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Synthesis, characterisation and some reactions of alkynyl derivatives [Ni(η^5-C_5H_5)(PPh_3)C≡CX]

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Oxalic acid catalyses the hydrolysis of the Ni(II) acetylide [Ni(η^5-C_5H_5)(PPh_3)C≡CCH($OEt)_2$] **1**, to the alkynylaldehyde [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2**, in high yield. Condensation reactions of **2** with phenylhydrazine and dinitrophenylhydrazine in the presence of acetic acid, and with malononitrile and 3-phenyl-5-isoxazolone ($C_9H_7NO_2$) in the presence of triethylamine yield [Ni(η^5-C_5H_5)(PPh_3)C≡CX] derivatives where X = CH=NNHC$_6$H$_5$ **3**, CH=NNH-C$_6$H$_3$(NO$_2$)$_2$-2,4 **4**, CH=C(CN)$_2$ **5**, and CH=C$_9$H$_5$NO$_2$ **6**. The reactivity of [Ni(η^5-C_5H_5)(PPh_3)C≡CX] complexes towards [Co$_2$(CO)$_8$] is a function of X. Thus **1** and **2**, where X = CH(OEt)$_2$ or CHO, react readily to give the bridging alkyne derivatives [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCH(OEt)$_2$}{Co$_2$(CO)$_6$}] **7**, and [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)-C≡CCHO}{Co$_2$(CO)$_6$}] **8**, but **5**, where X is the strongly electron-withdrawing CH=C(CN)$_2$ group, does not react even after 24 h at room temperature. Furthermore, coordination of the alkyne to a Co$_2$(CO)$_6$ fragment appears to inhibit the normal reactions of the group X in **7** and **8**. Thus the acetal grouping in **7** does not undergo oxalic acid-catalysed hydrolysis to an aldehyde in **8**, and the aldehyde function in **8** does not undergo a Knoevenagel condensation with CH$_2$(CN)$_2$. The IR spectra of **1**, and **3**–**6** show a single ν(C≡C) band the frequency of which decreases along the series X = CH(OEt)$_2$ > CH=NNHC$_6$H$_5$ > CH=NNHC$_6$H$_3$(NO$_2$)$_2$-2,4 > CH=C(CN)$_2$ ≈ CH=C$_9$H$_5$NO$_2$; that of **2** is anomalous in that it can show two ν(C≡C) bands. The UV-visible spectra of **1**–**6** show a strong charge transfer absorption band which increases in wavelength **1** < **3** < **2** < **4** < **5** < **6**. These spectroscopic data and the ^{13}C chemical shifts suggest that the (η^5-C_5H_5)(Ph$_3$P)Ni moiety is a donor and, when X is an acceptor, charge separated cumulenic mesomers such as Ni$^+$=C=C=X$^-$ contribute to the description of the bonding in **1**–**6**. This is not reflected in the molecular dimensions of **1**, **2** and **5** as determined by X-ray diffraction. However, the crystal structure of [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCHO}{Co$_2$(CO)$_6$}], **8**, shows that the C$_2$Co$_2$ cluster core is severely distorted because of the strong donor (Ni) and acceptor (CHO) substituents on the acetylenic carbon atoms.

Introduction

Transition-metal σ-acetylide complexes have attracted considerable interest as precursors in the expanding field of organometallic derivatives that contain π-conjugated systems. These have potential applications in nonlinear optics,[1] liquid crystal technology, dendrimer science and nanostructured materials for molecular devices.[2,3] Attention has focused on the acetylide group because of its accessibility and the ease with which it can be incorporated into organometallic complexes and multimetallic assemblies, and because C≡C can provide a facile pathway for electron delocalization between interacting metal centres.[3–5] In this context, nickel cyclopentadienyl alkynyl derivatives having the general formulae [Ni(η^5-C_5H_5)(PR$_3$)C≡CR][6,7] are of current interest in donor–π-acceptor systems.[5,8–10]

Here, we report studies into the synthesis, structures, and spectra of a series of [Ni(η^5-C_5H_5)(PPh_3)C≡CX] complexes which were obtained from the alkynylaldehyde [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] by condensation reactions with hydrazines and some active methylene compounds (Scheme 1). We have found that some, but not all of these alkynes, form [(μ-alkyne){Co$_2$(CO)$_6$}] complexes, and that the presence of the Co$_2$(CO)$_6$ moiety appears to affect some of the characteristic reactions of the group X. The structures of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2**, [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=C(CN)$_2$] **5**, and [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCHO}{Co$_2$(CO)$_6$}] **8**, have been determined by single crystal X-ray diffraction and compared with those of related compounds.[8–12]

Experimental

[Ni(η^5-C_5H_5)(PPh_3)Br] was prepared according to literature methods.[13] Other chemicals were purchased from the usual sources.

All reactions were carried out under N$_2$ in dried and deoxygenated solvents unless stated otherwise. They were monitored by IR or NMR spectroscopy where appropriate.

IR spectra were recorded on a Perkin-Elmer 1710 FT spectrometer (peak positions are in cm^{-1} with relative peak heights in parentheses) and UV-visible spectra were recorded on a UNICAM UV2 spectrometer (band positions are in nm with intensities ε in dm^3 mol^{-1} cm^{-1}). NMR spectra were obtained in CDCl$_3$ solution on a Jeol JNM-GX270 FT-NMR spectrometer. ^{1}H (270 MHz) and ^{13}C (67.8 MHz) chemical shifts are reported downfield from tetramethylsilane as internal standard; ^{31}P (109.3 MHz) spectra are referenced to 85% phosphoric acid with downfield shifts reported as positive. Analyses were carried out in the Microanalytical Laboratory, University College Dublin.

Preparation of [Ni(η^5-C_5H_5)(PPh_3)C≡CCH(OEt)$_2$], 1

A solution of CuI (5 mg, 0.026 mmol), [Ni(η^5-C_5H_5)(PPh_3)Br] (0.5 g, 1.1 mmol) and HC≡CCH(OEt)$_2$ (0.14 g, 1.1 mmol) in Et$_3$N (50 cm^3) was stirred overnight. The solvent was removed under reduced pressure and the residue dissolved in Et$_2$O. This solution was filtered, chromatographed (basic alumina/Et$_2$O),

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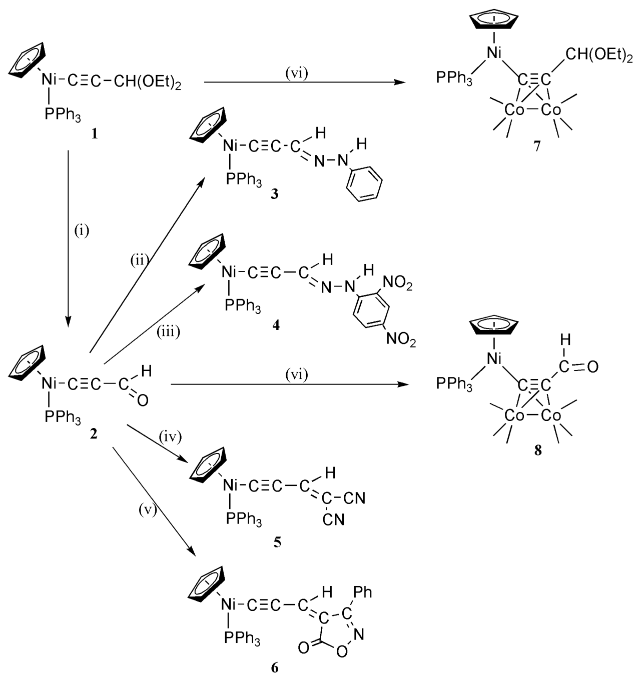


Scheme 1 Synthetic route to the complexes **1**–**8** (CO ligands have been omitted from the $Co_2(CO)_6$ moiety for the sake of clarity). (i) H_2O/oxalic acid; (ii) $PhNHNH_2/H^+$; (iii) $C_6H_3(NO_2)_2NHNH_2/H^+$; (iv) $CH_2(CN)_2/Et_3N$; (v) $C_9H_7NO_2/Et_3N$; (vi) $Co_2(CO)_8$.

and recrystallized from Et_2O–hexane to give green crystals of [Ni(η^5-C_5H_5)(PPh_3)C≡CH$(OEt)_2$] **1** (0.43 g, 80%), mp 76–77 °C (Found: C, 70.6; H, 6.0%. $C_{30}H_{31}NiO_2P$ requires C, 70.2; H, 6.1%). ν_{max}/cm^{-1} (C≡C) 2112 (CH_2Cl_2); (C≡C) 2109 (KBr); λ_{max}/nm (CH_2Cl_2) 305 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 15 200); λ_{max}/nm (CH_3CN) 303 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 14 900); $\delta_H(CDCl_3)$ 7.26–7.72 [15 H, m, Ph], 5.16 [5 H, s, C_5H_5], 4.92 [1 H, s, C≡CCH], 3.10 [4 H, q, *J*(HH) 6.8 Hz, OCH_2] and 0.89 [6 H, t, *J*(HH) 6.8 Hz, CH_3]; $\delta_C(CDCl_3)$ 134.0 [d, *J*(CP) 11 Hz, *o*-Ph], 133.9 [d, *J*(CP) 48 Hz, *i*-Ph], 130.2 [d, *J*(CP) 2 Hz, *p*-Ph], 128.2 [d, *J*(CP) 10 Hz, *m*-Ph], 114.2 [s, NiC≡*C*], 92.7 [s, η^5-C_5H_5], 82.0 (d, *J*(CP) 40 Hz, Ni*C*≡C], 71.7 [s, C≡C*C*H], 59.3 s, OCH_2] and 15.1 [s, CH_3]; $\delta_P(CDCl_3)$ 41.24.

Preparation of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO], 2

A solution of oxalic acid (0.03 g, 0.21 mmol) in H_2O (10 cm^3) was added to one of [Ni(η^5-C_5H_5)(PPh_3)C≡CH$(OEt)_2$] **1** (0.1 g, 0.2 mmol) in tetrahydrofuran (10 cm^3). The reaction mixture was stirred for 1 h at room temperature and then shaken with $CHCl_3$ (100 cm^3) and water (50 cm^3). The $CHCl_3$ layer was washed with water, dried with magnesium sulfate, and chromatographed (alumina/CH_2Cl_2–Et_2O). The green band was evaporated to dryness and the residue crystallised from dichloromethane–hexane mixtures to give green crystals of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2** (0.07 g, 80%), mp 118–119 °C (Found: C, 71.6; H, 5.0%. $C_{26}H_{21}NiOP$ requires C, 71.1; H, 4.8%); ν_{max}/cm^{-1} (C≡C) 2079(7) and 2034(3), (CO) 1625(10), 1622(10) (CH_2Cl_2); (C≡C) 2081(7) and 2034(3), (CO) 1627(10) (KBr); λ_{max}/nm (CH_2Cl_2) 364 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 16 100); λ_{max}/nm (CH_3CN) 359 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 16 000); $\delta_H(CDCl_3)$ 8.41 [1 H, s, CHO], 7.37–7.70 [15 H, m, Ph] and 5.22 [5 H, s, C_5H_5]; $\delta_C(CDCl_3)$ 174.4 [s, CHO], 133.7 [d, *J*(CP) 11 Hz, *o*-Ph], 132.9 (d, *J*(CP) 49 Hz, *i*-Ph], 130.5 (d, *J*(CP) 2 Hz, *p*-Ph), 128.3 (d, *J*(CP) 11 Hz, *m*-Ph], 124.6 [s, NiC≡*C*], 122.8 (d, *J*(CP) 43 Hz, Ni*C*≡C] and 93.27 [s, C_5H_5]; $\delta_P(CDCl_3)$ 42.64.

The reaction of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] with hydrazines

[Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2** (0.5 g, 1.1 mmol) and phenylhydrazine, $H_2NNHC_6H_5$ (0.11 g, 1.1 mmol), were dissolved in dichloromethane (50 cm^3). A few drops of glacial acetic acid were added to the mixture which was then stirred for 2 h at 35 °C. The solution colour changed from brown to red. The solvent was removed *in vacuo* and the residue dissolved in CH_2Cl_2, layered with n-hexane and stored at −20 °C overnight. Filtration gave [Ni(η-C_5H_5)(PPh_3)C≡CCH=NNHC_6H_5] **3** as a brick-red powder (0.55 g, 90%), decomp. > 150 °C (Found: C, 72.1; H, 5.1; N, 5.4%. $C_{32}H_{27}NiN_2P$ requires C, 72.6; H, 5.1; N, 5.3%); ν_{max}/cm^{-1} (C≡C) 2090(4.5), (C=N) 1593(10) (CH_2Cl_2); (C≡C) 2091(4.3), (C=N) 1595(10) (KBr); λ_{max}/nm (CH_2Cl_2) 350 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 12 200); λ_{max}/nm (CH_3CN) 354 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 10 100); $\delta_H(CDCl_3)$ 6.51–7.76 [20 H, m, Ph and Ph_3P), 5.25 [5 H, s, C_5H_5], 5.09 [1 H, s, NNH] and 4.22 [1 H, s, CH]; $\delta_C(CDCl_3)$ 120.1–143.0 (Ph, PPh_3), 113.0 [s, CH=N], 93.1 [s, NiC≡*C*], 92.4 [s, η^5-C_5H_5] and 91.4 [d, *J*(CP) 48 Hz, Ni*C*≡C].

A similar procedure but with $NH_2NHC_6H_5$ replaced by $NH_2NHC_6H_3(NO_2)_2$-2,4 gave [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=NNH$C_6H_3(NO_2)_2$-2,4] **4** (0.67 g, 95%) decomp. > 150 °C (Found: C, 61.2; H, 4.0; N, 8.7%. $C_{32}H_{25}NiN_4O_4P$ requires C, 62.1; H, 4.1; N, 9.0%); ν_{max}/cm^{-1} (C≡C) 2082 and (NO_2) 1617, 1600 (CH_2Cl_2); (C≡C) 2082 and (NO_2) 1615, 1601, (KBr); λ_{max}/nm (CH_2Cl_2) 394 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 19 600); λ_{max}/nm (CH_3CN) 394 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 18 500); $\delta_H(CDCl_3)$ 9.17 [1 H, s, CH=N], 8.26 [3 H, m, C_6H_3], 6.50–7.81 [15 H, m Ph_3P], 6.23 [1 H, m, NNH) and 5.20 [5 H, s, C_5H_5]; δ_C 118–144.4 [m, *C*$_6H_3(NO_2)_2$], 133.8 [d, *J*(CP) 41 Hz, *o*-Ph), 133.1 [d, *J*(CP) 50 Hz, *i*-Ph], 130.5 [d, *J*(CP) 2 Hz, *p*-Ph], 128.2 [d, *J*(CP) 11 Hz, *m*-Ph], 117.0 [s, CH=N], 110.9 [s, NiC≡*C*], 108.3 [d, *J*(CP) 48 Hz, Ni*C*≡C] and 93.5 [s, η^5-C_5H_5].

The reaction of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] with malononitrile and 3-phenyl-5-isoxazolone

A solution of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2** (0.1 g, 0.22 mmol) and $CH_2(CN)_2$ (0.015 g, 0.22 mmol) in CH_2Cl_2 (10 cm^3) was stirred for 10 min. Et_3N (3 drops) was added. A rapid colour change from green to deep red took place. The mixture was stirred for 2 h, and then the solvent removed at reduced pressure. The residue was crystallised from chloroform–hexane mixtures at −20 °C overnight and then filtered to give a red powder, [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=C$(CN)_2$] **5** (0.098 g, 90%), decomp. > 150 °C (Found: C, 71.4; H, 4.4; N, 5.8%. $C_{29}H_{21}N_2NiP$ requires C, 71.4; H, 4.3; N, 5.7%); ν_{max}/cm^{-1} (C≡C) 2050(10), (CN) 2218(1), 2226(1), (C=C) 1534(2.1) (CH_2Cl_2); (C≡C) 2049(10), (CN) 2216(1), 2225(1), (C=C) 1532(2.4) (KBr); λ_{max}/nm (CH_2Cl_2) 469 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 13 000); λ_{max}/nm (CH_3CN) 463 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 11 200); $\delta_H(CDCl_3)$ 7.33–7.62 [15 H, m, Ph_3P], 6.43 [1 H, s, CH], 5.25 [5H, s, C_5H_5]; $\delta_C(CDCl_3)$ 152.8 [d, *J*(CP) 48 Hz, Ni*C*≡C], 143.7 [s, H*C*=C], 134.1 [d, *J*(CP) 11 Hz, *o*-Ph], 133.2 (d, *J*(CP) 50 Hz, *i*-Ph], 131.4 (d, *J*(CP) 3 Hz, *p*-Ph], 129.1 [d, *J*(CP) 11 Hz, *m*-Ph], 121.5 [s, NiC≡*C*], 114.5 [s, *C*≡N], 114.9 [s, *C*≡N], 94.2 [s, η^5-C_5H_5] and 86.3 [d, *J*(CP) 2.1 Hz, *C*$(CN)_2$].

Using the same procedure 3-phenyl-5-isoxazolone, $C_9H_7NO_2$ and [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2** gave purple [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=$C_9H_5NO_2$] **6** (0.11g, 85%), decomp. > 50 °C (Found: C, 72.1; H, 4.5; N, 2.3%. $C_{32}H_{25}NiN_4O_4P$ requires C, 72.2; H, 4.5; N, 2.4%); ν_{max}/cm^{-1} (C≡C) 2050(6), (CO) 1690(10) (CH_2Cl_2); (C≡C) 2051(6), (CO) 1692(10), (KBr); λ_{max}/nm (CH_2Cl_2) 511 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 27 800); λ_{max}/nm (CH_3CN) 507 ($\varepsilon/dm^3\ mol^{-1}\ cm^{-1}$ 26 600); $\delta_H(CDCl_3)$ 6.95–7.59 [21 H, m, Ph_3P, Ph, CH=] and 5.22 [5H, s, C_5H_5]; $\delta_C(CDCl_3)$ 140.3 [d, *J*(CP) 48 Hz, Ni*C*≡C], 133.9 [d, *J*(CP) 12 Hz, *o*-Ph], 133.0 (d, *J*(CP) 50 Hz, *i*-Ph], 128.7–131.4 [m, Ph, isoxazolone], 130.7 [d, *J*(CP) 2 Hz, *p*-Ph], 128.6 [d, *J*(CP) 11 Hz, *m*-Ph], 120.7 [s, NiC≡*C*] and 96.7 [s, η^5-C_5H_5].

The reaction of [Ni(η^5-C_5H_5)(PPh_3)C≡CX] {X = CH$(OEt)_2$, CHO and CHC$(CN)_2$} with [$Co_2(CO)_8$]

[$Co_2(CO)_8$] (0.07 g, 0.22 mmol) was added to a solution of [Ni(η^5-C_5H_5)(PPh_3)C≡CX] {0.22 mmol; X = CH$(OEt)_2$ and

Table 1 Crystal data and structure refinement for [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2**, [Ni(η^5-C_5H_5)(PPh_3)C≡CCHC$(CN)_2$] **5**, and [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCHO}{$Co_2(CO)_6$}] **8**

	2	**5**	**8**
Empirical formula	$C_{26}H_{21}NiOP$	$C_{29}H_{21}N_2NiP$	$C_{32}H_{21}Co_2NiO_7P$
Formula weight	439.11	487.16	725.03
Temperature/K	297(2)	290(1)	294(2)
Wavelength/Å	0.71073	0.71073	0.71073
Crystal system, space group	Orthorhombic, *Pbca*	Triclinic, $P\bar{1}$	Monoclinic, *I*2/*a*
a/Å	10.2026(14)	10.6684(9)	18.698(3)
b/Å	16.4365(18)	11.0455(10)	16.8087(11)
c/Å	26.152(2)	11.7757(8)	21.090(3)
α/°	90	95.774(7)	90
β/°	90	113.486(7)	109.150(14)
γ/°	90	106.520(8)	90
Volume/Å^3	4385.5(8)	1183.46(17)	6261.3(14)
Z, Calculated density/Mg m^{-3}	8, 1.330	2, 1.367	8, 1.538
Absorption coefficient/mm^{-1}	0.971	0.907	1.739
Reflections collected/unique	6439/5249	4396/3658	7152/7152
Final R indices $\{I > 2\sigma(I)\}$	$R_1 = 0.062$, $wR_2 = 0.099$	$R_1 = 0.037$, $wR_2 = 0.046$	$R_1 = 0.047$, $wR_2 = 0.078$
R indices (all data)	$R_1 = 0.168$, $wR_2 = 0.129$	$R_1 = 0.093$, $wR_2 = 0.096$	$R_1 = 0.143$, $wR_2 = 0.092$

CHO} in tetrahydrofuran (20 cm^3). After 2 h the solution was filtered, the solvent removed at reduced pressure and the residue chromatographed (alumina/petroleum ether, bp 40–60 °C). The product was recrystallised from ether–hexane mixtures to give red crystals.

There was no reaction between [$Co_2(CO)_8$] and **5** where X = CHC$(CN)_2$.

[{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCH$(OEt)_2$}{$Co_2(CO)_6$}] **7** (0.14 g, 80%), decomp. > 200 °C (Found: C, 63.1; H, 4.5%. $C_{36}H_{31}O_8PCo_2Ni$ requires C, 63.5, H, 4.6%); ν_{max}/cm^{-1} terminal (CO) 2058(8), 2031(6) and 1997(10) (CH_2Cl_2); terminal (CO) 2056(8), 2031(6) and 1998(10) (KBr); λ_{max}/nm (CH_2Cl_2) 400 (ε/dm^3 mol^{-1} cm^{-1} 12 900); λ_{max}/nm (CH_3CN) 401 (ε/dm^3 mol^{-1} cm^{-1} 13 300); δ_H($CDCl_3$) 7.24–7.75 [15 H, m, Ph_3P], 5.17 [5 H, s, C_5H_5], 4.90 [1 H, s, C*H*$(OEt)_2$], 3.05 [4 H, q, *J*(HH) 7.3 Hz, CH_2] and 0.9 [6 H, t, *J*(HH), CH_3]; δ_C($CDCl_3$) 206.4 [s, terminal-CO], 134.2 [d, *J*(CP) 12 Hz, *o*-Ph], 133.6 [d, *J*(CP) 50 Hz, *i*-Ph], 130.5 [d, *J*(CP) 2 Hz, *p*-Ph], 128.0 [d, J(CP) 11 Hz, *m*-Ph], 106.5 [s, NiC≡C], 96.0 [s, *C*$_5H_5$], 75.2 [d, *J*(CP) 48 Hz, NiC≡C], 70.3 [s, *C*H$(OEt)_2$], 60.1 [s, *C*H$_2$CH$_3$] and 15.1 [s, CH$_2$*C*H$_3$].

[{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCHO}{$Co_2(CO)_6$}] **8** (0.14 g, 85%), decomp. 150 °C (Found: C, 53.0; H, 3.0%. $C_{32}H_{21}O_7P$-Co_2Ni requires C, 53.0, H, 2.9%); ν_{max}/cm^{-1} terminal (CO) 2072(6), 2034(6) and 2007(10), (CHO) 1654(8) (CH_2Cl_2); terminal (CO) 2071(6), 2032(6) and 2006(10), (CHO) 1654(1) (KBr); λ_{max}/nm (CH_2Cl_2) 406 (ε/dm^3 mol^{-1} cm^{-1} 12 000); λ_{max}/nm (CH_3CN) 402 (ε/dm^3 mol^{-1} cm^{-1} 14 300); δ_H($CDCl_3$) 8.43 [1 H, s, CHO], 7.42–7.70 [15 H, m, Ph_3P] and 5.18 [5 H, s, C_5H_5]; δ_C($CDCl_3$) 201.8 [s, terminal CO], 185.7 [s, CHO], 133.8 [d, *J*(CP) 11 Hz, *o*-Ph], 132.5 [d, *J*(CP) 50 Hz, *i*-Ph], 131.2 [d, *J*(CP) 2 Hz, *p*-Ph], 128.8 [d, *J*(CP) 10 Hz, *m*-Ph], 118.0 [s, NiC≡*C*], 107.1 [d, *J*(CP) 48 Hz, Ni*C*≡C] and 96.6 [s, C_5H_5].

Structures of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] 2, [Ni(η^5-C_5H_5)(PPh_3)C≡CCH=C$(CN)_2$] 5, and [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCHO}{$Co_2(CO)_6$}] 8

The crystal data for **2**, **5** and **8** are summarised in Table 1. The structures were solved using the Patterson function of SHELXS97,[14] and refined by full-matrix least squares using SHELXL97.[14] The diagrams were obtained using the PLATON[15] and ORTEX[16] programs. The molecular structures and atom labelling for **2**, **5** and **8** are illustrated in Figs. 1, 2 and 3, respectively. Selected bond lengths and angles are listed in Table 2 together with those previously reported for **1**.[10]

CCDC reference numbers 165064–165066.

See http://www.rsc.org/suppdata/dt/b1/b104442g/ for crystallographic data in CIF or other electronic format.

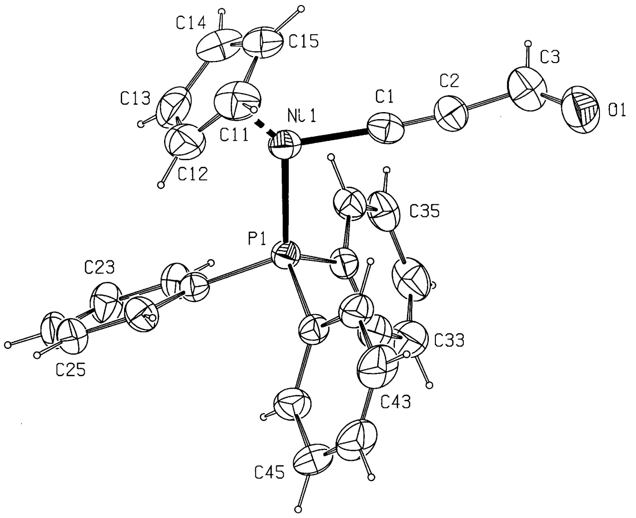


Fig. 1 Molecular structure and atom labeling for [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] **2**. Displacement ellipsoids are drawn at the 30% probability level.

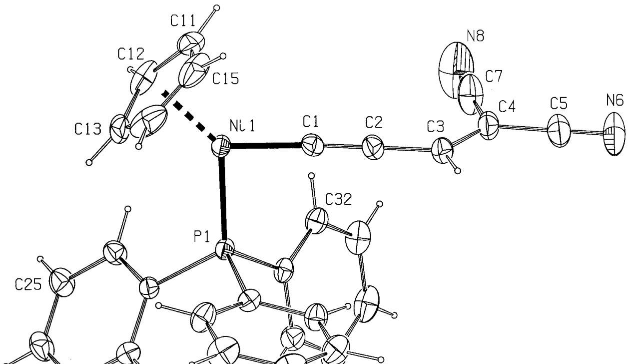


Fig. 2 Molecular structure and atom labeling for [Ni(η^5-C_5H_5)(PPh_3)C≡CCHC$(CN)_2$] **5**. Displacement ellipsoids are drawn at the 30% probability level.

Results and discussion

Synthesis and reactivity studies

Transition metal acetylides of the general type MC≡CX provide an attractive starting point for the synthesis of organometallic donor–π-acceptor systems. They may often be easily prepared

Table 2 Selected molecular dimensions, bond lengths in Å, bond angles in °, for [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCH(OEt)$_2$] **1**, [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCHO] **2**, [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCH=C(CN)$_2$] **5**, and [{μ-η^1:η^1-Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCHO}{Co$_2$(CO)$_6$}] **8**

	1	**2**	**5**	**8**[b]
Ni1–P1	2.1376(10)	2.1418(11)	2.1451(6)	2.1430(11)
Ni1–C1	1.840(5)	1.830(5)	1.833(2)	1.867(4)
C1–C2	1.193(5)	1.205(6)	1.214(3)	1.333(5)
C2–C3	1.474(5)	1.432(8)	1.402(3)	1.460(5)
C11–C12	1.391(5)	1.364(7)	1.346(5)	1.386(6)
C12–C13	1.389(5)	1.418(7)	1.385(5)	1.376(6)
C13–C14	1.406(6)	1.370(7)	1.391(5)	1.400(6)
C14–C15	1.369(6)	1.398(7)	1.356(5)	1.373(6)
C11–C15	1.396(6)	1.426(7)	1.394(5)	1.405(6)
Ni1–C11	2.059(4)	2.127(5)	2.111(3)	2.099(4)
Ni1–C12	2.128(4)	2.099(6)	2.123(3)	2.152(4)
Ni1–C13	2.094(4)	2.097(5)	2.062(30)	2.084(4)
Ni1–C14	2.133(4)	2.121(5)	2.134(30)	2.119(4)
Ni1–C15	2.128(4)	2.066(4)	2.101(3)	2.144(4)
Ni1–Cg1[a]	1.7458(4)	1.7354(6)	1.7523(4)	1.7612(6)
C3–O1/C3–C4*		1.147(6)	1.345(4)*	1.179(5)
C3–H3		0.93(3)	0.96(3)	0.93
Others			C4–C5 1.434(4)	Co1–Co2 2.4854(11)
			C4–C7 1.419(5)	Co1–C1 2.084(3)
			C7–N8 1.134(5)	Co2–C1 2.053(4)
				Co1–C2 1.934(4)
				Co2–C2 1.969(5)
P1–Ni1–C1	90.90(10)	95.65(14)	89.93(7)	93.34(11)
Ni1–C1–C2	178.7(3)	176.4(4)	176.6(2)	154.2(3)
Cg1–Ni1–P1	136.6	134.24(4)	137.27(3)	131.19(4)
Cg1–Ni1–C1	132.6	130.10(13)	131.92(9)	135.46(10)
C1–C2–C3	173.9(4)	174.6(6)	177.8(3)	145.0(4)
C2–C3–O1 (C4)*		130.8(6)	125.0(3)*	126.3(5)
Ni1–C1–Co1				128.5(2)
Ni1–C1–Co2				134.3(2)

[a] Cg1 is the centroid of the η^5–C$_5$H$_5$ ligand. [b] The range of bond lengths for Co–CO is 1.765(6) to 1.815(6) Å and for C≡O is 1.126(6) to 1.144(5) Å and the Co–C≡O bond angles are in the range 176.2(6)–178.7(6)° (*cf.* refs. 20, 24–26). Co1–C1–C2 64.6(2), Co2–C1–C2 67.2(3), Co1–C2–C1 76.8(2), Co2–C2–C1 74.1(3)°.

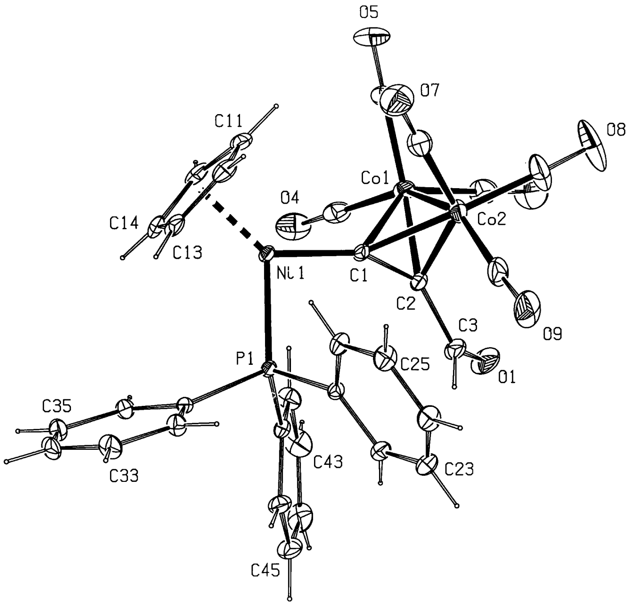


Fig. 3 Molecular structure and atom labeling for [{μ-η^1:η^1-Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCHO}{Co$_2$(CO)$_6$}] **8**. Displacement ellipsoids are drawn at the 10% probability level.

from a CuI–catalysed reaction of metal halides with terminal alkynes HC≡CX,[7] and when X contains a suitable functional group, it may be modified by conventional organic reactions. In the present work, the reaction of [Ni(η^5-C$_5$H$_5$)(PPh$_3$)Br] with the alkyne acetal HC≡CCH(OEt)$_2$ gives [Ni(η^5-C$_5$H$_5$)(PPh$_3$)-C≡CCH(OEt)$_2$] **1**, which is hydrolysed in the presence of oxalic acid to the aldehyde [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCHO] **2**. This undergoes condensation reactions with hydrazines in the presence of acetic acid to give the hydrazones [Ni(η^5-C$_5$H$_5$)-(PPh$_3$)C≡CCH=NNHAr] {Ar = C$_6$H$_5$ **3**, or C$_6$H$_3$(NO$_2$)$_2$-2,4 **4**}, and with active methylene compounds such as malononitrile or phenylisoxazolone in the presence of triethylamine to give [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCH=C(CN)$_2$] **5**, and [Ni(η^5-C$_5$H$_5$)-(PPh$_3$)C≡CCH=C$_9$H$_5$NO$_2$] **6**, respectively (Scheme 1).

Compounds **1**–**6** are alkynes and would be expected to react with [Co$_2$(CO)$_8$] to give the well-known alkyne complexes [(μ^2-alkyne)Co$_2$(CO)$_6$]. Thus **1** and **2**, respectively, gave the derivatives [{μ-η^1:η^1-Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCH(OEt)$_2$}{Co$_2$-(CO)$_6$}] **7**, and [{μ-η^1:η^1-Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CCHO}{Co$_2$-(CO)$_6$}] **8**, within two hours. However **5**, [Ni(η^5-C$_5$H$_5$)-(PPh$_3$)C≡CCHC(CN)$_2$], does not undergo this reaction even after 24 h at room temperature, so clearly the ability of the alkynes [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CX] to react with [Co$_2$(CO)$_8$] depends on X and is inhibited by the strongly electron-withdrawing C(CN)$_2$ group. Furthermore, some characteristic reactions of X appear to be affected by complexation of C≡C to the {Co$_2$(CO)$_6$} moiety so that the acetal group in **7** is not hydrolysed to the aldehyde in the presence of oxalic acid, and the aldehyde group in **8** does not undergo a Knoevenagel condensation with CH$_2$(CN)$_2$ or react with the Wittig reagent prepared from [Ph$_3$PCH$_2$Br]Br and ^{n}BuLi. These reactions are facile for the free [Ni(η^5-C$_5$H$_5$)(PPh$_3$)C≡CX].

A rationalization of these observations will be discussed below.

Spectra and bonding

The IR spectra of complexes **1**–**8** show many absorption bands, but the ones which yield useful structural information are those due to the *ν*(C≡C), aldehyde *ν*(CO) and *ν*(CN) modes of the C≡CX moieties and the *ν*(CO) vibrations of the Co$_2$(CO)$_6$ groups.

Table 3 IR, ^{13}C NMR and UV/visible spectroscopic data for [Ni(η^5-C_5H_5)(PPh_3)C≡CX] complexes

	IR spectra[a]		^{13}C spectra[b]			UV/visible spectra[c]	
X	ν(C≡C)[d]	ν(C≡C)[e]	C_1	C_2	C_5H_5	λ_{max} (ε)[e]	λ_{max} (ε)[f]
$CH(OEt)_2$, **1**	2109	2112	82.0 (d, 40)	114.2	92.7	305 (15.2)	303 (14.9)
CHO, **2**	2081 (2), 2034 (3)	2079 (2), 2034 (3)	122.8 (d, 43)	124.6	93.3	364 (16.1)	359 (16.0)
$CHNNHC_6H_5$, **3**	2091	2090	91.4 (d, 48)	93.1	92.4	350 (12.0)	354 (10.1)
$CHNNHC_6H_3(NO_2)_2$-2,4, **4**	2082	2082	108.3 (d, 48)	110.9	93.5	394 (19.6)	394 (18.5)
$CHC(CN)_2$, **5**	2049	2050	152.8 (d, 48)	121.5	94.2	469 (13.0)	463 (11.2)
$CHC_9H_5NO_2$, **6**	2051	2050	140.3 (d, 48)	120.7	96.7	511 (27.8)	507 (26.6)

[a] Peak positions in cm^{-1} with relative peak heights in parentheses for **2**. [b] Chemical shifts in ppm downfield from Me_4Si as an internal standard. In parentheses are multiplicity (d = doublet) and coupling constants J_{PC} in Hz. Other resonances are singlets. Spectra recorded in $CDCl_3$ solution. [c] Absorption band maxima in nm with band intensities in parentheses in 10^3 dm^3 mol^{-1} cm^{-1}. [d] Spectra measured as KBr discs. [e] Spectra measured in CH_2Cl_2 solution. [f] Spectra measured in CH_3CN solution.

The bands due to the ν(C≡C) vibrations of the [Ni(η^5-C_5H_5)(PPh_3)C≡CX] complexes are readily identified. Their frequencies (Table 3) decrease along the series X = $CH(OEt)_2$ > CH=NNHC$_6$H$_5$ > CH=NNHC$_6$H$_3$(NO$_2$)$_2$ > CH=C(CN)$_2$ ≈ CH=C$_9$H$_5$NO$_2$. This may be correlated with the increasing electron-withdrawing power of X and rationalized by assuming that the ground state electronic structure of these complexes may be described as a resonance hybrid of three mesomers: the acetylenic form ***A*** and charge-separated forms ***B***, ***C*** and ***D*** (Fig. 4).

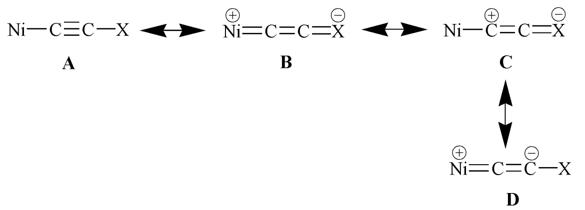


Fig. 4 Resonance structures of the [Ni(η^5-C_5H_5)(PPh_3)C≡CX] complexes.

A is always the most important, but there will be an increasing contribution from ***B***, ***C*** and ***D*** as the electron-withdrawing ability of X increases. The decreasing C≡C bond order results in a lower ν(C≡C) frequency as has been observed by Gladysz and co-workers in the metalloalkynes Re(η^5-C_5Me_5)(NO)(PPh_3)C≡CC≡CC(OMe)(fluorenyl)[17] which show ν(C≡C) bands at 2018 and 2172 cm^{-1} whereas in [Re(η^5-C_5Me_5)(NO)(PPh_3)-C≡CC≡CAr$_2$]$^+$ they are found at 1993 and 1902 cm^{-1} (H_2CAr_2 = fluorene).[17]

The IR spectrum of **2** (X = CHO) (Table 4) is different from those of **1**, and **3**–**6**. It displays two ν(C≡C) absorption bands in the solid state at 2034 and 2081 cm^{-1} (intensity ratio 1 : 3). In solution, the relative intensities vary with the *ca.* 2080 cm^{-1} band increasing in importance along the series MeCN ≈ CH_2Cl_2 (1 : 3) < toluene ≈ tetrahydrofuran (1 : 5) < hexane (0 : 1) so that for the latter solvent the *ca.* 2030 cm^{-1} band is absent. These changes are reversible. The aldehydic ν(CO) band of **2** has two equal components in acetonitrile or dichloromethane solutions *ca.* 1621 and 1626 cm^{-1}, but not in toluene, tetrahydrofuran, hexane, or in the solid state. Its frequencies are very low even when compared with that of benzaldehyde (1714 and 1702 cm^{-1} in hexane and CH_2Cl_2, respectively) and PhC≡CCHO (1661 and 1672 cm^{-1}). This frequency variation may be attributed to (a) coupling of the ν(C≡C) and ν(C=O) vibrations which would raise the frequency of the former and lower that of the latter but which is likely to be limited, and (b) the contribution made to the ground state electronic structure of **2** by the cumulenic mesomers ***B*** and ***C*** (Fig. 4) with their CO$^-$ moieties. The latter also accounts for the marked solvent-dependence of this absorption band. Hydrogen-bonding of the negatively charged oxygen atom to solvents such as dichloromethane and acetonitrile (but not hexane) would be expected to lower the frequency of the ν(CO) vibration still further. However, we are unable to account for the presence of two ν(C≡C) bands in the spectrum of **2**. This feature is commonly observed for MC≡CX complexes and is usually attributed to Fermi resonance [*e.g.* ref. 18]. It may be due to the presence of two species, but there is no evidence for this in the case of **2** either in the solid state (X-ray crystallography) or in solution (NMR spectra).

Table 4 The effect of solvent on the ν(CC) and ν(CO) absorption bands in the IR spectrum of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO]

Solvent	ν(C≡C) absorption bands[a]	ν(CO) absorption bands[a]
CH_3CN	2078, 2031 (3 : 1)	1626, 1621 (1 : 1)
CH_2Cl_2	2079, 2034 (3 : 1)	1625, 1622 (1 : 1)
$C_6H_5CH_3$	2082, 2026 (5 : 1)	1635
THF	2082, 2026 (5 : 1)	1635
Hexane	2086	1645
KBr	2081, 2034 (3 : 1)	1627
CH_2Cl_2[b]	2192	1661
$CH_3C_6H_5$[b]	2190	1664
Hexane[b]	2193	1672

[a] Frequency (cm^{-1}) with relative peak heights in parentheses. [b] Values for PhC≡CCHO.

The IR spectra of **7** and **8** show absorption bands due to the ν(CO) ligands of the $Co_2(CO)_6$ moiety (Table 5). Their frequencies are a function of X and are *ca.* 10 cm^{-1} higher when X is the electron-withdrawing CHO group as compared with $CH(OEt)_2$. This is attributed to the contribution that mesomers such as ***G*** (Fig. 5) make to the electronic structure of these complexes. The same frequency relationship is observed for the ν(CO) bands of [{μ-PhC≡CX}{$Co_2(CO)_6$}] (X = $CH(OEt)_2$ **9**, and CHO **10**),[19] but whereas the frequencies for **9** and **10** are similar to those of other [(μ-alkyne)$Co_2(CO)_6$] derivatives,

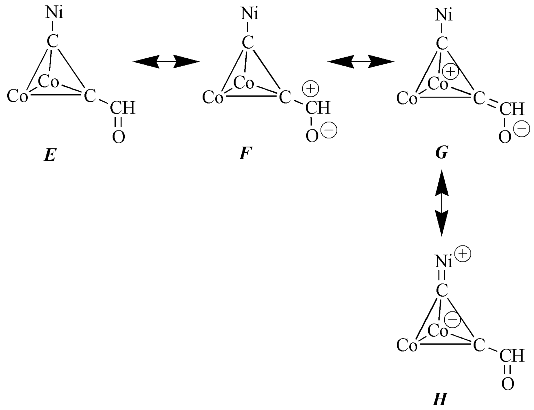


Fig. 5 Resonance structures of [{μ-η^1-η^1-Ni(η^5-C_5H_5)(PPh_3)-C≡CCHO}{$Co_2(CO)_6$}].

Table 5 C–O stretching frequencies in the IR spectra of [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CX}{$Co_2(CO)_6$}] {X = $CH(OEt)_2$ **7** and CHO **8**} and [{μ-η^1:η^1-PhC≡CX}{$Co_2(CO)_6$}] {X = $CH(OEt)_2$ **9** and CHO **10**}

Compound	Absorption bands				
7 {X = $CH(OEt)_2$}	2058 (8)	2031 (6)	1997 (10, br)		
8 {X = CHO}	2072 (6)	2034 (6)	2007 (10, br)		1654 (1)
9 {X = $CH(OEt)_2$}	2093 (3)	2056 (10)	2030 (8)	2024 (10)	
10 {X = CHO}	2102 (4)	2067 (10)	2041 (10)	2035 (sh)	1663 (1)

[a] Peak positions (cm^{-1}) with relative peak heights in parentheses. The bands at *ca.* 1660 cm^{-1} are due to the aldehyde group.

they are *ca.* 30 cm^{-1} higher on average than are those of **7** and **8**. This is attributed to the electron-donating ability of the (η^5-C_5H_5)(Ph_3P)Ni moiety and the contribution made by mesomers such as ***H*** to an overall description of the bonding in **7** and **8** (Fig. 5). Similar mesomers clearly do not contribute to the bonding of **9** and **10**. Similar effects have been observed for [{μ-η^1:η^1-(η^5-C_5H_5)$(OC)_2$FeC≡CH}{$Co_2(CO)_6$}] {ν(CO) = 2060, 2011, 1986, 1961 cm^{-1}}.[20] The spectra of **8** and **10** also show an additional weaker band at 1654 and 1663 cm^{-1} respectively due to their aldehydic ν(CO) vibration. This is much higher than that of the uncomplexed aldehyde **2** but very little changed from PhC≡CCHO. The relative frequencies reflect the greater electron-richness of the Co_2C_2 cluster in **8** as compared with **10**. It points to some Ni · · · CHO electronic interaction in **8** that is greatly reduced as compared with that in the parent alkyne **2**.

The ^{1}H NMR spectra of **1**–**8** show the resonances characteristic of the η^5-C_5H_5 and PPh_3 ligands, and the group X. They require no further discussion.

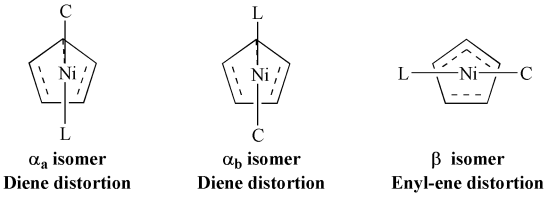
The ^{13}C NMR spectra show the anticipated resonances. The most interesting are two due to the alkynyl C atoms (Table 3). One is a doublet. It is assigned to the Ni–C_1 atom coupled to the coordinated P atom. The other is a singlet and is assigned to the remote Ni–C≡C_2 atom as there is no coupling to ^{31}P. The chemical shifts of both are a function of X so that when X is electron-donating such as $CH(OEt)_2$, the C_1 resonance is found upfield (δ 82.0) of that due to C_2 (δ 114.2). Both carbon atoms are deshielded when X is electron-withdrawing, but C_1 is affected more than C_2 so that when X is, for example, CH=C$(CN)_2$, the C_1 resonance is found downfield (δ 152.8) of that due to C_2 (δ 121.5). C_1 is increasingly deshielded along the series X = $CH(OEt)_2$, CH=NNHC_6H_5, CH=NNH$C_6H_3(NO_2)_2$-2,4, CHO, CH=$C_9H_5NO_2$, CH=C$(CN)_2$. These effects are consistent with the suggestion made above that the charge separated mesomers ***B***, ***C*** and ***D*** (Fig. 4) make an increasing contribution to the ground state structure of these complexes as the electron-withdrawing ability of X increases. The series for C_1 arises, in part, from its increasing carbene character/decreasing alkyne character as a consequence of rehybridisation of the NiCCX chain, and, in part, from its increasing positive charge as a consequence of charge separation. The series is very similar to that observed for the effect of X on the ν(C≡C) frequency except for the anomalous IR spectrum of **2**. C_2 becomes increasingly deshielded for X = CH=NNHC_6H_5, CH=NNH$C_6H_3(NO_2)_2$-2,4, $CH(OEt)_2$, CH=$C_9H_5NO_2$, CH=C$(CN)_2$, CHO. This is a somewhat different series from that for C_1, but similarly it has the electron-withdrawing X giving rise to the most deshielded carbon atoms. The differences between the two series are probably a reflection of the differing contributions made by mesomers ***A***–***D***.

The UV-visible spectrum of **1** (Table 3) shows a relatively intense absorption band at 305 nm. It is present in the spectra of **2**–**6** but its wavelength increases with the increasing electron-withdrawing ability of X to 469 nm when X = CHC$(CN)_2$ and 511 nm when X = CH$C_9H_5NO_2$. It is assigned to an electronic transition from the ground state of these complexes to an excited state. As discussed above, the electronic structure of the ground state may be described as a resonance hybrid in which the alkynyl mesomer ***A*** predominates over the charge separated cumulenic mesomers. In the excited state, the same mesomers probably contribute to an overall description of the bonding but ***B***, ***C*** and ***D*** are now the more important. Consequently, the electron-withdrawing groups X preferentially stabilise the excited state, reduce the energy of the electronic transition and increase the wavelength of the observed absorption band. The increasing conjugation present in **5** and **6** may also contribute to lowering the energy of this electronic transition as may the presence of the NH$C_6H_3(NO_2)_2$-2,4 moiety in **4**.

The NMR and UV-visible spectra of **7** and **8** are similar to those of other [μ-(alkyne)$Co_2(CO)_6$] species and will not be discussed further.

Crystal structures of [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] 2, [Ni(η^5-C_5H_5)(PPh_3)C≡CCHC$(CN)_2$] 5, and [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡CCHO}{$Co_2(CO)_6$}] 8

The structures of **2**, **5** and **8** are illustrated in Figs. 1, 2 and 3, respectively, and selected molecular dimensions are listed in Table 2 together with those previously reported for **1** (isomer **B**). All four compounds have the expected half-sandwich structures in which the C_5 and P–Ni–C planes are virtually orthogonal. The P–Ni–C plane may be coincident with a σ_v plane of the C_5 ring (α isomers in Fig. 6) or perpendicular to it (β isomer in Fig. 6). There are two possible α isomer (Fig. 6) and intermediate situations are possible. Complex **2** adopts the α_a structure, **5** the α_b structure, and **1B** and **8** the β structure but not completely so. The α isomers show a distortion of the C_5 ring towards a diene with two short non-adjacent C–C bonds (C_{11}–C_{12}/C_{13}–C_{14} in **2**, and C_{11}–C_{12}/C_{14}–C_{15} in **5**) and one particularly short Ni–C_{ring} bond (to C_{15} in **2** and C_{13} in **5**). The β isomers show distortions of the ring towards an ene-allyl with a short ene C–C bond (C_{14}–C_{15} in both **1B** and **8**) and two longer bonds (C_{11}–C_{15}/C_{13}–C_{14}) and two Ni–C_{ring} ring bonds (to C_{11} and C_{13}) which are shorter than the other three; differences which are less marked for **1B** than for **8**. These distortions are a reflection of the loss of degeneracy of the cyclopentadienyl E_1 and E_2 π orbitals, their different energies and their differential occupancy in these complexes. This has been discussed in ref. 21 and many other papers cited therein.



α_a isomer
Diene distortion

α_b isomer
Diene distortion

β isomer
Enyl-ene distortion

Fig. 6 Distortions of the η^5-C_5H_5 ligand in the [Ni(η^5-C_5H_5)(PPh_3C≡CX] complexes.

The P–Ni–C angles lie in the range 89.9–95.7° and are comparable with values of 93.47(5)° in [Ni(η^5-C_5H_5)(PPh_3)-C≡CC≡CH],[9] 93.30(10)° in [Ni(1-Me-indenyl)(PPh_3)C≡C-C_6H_5],[11] and 95.4(7)° in the benzonitrile derivative [Ni(η^5-C_5H_5)(PPh_3)NC$C_6H_4NH_2$][PF_6].[12] The Ni–P distances lie in the range 2.1376(10)–2.1451(6) Å. They are identical within experimental error and similar to those of related compounds.[8–11]

The Ni–C–C–X systems are almost linear for **1**, **2** and **5** with Ni–C_1–C_2 and C_1–C_2–C_3 angles lying between 173.9(4)° and 178.7(3)°. Their Ni–C_1 distances are, within experimental error, independent of X, and although their C_1–C_2 bond lengths increase along the series **1** < **2** < **5**, the changes are small and scarcely outside of experimental error, but they do follow the trend expected if the mesomeric form ***B*** makes an increasing contribution to the overall bonding with increasing electron-withdrawing power of X. However, our observations are essentially in agreement with those of Humphrey and co-workers who showed that Ni–$C_{alkynyl}$ and C≡C bond lengths do not vary significantly in a series of [Ni(η^5-C_5H_5)(PPh_3)(L)C≡CAr] complexes with NO_2 substituents on the aromatic groups Ar.[8]

In **5** the CHC$(CN)_2$ moiety is planar and oriented almost orthogonal {81.53(10)°} to the P–Ni–C plane. The same is observed for the CHO group in **2**, which contrasts with the situation in [Ni(η^5-C_5H_5)(PPh_3)C≡CPh] derivatives where the P–Ni–C plane and the C_6 ring tend towards coplanarity.[22] The C_2–C_3 distance in **2** {1.432(8) Å} is longer than that in **5** {1.402(3) Å}, which is consistent with the increasing contribution that mesomer ***B*** makes toward the bonding in **5** as compared with **2** (Fig. 4).

There are no intramolecular interactions of note in **5** and this is primarily due to the orientation of the rigid dicyanovinyl ligand with respect to the Ni(η^5-C_5H_5)(PPh_3) group; this contrasts with the acetal derivative [Ni(η^5-C_5H_5)(PPh_3)C≡CCH$(OEt)_2$][10] where the flexible CH$(OEt)_2$ group interacts with the PPh_3 ligand. An intermolecular interaction C_{23}–H_{23} ··· π(C≡C)^i (i = 1 + *x*, *y*, *z*) involving the alkynyl C_1≡C_2–C_3, with C_{23}–H_{23} ··· C_2 146°, H_{23} ··· C_2 2.63 Å and C_{23} ··· C_2 3.438(5) Å, is comparable to similar C–H ··· π(C≡C) interactions reported in Ni(η^5-C_5H_5)(PPh_3)-C≡CC≡CH,[9] and by Desiraju and Steiner.[23] There are two other intermolecular interactions of note C_{43}–H_{43} ··· {C_{31}, ··· C_{36}}^{ii} (ii = *x*, *y*, 1 + *z*) and C_{45}–H_{45} ··· {C_{21}, ··· C_{26}}^{iii} (iii = 1 − *x*, 1 − *y*, 1 − *z*).

The overall structure of [{μ-η^1:η^1-Ni(η^5-C_5H_5)(PPh_3)C≡C-CHO}{$Co_2(CO)_6$}], **8**, (Fig. 3) is similar to that of other [(μ-η^1:η^1-alkyne)$Co_2(CO)_6$] complexes[20,24–26] with a Co_2C_2 tetrahedral core. However, inspection of bond angles and bond lengths within this core reveals some interesting distortions. The Co–C distances to C_1 (average 2.068 Å) are considerably longer than those to C_2 (average 1.952 Å). A similar distortion is observed in [{μ-η^1:η^1-(η^5-C_5H_5)$(OC)_2$FeC≡CH}{$Co_2(CO)_6$}][20] whereas in [{μ-η^1:η^1-Bu^{t}C≡CBu^t}{$Co_2(CO)_6$}] Co–C are comparable at 1.999 and 1.985 Å.[24] It is a reflection of the electron-donating character of (η^5-C_5H_5)(Ph_3P)Ni and the electron-withdrawing character of CHO. It is consistent with the supposition that the alkyne–Co_2 bonding consists of donation of the alkyne π-electrons to the metal atoms and back-donation of electrons from the metal atoms into the two vacant alkyne π* orbitals in which the latter is the more important and would be preferentially directed to the C atom bearing the most electronegative substituent. There is a second but minor distortion of the Co_2C_2 core as each C is bonded unequally to the two Co atoms with C_1–Co_1 > C_1–Co_2 and C_2–Co_1 < C_2–Co_2 so that the Co–Co and C–C axes are not orthogonal. These solid-state differences involving the (μ-η^1:η^1-C_2)/$Co_2(CO)_6$ system in **8** may support evidence for predisposed substitution sites in unsymmetrical alkynyl systems in Pauson–Khand reactions.[27–30]

As would be expected, the C_1–C_2 bond length in **8** {1.333(5) Å} is much longer than in **2** {1.205(6) Å} but well short of a normal C–C single bond of 1.53 Å.[31] It is comparable to that found in most complexes of this class of compound[24] but it is longer than that in [{μ-η^1:η^1-(η^5-C_5H_5)$(OC)_2$FeC≡CH}{$Co_2(CO)_6$}]{1.305(5) Å}.[20] The Ni–C≡C and C≡C–C angles of 154.2(3)° and 145.0(4)° in **8** differ greatly as is usually the case where the substituents on the coordinated C≡C differ greatly in their electron-withdrawing capabilities, (*e.g.* ref. 25). They are different from the near linear 176.4(4) and 174.6(6)° angles in **2**. The Ni–C and aldehyde C=O bond lengths of 1.867(4) Å and 1.179(5) Å, however, are longer in **8** than in **2** as a direct consequence of the μ-η^1 : ^{1}-(C_2) moiety bonding with the Co_2 group. The orientation of the η^5-C_5H_5 ring and the P–Ni–C fragment is of the β type with ene-allyl distortions within the cyclopentadienyl ring (see above). The Ni–C_{cp} bond lengths in **8** {2.084(4)–2.152(4) Å} are lengthened when compared with those in **2** {2.066(4)–2.127(5) Å} and so is the nickel to cyclopentadienyl ring centroid distance, Ni1 ··· Cg1 is 1.7612(6) Å in **8** and 1.7354(6) Å in **2**.

Conclusions

In [Ni(η^5-C_5H_5)(PPh_3)C_1≡C_2X] complexes the (η^5-C_5H_5)(Ph_3P)-Ni acts as an electron donor. When X is a suitable electron acceptor, the electronic interaction between the two results in a lowering of the *ν*(C≡C) frequency, a deshielding of the C_1 and C_2 resonances (particularly the former), and an increase in the wavelength of the lowest energy charge transfer transition of the NiC≡CX system. In the broadest terms, these effects increase in importance as the electron-withdrawing ability of X increases. Although the ordering of X is not the same for each spectroscopic parameter, it is clear that the more strongly electron-withdrawing X [CHO, CH=C$(CN)_2$ and CH=C_9-H_5NO_2] have a greater effect than the less strongly electron-withdrawing [CH$(OEt)_2$, CH=NNHPh and CH=NNHC_6-$H_3(NO_2)_2$-2,4]. The two least ambiguous of the parameters are the *ν*(C≡C) frequencies which provide a direct measure of the C≡C bond order, and the chemical shift of C_1 which depends on the charge separation in the molecule as well as hybridisation at C_1. Both suggest that the electron withdrawing ability of X increases along the series CH$(OEt)_2$ < CH=NNHPh < CH=NNHC_6H_3-$(NO_2)_2$-2,4 < CHO < CH=$C_9H_5NO_2$ ≈ CH=C-$(CN)_2$. The spectroscopic changes are attributed to the increasing contribution that charge-separated mesomers make to the overall electronic structure of these compounds, but the crystal structures of [Ni(η^5-C_5H_5)(PPh_3)C≡CCH$(OEt)_2$], [Ni(η^5-C_5H_5)(PPh_3)C≡CCHO] and [Ni(η^5-C_5H_5)(PPh_3)C≡CCHC$(CN)_2$] show that this is not reflected in any significant structural changes in the Ni–C≡C–C system.

Although **1**–**8** are alkynes, not all of them form [{μ-η^1:η^1-Ni-(η^5-C_5H_5)(PPh_3)C_1≡C_2X}{$Co_2(CO)_6$}] derivatives on reaction with [$Co_2(CO)_8$]. Such compounds may be isolated when X = CH$(OEt)_2$ **7**, or CHO **8**, but not when X is the strongly electron-withdrawing CH$(CN)_2$. This is attributed to the relatively low C≡C bond order in **6** as evidenced by its low *ν*(C≡C) frequency. The donor capability of the (η^5-C_5H_5)(PPh_3)Ni substituents greatly affects the *ν*(CO) frequencies of **7** and **8** which are lowered by *ca.* 35 cm^{-1} as compared with their [(μ-PhC≡CX)-{$Co_2(CO)_6$}] counterparts, and in **8** where one cluster C atom is substituted by the electron donating (η^5-C_5H_5)(PPh_3)Ni and the other by the electron withdrawing CHO groups, the C_2Co_2 core is greatly distorted with significantly different C–Co distances. Furthermore, complexation of [Ni(η^5-C_5H_5)(PPh_3)C≡CX] to a $Co_2(CO)_6$ moiety appears to affect the reactivity of X, but the electronic communication between Ni and X is still apparent and has spectroscopic implications.

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