_4=C(CN)_2\}-Ni(\eta^5-C_5H_5)(PPh_3)$  (**7c**)

Anal. Calc. for  $C_{80}H_{52}N_8Ni_2P_2$ : C, 73.6; H, 4.0; N, 8.6. Found: C, 73.7; H, 4.0; N, 8.5%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv N)$  2212

( $CH_2Cl_2$ );  $\nu(C\equiv N)$  2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.77–8.02 [42H, m,  $C_6H_4$ ,  $C_6H_4$ , and  $PPh_3$ ], 5.26 [10H, s,  $C_5H_5$ ].  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 473 (42200) 555 (sh, 19000) in  $CH_2Cl_2$ ; 473 (43000), 553 (sh, 19600) in  $CH_3CN$ .

2.4.8.  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-(4,4'-C_6H_4-C_6H_4)-C\{=C(CN)_2\}-C\{=C_6H_4=C(CN)_2\}-Ni(\eta^5-C_5H_5)(PPh_3)$  (**7d**)

Anal. Calc. for  $C_{86}H_{56}N_8Ni_2P_2$ : C, 74.8; H, 4.1; N, 8.1. Found: C, 74.8; H, 4.1; N, 8.1%. IR  $\nu/cm^{-1}$ :  $\nu(C\equiv N)$  2212 ( $CH_2Cl_2$ );  $\nu(C\equiv N)$  2213 (KBr).  $^1H$  NMR ( $CDCl_3$ ):  $\delta$  6.84–7.96 [46H, m,  $C_6H_4$ ,  $C_6H_4C_6H_4$ , and  $PPh_3$ ], 5.20 [10H, s,  $C_5H_5$ ].  $^{13}C$  NMR ( $CDCl_3$ ):  $\delta$  202.4 [d,  $J = 25$  Hz], 156.8, 144.9, 143.6, 121–134, 115.5, 115.4, 114.1, 114.0, 96.7, 69.95.  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) 477 (30400) 562 (sh, 12000) in  $CH_2Cl_2$ ; 474 (29800), 553 (sh, 13200) in  $CH_3CN$ .

2.5. Crystal structure determinations of  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C_6H_5$  (**4a**),  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C_6H_4-C_6H_5-4$  (**4b**) and  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-H.0.5(C_2H_5)_2O$  (**4l**)

Crystals of **4a** (black blocks), **4b** (black plates) and **4l** · 0.5( $C_2H_5$ )<sub>2</sub>O (purple plates) were grown from acetonitrile/ether. Data were collected for **4a** and **4l** at 88(2) K on a Bruker APEXII CCD diffractometer and for **4b** at

Table 1

Crystal data for  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C_6H_5$  (**4a**),  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-C_6H_4-C_6H_5-4$ , **4b**, and  $Ni(\eta^5-C_5H_5)(PPh_3)-C\{=C_6H_4=C(CN)_2\}-C\{=C(CN)_2\}-H \cdot 1/2(C_2H_5)_2O$ , **4l** · 1/2( $C_2H_5$ )<sub>2</sub>O

Compound	<b>4a</b>	<b>4b</b>	<b>4l</b> · 1/2( $C_2H_5$ ) <sub>2</sub> O
Chemical formula	$C_{43}H_{29}N_4NiP$	$C_{49}H_{33}N_4NiP$	$C_{39}H_{30}N_4O_{0.5}NiP$
Formula weight	691.38	767.47	652.35
$T$ (K)	90(2)	163(2)	90(2)
$\lambda$ (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$Pca2(1)$	$C2/c$
$a$ (Å)	10.3756(8)	26.263(9)	13.4239(3)
$b$ (Å)	10.1379(8)	11.347(4)	22.6219(6)
$c$ (Å)	32.667(2)	26.306(9)	21.9641(5)
$\alpha$ (°)	90	90	90
$\beta$ (°)	98.225(5)	90	95.641(1)
$\gamma$ (°)	90	90	90
$V$ (Å <sup>3</sup> )	3400.8(5)	7839(5)	6637.6(3)
$Z$	4	8	8
$D_{calc}$ ( $Mg m^{-3}$ )	1.350	1.301	1.306
$\mu$ ( $mm^{-1}$ )	0.655	0.576	0.668
Transmission factors ( $T_{min}$ , $T_{max}$ )	0.981, 0.711	0.960, 0.877	0.980, 0.902
Reflections collected	20995	96160	68746
Independent reflections [ $R_{int}$ ]	6670 [0.0866]	15876 [0.0697]	9342 [0.0531]
Observed reflections $I > 2\sigma(I)$	4667	11363	6760
$\theta_{max}$ (°)	26.26	26.43	31.02
Final $R$ indices <sup>a</sup> [ $I > 2\sigma(I)$ ]	$R_1 = 0.0800$ , $wR_2 = 0.2038$	$R_1 = 0.0339$ , $wR_2 = 0.0642$	$R_1 = 0.0412$ , $wR_2 = 0.1139$
$R$ indices (all data) <sup>a</sup>	$R_1 = 0.1113$ , $wR_2 = 0.2184$	$R_1 = 0.0594$ , $wR_2 = 0.0689$	$R_1 = 0.0642$ , $wR_2 = 0.1238$
Largest difference in peak and hole ( $e \text{ \AA}^{-3}$ )	2.300 and $-0.591$	0.703 and $-0.279$	1.061 and $-0.827$

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (0.0944P)^2 + 10.5457P]$  where  $P = (F_o^2 + 2F_c^2)/3$  for **4a**;  $w = 1/[\sigma^2(F_o^2) + (0.0327P)^2]$  where  $P = (F_o^2 + 2F_c^2)/3$  for **4b**;  $w = 1/[\sigma^2(F_o^2) + (0.0710P)^2 + 1.0322P]$  where  $P = (F_o^2 + 2F_c^2)/3$  for **4l** · 1/2( $C_2H_5$ )<sub>2</sub>O.

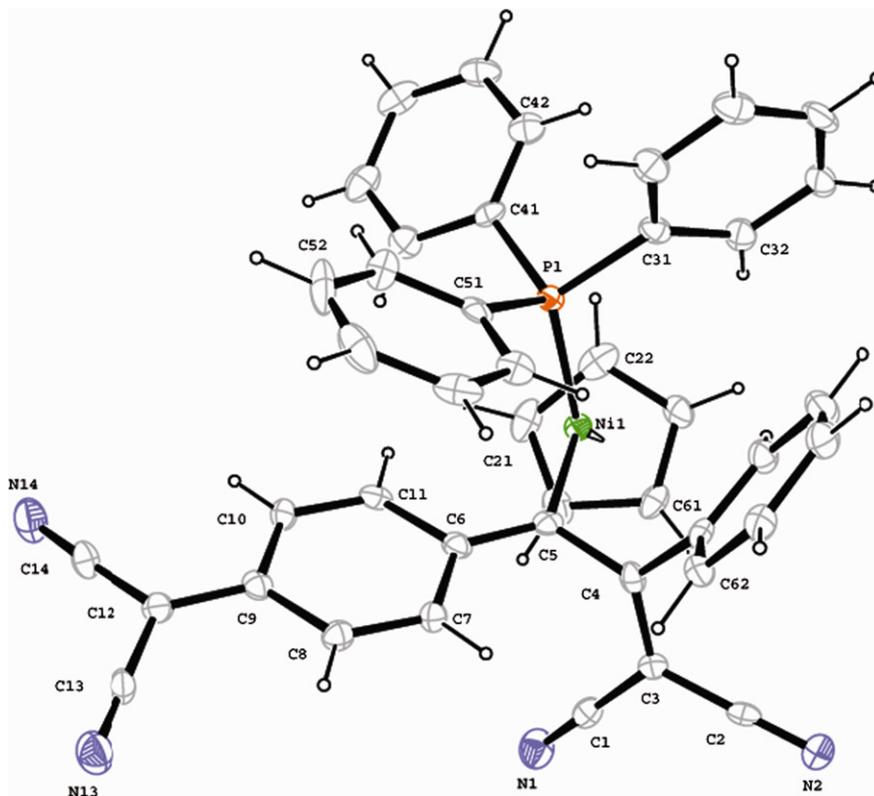


Fig. 1. The molecular structure and atom labelling of  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}(\text{=C}_6\text{H}_4\text{=C}(\text{CN})_2)\text{-C}(\text{=C}(\text{CN})_2)\text{-C}_6\text{H}_5$  (**4a**). For clarity, only two C atoms of the consecutively numbered cyclopentadienyl and phenyl rings are labelled.

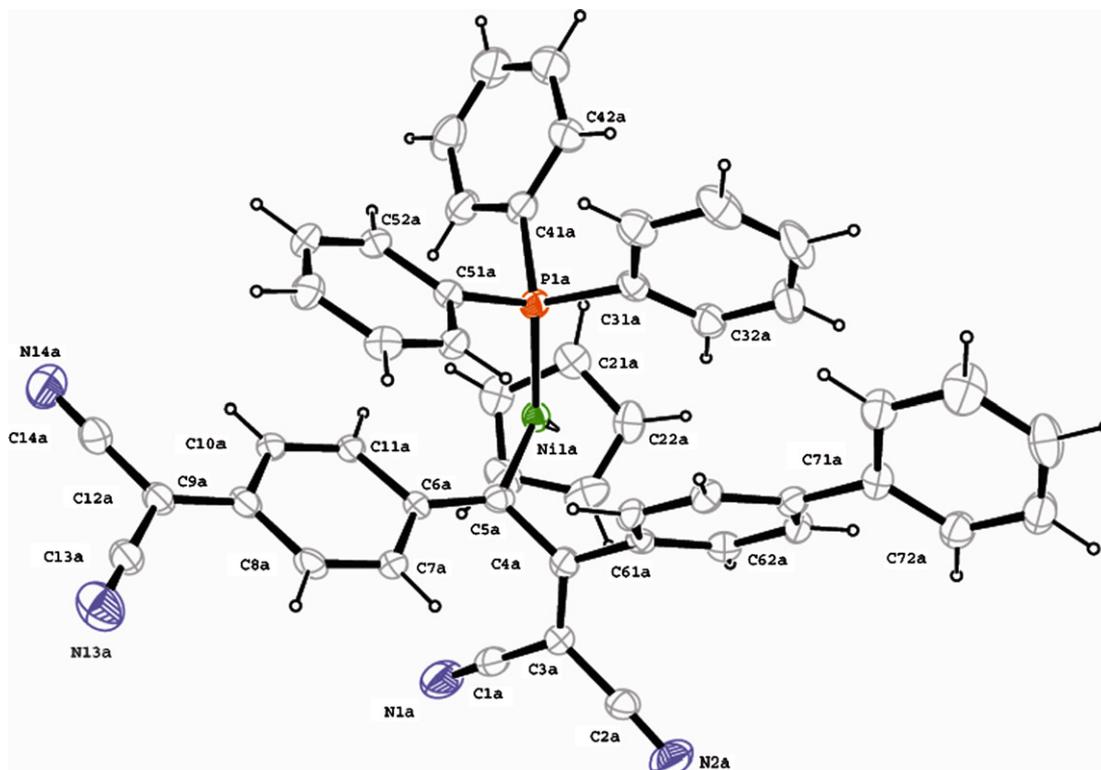


Fig. 2. The molecular structure and atom labelling of Molecule 1 of  $\text{Ni}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{-C}(\text{=C}_6\text{H}_4\text{=C}(\text{CN})_2)\text{-C}(\text{=C}(\text{CN})_2)\text{-C}_6\text{H}_4\text{-C}_6\text{H}_5\text{-4}$  (**4b**). For clarity, only two C atoms of the consecutively numbered cyclopentadienyl and phenyl rings are labelled.



Table 2

Selected bond lengths (Å) and bond angles (°) for Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub>}C{C(CN)<sub>2</sub>}C<sub>6</sub>H<sub>5</sub> (**4a**), Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)C{C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub>}C{C(CN)<sub>2</sub>}C<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>-4 (**4b**) (molecule A only; molecule B is very similar) and Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)C{C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub>}C{C(CN)<sub>2</sub>}H · 1/2(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O (**4l**) · 1/2(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O

	<b>4a</b>	<b>4b</b> (molecule A)	<b>4l</b> · 1/2(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> O
<i>Coordination about Ni</i>			
Ni(1)–P(1)	2.1818(15)	2.1960(10)	2.1536(5)
Ni(1)–C(5)	1.1912(5)	1.911(3)	1.8798(18)
Ni(1)–C(21)	2.135(6)	2.113(3)	2.142(2)
Ni(1)–C(22)	2.094(6)	2.194(3)	2.1019(19)
Ni(1)–C(23)	2.164(5)	2.137(4)	2.152(2)
Ni(1)–C(24)	2.136(5)	2.122(3)	2.080(2)
Ni(1)–C(25)	2.109(6)	2.151(3)	2.130(2)
C(21)–C(22)	1.403(9)	1.421(4)	1.442(3)
C(22)–C(23)	1.434(8)	1.388(5)	1.409(3)
C(23)–C(24)	1.388(8)	1.456(5)	1.397(3)
C(24)–C(25)	1.455(8)	1.472(4)	1.438(3)
C(21)–C(25)	1.395(9)	1.418(4)	1.376(3)
P(1)–Ni(1)–C(5)	100.29(16)	98.98(9)	97.66(6)
<i>C=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub> fragment</i>			
C(5)–C(6)	1.367(7)	1.391(4)	1.375(3)
C(6)–C(7)	1.449(7)	1.448(4)	1.447(3)
C(7)–C(8)	1.350(7)	1.357(4)	1.353(3)
C(8)–C(9)	1.435(7)	1.435(5)	1.430(3)
C(9)–C(10)	1.441(7)	1.446(5)	1.440(3)
C(10)–C(11)	1.349(8)	1.355(5)	1.349(3)
C(6)–C(11)	1.445(7)	1.457(4)	1.439(3)
C(9)–C(12)	1.392(7)	1.385(5)	1.386(3)
C(12)–C(13)	1.434(8)	1.427(5)	1.426(3)
C(12)–C(14)	1.429(8)	1.445(5)	1.424(3)
C(13)–N(13)	1.146(7)	1.161(5)	1.146(3)
C(14)–N(14)	1.161(7)	1.142(4)	1.153(3)
Ni(1)–C(5)–C(4)	113.5(4)	112.7(2)	105.13(13)
Ni(1)–C(5)–C(6)	120.6(5)	126.4(2)	130.46(14)
C(4)–C(5)–C(6)	121.0(5)	120.9(3)	124.16(17)
C(5)–C(6)–C(7)	124.3(5)	123.3(3)	122.34(17)
C(6)–C(7)–C(8)	122.5(5)	121.7(3)	121.84(18)
C(7)–C(8)–C(9)	121.4(5)	121.9(3)	121.07(18)
C(8)–C(9)–C(10)	117.1(5)	116.7(3)	117.79(17)
C(9)–C(10)–C(11)	121.1(5)	122.1(3)	120.88(17)
C(6)–C(11)–C(10)	122.8(5)	121.1(4)	122.19(17)
C(8)–C(9)–C(12)	122.4(5)	121.9(3)	120.94(17)
C(10)–C(9)–C(12)	120.4(5)	121.4(3)	121.27(18)
C(9)–C(12)–C(13)	123.2(5)	123.0(3)	120.95(13)
C(9)–C(12)–C(14)	120.0(5)	121.1(3)	122.06(18)
C(13)–C(12)–C(14)	116.7(5)	115.8(3)	116.99(18)
C(12)–C(13)–N(13)	178.9(6)	179.0(4)	179.3(3)
C(12)–C(14)–N(14)	177.1(6)	179.1(4)	179.6(3)
<i>C=C(CN)<sub>2</sub> fragment</i>			
C(3)–C(4)	1.361(8)	1.353(4)	1.363(3)
C(4)–C(5)	1.472(7)	1.478(4)	1.441(3)
C(4)–C(61)	1.497(7)	1.494(4)	
C(1)–C(3)	1.450(8)	1.444(5)	1.434(3)
C(2)–C(3)	1.442(8)	1.440(4)	1.438(3)
C(1)–N(1)	1.149(7)	1.142(4)	1.136(3)
C(2)–N(2)	1.152(7)	1.142(4)	1.144(3)
C(3)–C(4)–C(5)	122.6(5)	120.3(3)	124.55(17)
C(3)–C(4)–C(61)	119.1(5)	119.8(2)	
C(5)–C(4)–C(61)	118.4(5)	119.8(3)	
C(1)–C(3)–C(4)	121.4(5)	122.6(3)	120.79(17)
C(2)–C(3)–C(4)	121.0(5)	122.6(3)	122.46(18)
C(1)–C(3)–C(2)	117.6(5)	114.8(3)	116.73(16)
N(1)–C(1)–C(3)	179.0(6)	178.1(4)	179.3(2)
N(2)–C(2)–C(3)	179.4(6)	177.7(4)	176.9(2)

slowly. Consequently, although the reactions which form **3–7** appear to be close to quantitative, purification results in loss of product and the yields of the pure compound are lower but always >80%.

### 3.1. Structures of **4a**, **4b** (molecule A) and **4l**

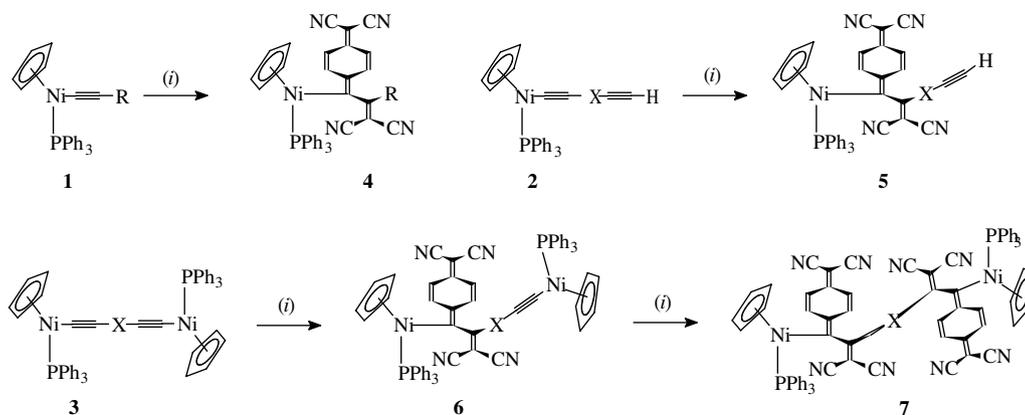
The spectroscopic data discussed below does not allow the molecular structures of **4–7** to be deduced unambiguously, although it does confirm that all have similar structures. Consequently the structures of three were determined by X-ray crystallography, **4a** (R = Ph), **4b** (R = 4-Ph-C<sub>6</sub>H<sub>4</sub>) and **4l** (R = H). The molecular structures and atom labelling of **4a**, **4b** and **4l** are illustrated in Figs. 1–3, respectively, whilst selected bond lengths and angles are summarised in Table 2. In the discussion that follows **4a** will be used as the generic example for the aryl derivatives as its structure is closely similar to that of **4b**. Complex **4b** crystallises with two unique molecules in the asymmetric unit, small differences between the two can be ascribed to crystal packing effects. The structure of **4l** is somewhat different and will be discussed separately.

The crystal structure of **4e** (R = 2-C<sub>10</sub>H<sub>7</sub>) was also determined, but is not reported because of disorder within the naphthyl group that it was not possible to model effectively. However, the principal molecular parameters for **4e** are very similar to those of **4a** and the two independent molecules of **4b**.

In **4a**, **4b** and **4l** the alkyne C≡C has inserted into a C=C bond linking one C(CN)<sub>2</sub> moiety to the quinonoid ring of TCNQ. There are two possible isomeric products from this reaction, but the only one observed has the C(CN)<sub>2</sub> residue attached to C<sub>2</sub> of Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C<sub>1</sub>≡C<sub>2</sub>-R and C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub> to C<sub>1</sub>, both by C=C bonds. The same isomer was obtained from the reaction of TCNQ with *trans*-Pt(PMe<sub>3</sub>)<sub>2</sub>(C≡C-Me)<sub>2</sub> [13,14].

In **4l** the coordination about Ni is similar to that found in many other [Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)X] derivatives with the P–Ni–C plane ca. perpendicular to the cyclopentadienyl plane, 89.0(7)°. It is a  $\beta$  isomer (cf. Ref. [24] and references therein) with the P(1)–Ni–C(5) plane oriented so that it is also approximately perpendicular to the  $\sigma_v$  plane of the (idealised) ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Ni moiety and an ene/enyl distortion of the cyclopentadienyl ligand, C(21)–C(25)/C(22)–C(23)–C(24), respectively. The C(5)–Ni–P angle at 97.66(6)° is at the high end of expectations and larger than that in **1l**, 90.29(15)° [24]. The Ni(1)–P(1) distance, 2.1536(5) Å, is comparable those in related [Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(L)R] complexes, 2.13–2.16 Å [24,34–37].

The Ni–C(5) bond length, 1.8798(18) Å, is greater than that in **1l**, 1.850(5) Å [24], a difference which may be due to the sp<sup>2</sup> hybridised C(5) in **4l** and the sp hybridised C(1) in **1l**. The C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}C{C(CN)<sub>2</sub>}–H ligand is unusual in that all carbon atoms except those of the cyano groups are formally sp<sup>2</sup> hybridised, but the whole ligand is not planar. The (NC)<sub>2</sub>C(9)=C<sub>6</sub>H<sub>4</sub>=C(5)–Ni(1) part of **4l** is effectively planar with angles of 1.94(4)° and



Scheme 1. (i) TCNQ/30 °C/CH<sub>2</sub>Cl<sub>2</sub>. X = nothing, 1,4-C<sub>6</sub>H<sub>4</sub>, 1,3-C<sub>6</sub>H<sub>4</sub> and 4,4'-C<sub>6</sub>H<sub>4</sub>-C<sub>6</sub>H<sub>4</sub>.

1.48(3)° between the (NC)<sub>2</sub>C, C<sub>6</sub>H<sub>4</sub> and Ni(1)C(5)C(4)C(6) planes within it. It lies at 85.10(3)° to the P–Ni(1)–C(5) plane of coordination about Ni, and at 70.68(4)° to the second important plane within the ligand which is defined by C(4)C(3)(CN)<sub>2</sub>. The *cis* diene system C(3)=C(4)–C(5)=C(6) is non-planar with a torsion angle of 68.2(3)°. The C–C bond lengths lie in the ranges 1.349(3)–1.386(3) Å for those which are formally double bonds, and 1.426(3)–1.447(3) Å for those which are formally single bonds, and those of the C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub> moiety are similar to those of TCNQ itself [38]. Although most C–C bond angles lie close to 120°, coordination about C(5) is severely distorted with Ni(1)–C(5)–C(4) = 105.13(13)°, Ni(1)–C(5)–C(6) = 130.46(14)° and C(4)–C(5)–C(6) = 124.16(17)° (sum = 359.75°). This appears to be due to an interaction between the Ni centre and C(4) as the Ni...C(4) separation is only 2.6502(18) Å, whereas the sum of their Van der Waal's radii is 3.4 Å. The nature of the substituents on C(4) suggests that this is a Ni → C(4) donor–acceptor interaction.

In **4a** the H of **4l** is replaced by a phenyl group. Although the structures of the two are closely related, there are differences which are largely associated with that part of the molecule derived from the [Ni(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)CCR] precursor. **4a** is an α<sub>b</sub> isomer where the P–Ni–C plane is oriented so that the P atom eclipses C(22) of the η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub> ligand which is distorted towards a diene, C(21)–C(25)–C(24)–C(23). Both the Ni–P distance, 2.1818(15) Å, and C(5)–Ni–P angle at 100.29(16)° are even larger than those in **4l**, but the Ni–C(5) bond length, 1.912(5) Å, is comparable within experimental error. The (NC)<sub>2</sub>C(9)=C<sub>6</sub>H<sub>4</sub>=C(5)–Ni(1) part of **4a** is no longer planar with an angle of 6.8(7)° and of 5.2(4)°, respectively, between the (NC)<sub>2</sub>C(9), the C<sub>6</sub>H<sub>4</sub> and Ni(1)C(5)C(4)C(6) planes. The Ni(1)C(5)C(6) plane is at an angle of 69.9° to the P(1)–Ni(1)–C(5) plane. The Ni(1)–C(5)–C(6) plane lies at 73.7(3)° to the second important plane within the ligand which is defined by C(4)C(3)(CN)<sub>2</sub>, and this last plane lies at an angle of 79.0(1)° to the phenyl ring defined by C(61)–C(66). A similar situation has been encountered in derivatives of 1,1-dicyanobuta-1,3-dienes such as (MeS)<sub>2</sub>C=

CH–C(C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>-4)=C(CN)<sub>2</sub> where the phenyl ring is twisted out of the plane of the C=C(CN)<sub>2</sub> system by steric effects [39]. The *cis* diene system C(3)=C(4)–C(5)=C(6) is non-planar with a torsion angle of 75.8(7)°. The C–C bond lengths lie in the ranges 1.350(7)–1.392(7) Å for those which are formally double bonds, and 1.429(8)–1.450(8) Å for those which are formally single bonds. However, the two single bonds to C(4) are somewhat longer with C(4)–C(5) = 1.472(7) Å and C(4)–C(61)(phenyl) = 1.497(7) Å. Again, this implies reduced or absent conjugation across these bonds. The dimensions of the C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub> moiety are also similar to those of TCNQ itself [38]. The C–C–C bond angles lie between 112.7° and 126.4°, with particular distortion about C(5). C(4)–C(5)–C(6) is 121.0(5)°, but Ni(1)–C(5)–C(6) is 125.5(4)° and Ni(1)–C(5)–C(4) is 113.5(4)° (sum = 360°). This appears to be due to an interaction between Ni(1) and C(4), separation = 2.840(5) Å, which is similar to, but weaker than, that observed for **4l**.

It seems reasonable to suggest that the steric effects of the phenyl (or biphenyl) group are responsible for the structural differences between **4a** (or **4b**) and **4l**.

### 3.2. Spectra

The IR spectra of **4–7** are similar in that they all show a single strong absorption band at 2212 cm<sup>-1</sup> which often has a weaker shoulder at 2223 cm<sup>-1</sup>. These are assigned to the ν(CN) vibrations of the complexes; the shoulder occurs at the same frequency as the ν(CN) vibration of TCNQ itself. The spectra of **5** and **6** also show a band at ca. 2095 cm<sup>-1</sup> due to the ν(C≡C) mode of the unreacted C≡C, and for **5** there is another band at 3300 cm<sup>-1</sup> characteristic of a ν(H–CC) vibration.

With the exception of **4k**, the <sup>1</sup>H NMR spectra of all **4** show a singlet signal at δ 5.33–5.41 due to their (η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)Ni protons, but those due to the Ph<sub>3</sub>P, C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub> and aryl groups of **4a–4k** often overlap to such an extent that their unambiguous identification and assignment was usually not possible. However, when R = H, **4l**, the aryl group resonances are absent; the Ph<sub>3</sub>P ligand gives rise to

a complex multiplet between  $\delta$  7.2–7.6, the unique H to a singlet at  $\delta$  7.07, and the  $C_6H_4$  protons to four separate resonances. Those at  $\delta$  6.58 and 6.79 couple as do those at  $\delta$  7.06 and 7.78 ( $J = 9.5$  Hz). A further weak coupling is detectable with  $J = 1.3$  Hz to the  $\delta$  6.58/6.79 pair and  $J = 1.8$  Hz to the  $\delta$  7.06/7.78 pair. In **4k** with its ferrocenyl end group, the obscuring aryl group resonances are also absent and here the  $C_6H_4$  give rise to doublet resonances at  $\delta$  ( $J$  in Hz) 6.93 (9.1), 7.03(9.0), 7.12 (9.7) and 8.18 (9.4). These are somewhat more deshielded than those of **4l**, but are comparable to those of the phenanthryl derivative **4f** ( $\delta$  6.97, 7.04, 7.22, 8.24) and of other compounds where only some of these resonances could be identified.

The absence of the aryl group in **4l** also allows its  $^{13}C$  NMR spectrum to be assigned with confidence. The ( $\eta$ - $C_5H_5$ ) group gives rise to a singlet at  $\delta$  94.9, and the  $Ph_3P$  ligand to three strong signals. These comprise a singlet at  $\delta$  131.6 and two doublets at  $\delta$  128.9 ( $J = 10.8$  Hz) and 133.4 ( $J = 11$  Hz) plus a weaker doublet at  $\delta$  130.1 ( $J = 49$  Hz) which are due to *p*, *m*, *o* and *ipso* carbon atoms, respectively. The four cyano groups are responsible for the four signals at  $\delta$  112.7, 114.4, 114.7 and 114.8; comparable chemical shifts are found for other derivatives containing the  $=C(CN)_2$  group. A combination of NOESY, HSQC and gHMBC techniques allow the following  $^{13}C$  ( $^1H$ ) assignments C(3)  $\delta$  69.6 (–), C(4)  $\delta$  161.3 (7.07), C(5)  $\delta$  201.3 (–), C(6)  $\delta$  143.0 (–), C(7)  $\delta$  129.6 (6.56), C(8)  $\delta$  120.1 (6.78), C(9)  $\delta$  156.2 (–), C(10)  $\delta$  124.5 (7.04), C(11)  $\delta$  141.7 (7.77), C(12)  $\delta$  70.7 (–). The highly deshielded resonance due to C(5), is a very weak doublet with  $J = 26$  Hz, presumably due to coupling with  $^{31}P$ . It is also detectable through its correlation with H(4) in the gHMBC spectrum. In TCNQ itself, the observed resonances are  $\delta$  150.8 { $C=C(CN)_2$ }, 131.3 (C–H), 111.6 (CN) and 89.8 { $C=C(CN)_2$ } [40] whilst for 1,1-dicyanobuta-1,3-dienes of the general type  $MeS(D)C=C(H)-C^b(C_6H_4X)=C^a(CN)_2$  where  $D = MeS$  or  $Me_2N$  the chemical shifts  $\delta$  for  $CN = 113.3$ – $117.6$ ,  $C^a = 62.7$ – $78.6$ ,  $C^b = 163.9$ – $169.8$  [39], and for various  $M-C^3\{=C^4(CN)_2\}-\{C^2(Ph)=C^1(CN)_2\}$  derivatives where  $M = W(\eta^5-C_5H_5)(CO)_3$ ,  $Ru(\eta^5-C_5H_5)(DPPE)$  or  $Ru(\eta^5-C_5H_5)(CNBu^t)_2$  the chemical shifts  $\delta$  for resonances due to  $C^1 = 69.3$ – $77.4$ ,  $C^2 = 179.7$ – $182.8$ ,  $C^3 = 215.1$ – $226.2$  and  $C^4 = 90.8$ – $99.8$  [5].

In general, the  $^{13}C$  NMR spectra of **4** usually show fewer signals than would be expected, perhaps due to the poor solubility of some compounds and the long relaxation times of some of the tertiary carbon atoms. Furthermore, the presence of  $Ph_3P$ ,  $C_6H_4C(CN)_2$  and aryl groups can make it difficult to assign the observed resonances. Even for the simplest aryl group,  $C_6H_5$ , some of its  $^{13}C$  resonances lie very close to or coincide with those due to the  $Ph_3P$  ligand. However, the most obvious difference between the  $^{13}C$  NMR spectra of **4l** and the other **4** is the chemical shift of the  $Ni-C(4)=C(CN)_2$  resonance which has  $\delta$  161.3 for **4l** but  $\delta$  181–184 in other **4**. These chemical shifts should be compared with those for  $C^2$  in the

$M-C^3\{=C^4(CN)_2\}\{C^2(Ph)=C^1(CN)_2\}$  derivatives above,  $\delta$  179.7–182.8. The signals due to C(4) and C(5), now both quaternary, are very weak and not always observed. In favourable instances that at  $\delta$  ca. 200 due to C(5) can be resolved into doublet,  $J = 26$  Hz, as a consequence of  $C-^{31}P$  coupling, otherwise both are rather broad.

The NMR spectra of the di-nickel complexes **5**–**7** follow the same general pattern as those of **4**, but with predictable differences, and the often greater constraints due to solubility problems means that few are completely satisfactory  $^{13}C$  NMR spectra were obtained. **5** show resonances at ca.  $\delta$  1.53–1.70 ( $^1H$  NMR) and  $\delta$  ca. 80 ( $^{13}C$  NMR) characteristic of the  $H-C\equiv C$  group. For **6**, the two different  $Ni(\eta^5-C_5H_5)(PPh_3)$  moieties each give rise to a  $C_5H_5$  resonance, and the  $Ni-C_1\equiv C_2$  moieties gives rise to a doublet at ca.  $\delta$  83.5–88.6 ( $J = 48.1$  Hz) and a singlet at  $\delta$  100.4–118.4 due to  $C_1$  and  $C_2$ , respectively, (cf.  $\delta$  86.2 with  $J = 48$  Hz and 119.6 for **1a**). Unfortunately, in no case could the intrinsically weak signals at ca.  $\delta$  ca. 180 and  $\delta$  ca. 200 be detected.

The electronic spectra of all **4**–**7** show a broad intense absorption band at ca. 470–480 nm with a shoulder at ca. 580 nm. This suggests that all **4**–**7** contain similar or identical chromophores. There are additional absorption bands in the spectra of **4g** (394 nm), **4i** (455 nm) and **4k** (630 nm) which are probably due to low energy transitions that are essentially localised within the anthryl, perylenyl and ferrocenyl end-groups respectively. Such transitions are found at ca. 375 and 355 nm in anthracene, and ca. 434, 406 and 387 nm in perylene [41].

There are two potential Donor– $\pi$ –Acceptor moieties within the molecules of **4**–**7**,  $D-C(Y)=C(CN)_2$  and  $Ni-C(R')=C_6H_4=C(CN)_2$  where the acceptors are both  $C(CN)_2$  and the donors D or Ni;  $D = R, H, X-C\equiv CH, X-C\equiv C-Ni(\eta^5-C_5H_5)(PPh_3)$  or  $X-C\{=C(CN)_2\}-C\{=C_6H_4=C(CN)_2\}-Ni(\eta^5-C_5H_5)(PPh_3)$ . The first of these is unlikely to be the effective chromophore as the spectra are independent of D even when it is the powerful donor 4- $Me_2NC_6H_4$ . Furthermore, in the solid state at least for **4a** and **4b** the phenyl plane lies at ca. 58–80° to the plane of the  $RC=C(CN)_2$  chromophore which hinders the necessary conjugation between aryl donor and CN acceptor and results in a long C(4)–C(61) bond. Further evidence is provided by the spectrum of the ferrocenyl derivative **4k** which confirms that it does not contain a functioning  $Fc-C=C(CN)_2$  chromophore {for  $Fc-CH=C(CN)_2$ ,  $\lambda_{max}$  326 nm ( $\epsilon = 14000 M^{-1} cm^{-1}$ ), 534 nm ( $\epsilon = 2400 M^{-1} cm^{-1}$ )} [16]. Consequently the spectroscopic evidence suggests that  $Ni-C(R')=C_6H_4=C(CN)_2$  is the effective chromophore in **4**–**7**. This is supported by the crystallographic evidence which shows that in **4l** it is planar and in **4a** and **4b** it is close to planar, which allows effective  $\pi$ -communication between the electron-rich Ni donor and the cyano acceptors. This chromophore maybe described by a mixture of resonance forms, Fig. 4. Bond lengths suggest that in the ground state *A* predominates, but others are possible in which there is charge separation and of partic-

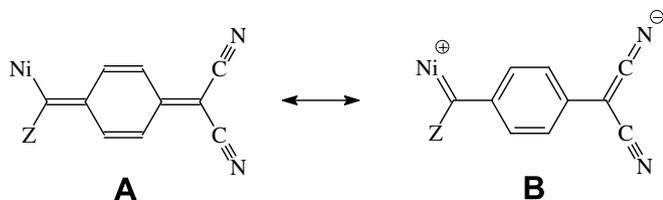


Fig. 4. Resonance forms of the Ni-C(Z)=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub> chromophore in 4–7.

ular importance will be those in which the C<sub>6</sub> ring is aromatic, e.g. **B**, Fig. 4. These charge-separated mesomers probably make a larger contribution to the excited states of the system than they do to the ground state.

### 3.3. Electrochemistry

The electrochemistries of **1** have been reported previously. **1a** and **1l** undergo a quasi-reversible oxidation with  $E_p = 0.81$  V and 0.83 V, respectively. For the TCNQ adducts, **4l** shows an irreversible oxidation,  $E_p = \text{ca. } 1$  V, and two reversible reductions at  $-0.26$  and  $-0.47$  V [vs. Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>] (Fig. 5). TCNQ itself shows two reversible reductions at 0.21 and  $-0.33$  V (vs. SCE) [42]. In contrast **4a**, chosen as typical of other **4**, shows a quasi reversible oxidation at ca. 1 V, which is characteristic of compounds containing the Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>) moiety, plus complicated reduction processes. Elucidation of such processes for **4a** and the apparently anomalous behaviour of **4l** are the subject of further investigation.

### 3.4. Reaction pathway

The reactions of **1–3** with TCNQ are fast with no evidence for the formation of intermediates such as the green paramagnetic compound or the cyclobutenyl derivative observed during the reaction of TCNE with W( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>-C≡C-Ph [5].

TCNQ inserts exclusively into the Ni-substituted C≡C of **2** rather than the C≡CH. The spectroscopic evidence

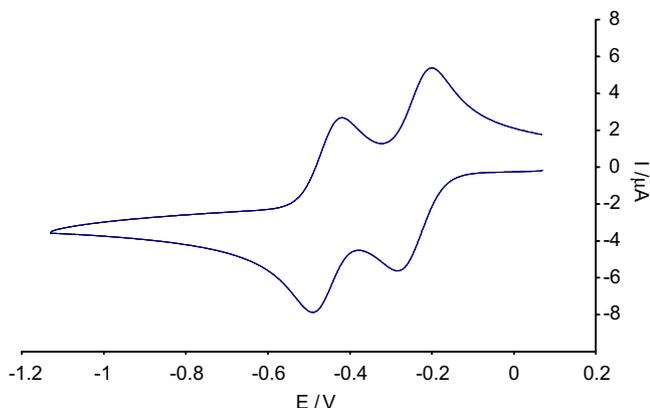


Fig. 5. Cyclic voltammogram of **4l** (Pt/acetone/0.1 M TEAP/ vs. [Fe( $\eta^5$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>]<sup>+/0</sup>, 0.0 V).

for this is unambiguous. The IR spectra of **5** all show an absorption band at ca. 3300 cm<sup>-1</sup> due the  $\nu(\text{H-CC})$  vibration, their <sup>1</sup>H NMR spectra show a H-C≡C resonance at ca.  $\delta$  1.6, and their <sup>13</sup>C NMR spectra (when obtainable) show singlet HC≡C resonances at ca.  $\delta$  80, respectively, rather than the doublet at ca.  $\delta$  87 and singlet at ca.  $\delta$  100–120 which would be expected for a Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C≡C moiety. This behaviour contrasts with that of W( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>-C≡C-C≡C-Fc (Fc = ferrocenyl) which reacts with TCNE to form W( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>3</sub>-C≡C-C(=C(CN)<sub>2</sub>)-C(=C(CN)<sub>2</sub>)-Fc i.e. the metal-attached C≡C is **not** the one which is attacked [11]. There is no reaction between TCNQ and Fc-C≡CH.

## 4. Conclusions

C≡C triple bonds in **1**, **2** and **3** (two) which are directly bonded to Ni are able to insert into one of the C=C(CN)<sub>2</sub> double bonds of 7,7,8,8-tetracyanoquinodimethane, TCNQ, to give complexes **4**, **5**, **6** and **7** containing the Ni-C{=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub>}-C{=C(CN)<sub>2</sub>}-X group (two such groups in **7**). However, no such reaction takes place between TCNQ and the C≡CH moieties of **2**, even though they are conjugated with Ni, or between TCNQ and normal alkynes such as PhC≡CH, PhC≡CPh, 1,4-C<sub>6</sub>H<sub>4</sub>(C≡CH)<sub>2</sub> and ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)Fe( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>C≡CH), (FcC≡CH). This contrasts with the reactions of C<sub>2</sub>(CN)<sub>4</sub>, TCNE, which with FcC≡CH, FcC≡CFc and one of the triple bonds of FcC≡C-C≡CFc to give tetracyanobutadiene derivatives [41]. Clearly, TCNQ is a less reactive electrophile than TCNE. Furthermore, only one of the two C=C(CN)<sub>2</sub> bonds of TCNQ reacts with **1–3** even when they are in excess.

Ni( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)-C{C<sub>6</sub>H<sub>4</sub>C(CN)<sub>2</sub>}-C{C(CN)<sub>2</sub>}-D complexes contain two potential chromophores, Ni-C=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub> and D-C=C(CN)<sub>2</sub>, but as all **4**, **5**, **6** and **7** have almost identical visible spectra which are different from those of known D-C=C(CN)<sub>2</sub> derivatives, only the first is effective. This is consistent with the molecular structures of **4a**, **4b** and **4l** which show the Ni(C<sub>β</sub>)=C<sub>6</sub>H<sub>4</sub>=C(CN)<sub>2</sub> moieties to be planar or close to it whilst the aryl groups are far from coplanar with the C=C(CN)<sub>2</sub> fragment. The X-ray diffraction studies also show that there is a significant Ni → C<sub>β</sub>=C(CN)<sub>2</sub> interaction which is greater for R = H than for R = Ph or 4-biphenyl.

## Acknowledgements

P.B. thanks Enterprise Ireland and Schering-Plough (Avondale) for financial support. We also thank the New Zealand Foundation for Research Science and Technology for a Postdoctoral Fellowship to C.J.M. and the Chemistry Department, University of Otago for financial assistance.

## Appendix A. Supplementary material

CCDC 660589, 660590 and 660591 contain the supplementary crystallographic data for **4a**, **4b** and **4l**. These data

can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.029](https://doi.org/10.1016/j.jorganchem.2007.11.029).

## References

- [1] A. Davidson, J. P. Solar, *J. Organomet. Chem.* 166 (1979) C13.
- [2] M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, *J. Chem. Soc., Chem. Commun.* (1981) 271.
- [3] P. Hong, K. Sonogashira, N. Hagihara, *J. Organomet. Chem.* 219 (1981) 363.
- [4] M.I. Bruce, T.W. Hambley, J.R. Rodgers, M.R. Snow, A.G. Swincer, *J. Organomet. Chem.* 226 (1982) C1.
- [5] M.I. Bruce, T.W. Hambley, M.R. Snow, A.G. Swincer, *Organometallics* 4 (1985) 501.
- [6] Y. Yamamoto, R. Satoh, T. Tanase, *J. Chem. Soc., Dalton Trans.* (1995) 307.
- [7] K. Onitsuka, S. Takahashi, *J. Chem. Soc., Chem. Commun.* (1995) 2095.
- [8] M.I. Bruce, M. Ke, P.J. Low, B.W. Skelton, A.H. White, *Organometallics* 17 (1998) 3539.
- [9] K. Onitsuka, N. Ose, E. Ozawa, S. Takahashi, *J. Organomet. Chem.* 578 (1999) 169.
- [10] M.I. Bruce, B.C. Hall, P.J. Low, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 59 (2001) 74.
- [11] M.I. Bruce, M.E. Smith, B.W. Skelton, A.H. White, *J. Organomet. Chem.* 637–639 (2001) 484.
- [12] Chao-Wan Chang, Ying-Chih Lin, Gene-Hsiang Lee, Yu Wang, *J. Chem. Soc., Dalton Trans.* (1999) 4223.
- [13] M. Masai, K. Sonogashira, N. Hagihara, *J. Organomet. Chem.* 34 (1972) 397.
- [14] K. Onuma, Y. Kai, N. Yasuoka, N. Kasai, *Bull. Chem. Soc. Jpn.* 48 (1975) 1696.
- [15] J.D. McKinney, P.A. Anderson, T.A. Hamor, C.J. Jones, A. Porch, *J. Organomet. Chem.* 558 (1998) 147.
- [16] J.F. Gallagher, R.D.A. Hudson, A.R. Manning, J. Simpson, Unpublished work.
- [17] K.W. Barnett, *J. Chem. Ed.* 519 (1974) 422.
- [18] S. Myano, I. Izumi, H. Hashimoto, *J. Chem. Soc., Dalton Trans.* (1995) 307.
- [19] M. Matsumoto, K. Kuroda, *Tetrahedron Lett.* 21 (1980) 4021.
- [20] L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 1988.
- [21] A.S. Hay, *J. Org. Chem.* 25 (1960) 637.
- [22] K. Sonogashira, Y. Yatake, Y. Tohoda, S. Takahashi, N. Hagihara, *J. Chem. Soc., Dalton Trans.* (1977) 291.
- [23] I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G.A. Heath, D. Bogsányi, *Organometallics* 16 (1997) 2631.
- [24] J.F. Gallagher, P. Butler, R.D.A. Hudson, A.R. Manning, *J. Chem. Soc., Dalton Trans.* (2002) 75; P. Butler, J.F. Gallagher, A.R. Manning, H. Mueller-Bunz, C.J. McAdam, J. Simpson, B.H. Robinson, *J. Organomet. Chem.* 690 (2005) 4545.
- [25] SMART: Area Detector Control; Bruker AXS, Madison, WI, USA, 1994.
- [26] APEXII V1.017, Diffractometer Control Software. Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
- [27] SAINT: Area detector integration software; Bruker AXS, Madison, WI, USA, 1994 and 2004.
- [28] SADABS (Absorption Correction for Area Detector Data); Bruker AXS, Madison WI, USA, 1997 and 2004.
- [29] G.M. Sheldrick, *SHELXS-97. A Program for the Solution of Crystal Structures from Diffraction Data*, University of Göttingen, Federal Republic of Germany, 1990.
- [30] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 26 (1993) 343–350.
- [31] G.M. Sheldrick, *SHELXL-97 A Program for the Refinement of Crystal Structures*, University of Göttingen, Federal Republic of Germany, 1997.
- [32] K.A. Hunter, J. Simpson, *TITAN2000 A molecular graphics program to aid structure solution and refinement with the SHELX suite of programs*, University of Otago, New Zealand, 1999.
- [33] H.D. Flack, *Acta Crystallogr. Sect. B39* (1983) 876.
- [34] R.H. Naulty, M.P. Cifuentes, M.G. Humphrey, S. Houbrechts, C. Boutton, A. Persoons, G.A. Heath, D.C.R. Hockless, B. Luther-Davies, M. Samoc, *J. Chem. Soc., Dalton Trans.* (1997) 4167.
- [35] I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, *Aust. J. Chem.* 51 (1998) 219.
- [36] P. Butler, J.F. Gallagher, A.R. Manning, *Inorg. Chem. Commun.* 1 (1998) 343.
- [37] J.F. Gallagher, P. Butler, A.R. Manning, *Acta Crystallogr. C54* (1998) 342.
- [38] R.E. Long, R.A. Sparks, K.N. Trueblood, *Acta Crystallogr.* 18 (1965) 876.
- [39] T. Freier, M. Michalik, K. Peseke, H. Reinke, *J. Chem. Soc., Perkin Trans. 2* (1999) 1265.
- [40] C.J. McAdam, Unpublished work.
- [41] E. Clar, *Polycyclic Hydrocarbons*, Academic Press, London, 1964.
- [42] T. Mochida, S. Yamazaki, *J. Chem. Soc., Dalton Trans.* (2002) 3559.