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Group 8 and 10 metal acetylide naphthalimide dyads

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Dedicated to Professor F.G.A. Stone

Abstract

[M]–C≡C–naphthalimide derivatives {[M] = CpNi(PPh$_3$), CpFe(dppe), CpRu(dppe) and Cp*Ru(dppe)} have been prepared and their X-ray structures determined. The structures show significant non-linearity of the acetylide link, with concomitant $\nu_{C\equiv C}$ at low energy and high intensity. Other properties confirm the strong-donor/strong-naphthalimide acceptor nature of the compounds. All the compounds exhibit an intense MLCT band in the visible spectrum that resolves into two bands in non-polar solvents. Spectroelectrochemistry of the CpFe species shows that the MLCT band disappears upon oxidation, and the appearance of a LMCT band at lower energy.

Keywords: Metal-acetylide; X-ray structure; Donor–acceptor; MLCT; Naphthalimide; Spectroelectrochemistry

1. Introduction

Organometallic architectures incorporating metal atoms in organic π networks have been receiving extensive interest due to their potential use in molecular-scaled electronics [1,2]. The attraction of having an organometallic component in these systems is the capacity for a range of accessible oxidation states and the tunability of properties by variation of the ligand environment. Our recent work has focussed on the effect of incorporation of ferrocenyl substituents on the absorption and emission characteristics of known fluorophores [3–6]. The chemistry of 1,8-naphthalimides has proved particularly fertile. We have synthesised ferrocenyl derivatives of these that retain significant fluorescence and shown that charge transfer properties in organic-donor/naphthalimide-acceptor arrays can be extended to organometallic/naphthalimide dyads [7].

Incorporation of the metal into the plane of the π-system should enhance its communication with the naphthalimide, and to this end, one group of compounds that appear particularly attractive are the Group 8 and 10 metal half-sandwich σ-acetylide complexes. The –C≡C–linkage in these provides facile electronic communication between the electron-rich metal donor and an acceptor moiety. Both mononuclear and multiple metal-centred compounds have been extensively studied [8–17] particularly with potential NLO properties in mind. IR spectroscopy has been used to investigate the bonding within the M–C≡C unit particularly the balance between acetylenic and cumulenic character in D–A assemblies [18–20].

This paper reports a series of 18-electron metal acetylide systems with a common naphthalimide acceptor terminus and metal donor functionality based on CpNi, CpFe, CpRu and Cp*Ru metal hubs.

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2. Experimental

2.1. General remarks

Solvents were dried and distilled by standard procedures, and all reactions were performed under nitrogen. 4-ethynyl-*N*-methyl-1,8-naphthalimide [7], CpNi(PPh_3)Br [21], CpFe(dppe)I [22], CpRu(dppe)Cl [23] and Cp*Ru(dppe)Cl [24] were prepared by literature methods. Microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago. Mass spectra were recorded on a Shimadzu LCMS-QP8000α. IR spectra were recorded on a Perkin–Elmer Spectrum BX FT-IR spectrometer, ^{1}H and ^{13}C NMR spectra on Varian Unity Inova 300 MHz and 500 MHz spectrometers in $CDCl_3$ (7.26 ppm) at 25 °C; electronic spectra were recorded on a Varian Cary 500 UV–Vis. Band maxima were obtained from convoluted spectra. Cyclic and square wave voltammetry in CH_2Cl_2 were performed using a three-electrode cell with a polished Pt 1 mm disk working electrode; solutions were $\sim10^{-3}$ M in electroactive material and 0.10 M in supporting electrolyte (recrystallised $TBAPF_6$). Data was recorded on a Powerlab/4sp computer-controlled potentiostat. Scan rates of 0.05–1 V s^{-1} were typically employed for cyclic voltammetry and for square-wave voltammetry, square-wave step heights of 5 mV, a square amplitude of 25 mV with a frequency of 15 Hz. All potentials are referenced to decamethylferrocene; $E_{1/2}$ for sublimed ferrocene was 0.55 V. UV–Vis OTTLE data were obtained from a standard cell with a platinum grid electrode.

2.2. CpNi(PPh_3)–C≡C–naphthalimide (**1**)

CpNi(PPh_3)Br (287 mg, 0.62 mmol) and 4-ethynyl-*N*-methyl-naphthalimide (145 mg, 0.62 mmol) were stirred 16 hours in N_2 degassed Et_3N (20 ml) with CuI (2.5 mol%). The dark precipitate obtained was dissolved in CH_2Cl_2 and filtered. Column chromatography (Al_2O_3/CH_2Cl_2) followed by crystallization from CH_2Cl_2/EtOH gave dark brown crystals of **2** (150 mg, 40%). *Anal.* Calc. for $C_{38}H_{28}NNiO_2P$: C, 73.58; H, 4.55; N, 2.26; P, 4.99. Found: C, 73.35; H, 4.58; N, 2.19; P, 4.71%. MS: *m*/*e* 620 (M^+). ^{1}H NMR (*δ*): 3.48 (s, 3H, N–Me), 5.32 (s, 5H, $-C_5H_5$), 7.11 [d (J = 8 Hz), naphth. *H3*], 7.21 [dd (J = 8, 7 Hz), naphth. *H6*], 7.4 (m, 9H, phenyl-*H*), 7.8 [(m, 6H, phenyl-*H*) + naphth. *H5*], 8.25 [d (J = 8 Hz), naphth. *H2*], 8.39 [dd (J = 7, 1 Hz), naphth. *H7*]. ^{13}C NMR (*δ*): 93.2 ($-C_5H_5$), 108.9 [d (J = 46 Hz), Ni–*C*≡C], 118.4 (Ni–C≡*C*). ^{31}P NMR (*δ*): 42.7. IR (KBr): $\nu_{C\equiv C}$ 2074, ν_{CO} 1692, 1648 cm^{-1}; (CH_2Cl_2): $\nu_{C\equiv C}$ 2079, ν_{CO} 1693, 1654 cm^{-1}; (cyclohex/benz): $\nu_{C\equiv C}$ 2084, ν_{CO} 1700, 1663 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} (ε) 304 (18800), 409 (10700), 484 (14400). E_{pa} 0.93 V, I_c/I_a = 0.7 (CH_2Cl_2 versus Fc* = 0.0 V).

2.3. CpFe(dppe)–C≡C–naphthalimide (**2**)

CpFe(dppe)I (97 mg, 0.15 mmol), NH_4PF_6 (29 mg, 0.18 mmol) and 4-ethynyl-*N*-methyl-naphthalimide (44 mg, 0.19 mmol) were heated at 40 °C in N_2 degassed MeOH (6 ml) 8 h. The MeOH was removed under vacuum and the brown vinylidene solid (**2v**) obtained converted to **2** by flash chromatography on (Al_2O_3/CH_2Cl_2). Crystallization from CH_2Cl_2/EtOH gave purple black crystals of **2** (12 mg, 10%). *Anal.* Calc. for $C_{46}H_{37}FeNO_2P_2$: C, 73.32; H, 4.95; N, 1.86; P, 8.22. Found: C, 72.92; H, 5.14; N, 1.95; P, 8.48%. MS: *m*/*e* 754 (MH^+). ^{1}H NMR (*δ*): 2.35, 2.64 [2 × (m, 2H, C_2H_4)], 3.49 (s, 3H, N–Me), 4.39 (s, 5H, $-C_5H_5$), 6.56 [d (J = 8 Hz), naphth. *H3*], 7.15 [dd (J = 8, 7 Hz), naphth. *H6*], 7.3–7.4 (m, 16H, phenyl-*H*), 7.70 [dd (J = 8, 1 Hz), naphth. *H5*], 7.90 (m, 4H, phenyl-*H*), 8.16 [d (J = 8 Hz), naphth. *H2*], 8.38 [dd (J = 7, 1 Hz), naphth. *H7*]. ^{31}P NMR (*δ*): 106.5. IR (KBr): $\nu_{C\equiv C}$ 2037 (sh), 2025, ν_{CO} 1692, 1649 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} (ε) 339 (12800), 544 (14200). $E°$ 0.31 V, I_c/I_a = 1.0 (CH_2Cl_2 versus Fc* = 0.0 V).

2.4. CpRu(dppe)–C≡C–naphthalimide (**3**)

CpRu(dppe)Cl (300 mg, 0.5 mmol), NH_4PF_6 (212 mg, 1.3 mmol) and 4-ethynyl-*N*-methyl-naphthalimide (294 mg, 1.25 mmol) were refluxed in MeOH (20 ml) for 2 h. The MeOH was removed under vacuum and the solid obtained redissolved in CH_2Cl_2 and filtered. Column chromatography (SiO_2) with CH_2Cl_2 eluent removed unreacted parent acetylene; the product eluted with CH_2Cl_2:EtOAc (10%). Crystallization from EtOH gave red crystals of **3** (72 mg, 18%). *Anal.* Calc. for $C_{46}H_{37}NO_2P_2Ru$: C, 69.17; H, 4.67; N, 1.75; P, 7.76. Found: C, 69.20; H, 4.68; N, 1.76; P, 7.99%. MS: *m*/*e* 800 (MH^+). ^{1}H NMR (*δ*): 2.4, 2.7 [2 (br m, 2H, $C_2\underline{H}_4$)], 3.48 (s, 3H, N–Me), 4.90 (s, 5H, $-C_5H_5$), 6.56 [d (J = 8 Hz), naphth. *H3*], 7.16 [dd (J = 8, 7 Hz), naphth. *H6*], 7.2–7.4 (m, 16H, phenyl-*H*), 7.61 [dd (J = 8, 1 Hz), naphth. *H5*], 7.93 (m, 4H, phenyl-*H*), 8.12 [d (J = 8 Hz), naphth. *H2*], 8.36 [dd (J = 7, 1 Hz), naphth. *H7*]. ^{31}P NMR (*δ*): 87.0. IR (KBr): $\nu_{C\equiv C}$ 2046, 2037 (sh), ν_{CO} 1687, 1647 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} (ε) 310 (13200), 493 (16800). $E°$ 0.65 V, I_c/I_a = 0.7 (CH_2Cl_2 versus Fc* = 0.0 V).

2.5. Cp*Ru(dppe)–C≡C–naphthalimide (**4**)

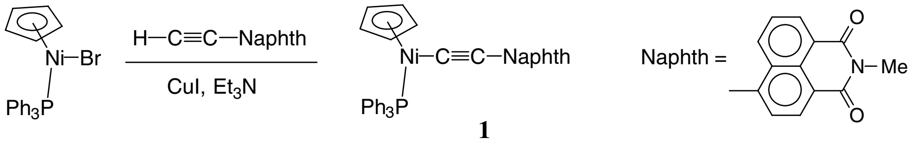
Cp*Ru(dppe)Cl (273 mg, 0.41 mmol), NH_4PF_6 (82 mg, 0.5 mmol) and 4-ethynyl-*N*-methyl-naphthalimide (118 mg, 0.5 mmol) were refluxed in MeOH (60 ml) 2 h. Solvent was removed under vacuum and the solid obtained was loaded dry onto a deactivated neutral alumina column. The column was flushed with toluene and then the product eluted with EtOAc. Crystallization from Et_2O/pentane gave dark red crystals of **4** (114 mg, 32%). *Anal.* Calc. for $C_{51}H_{47}NO_2P_2Ru$: C, 70.49; H, 5.45; N, 1.61; P, 7.13. Found: C, 70.55; H, 5.60; N, 1.60; P, 7.19%. MS: *m/e* 871 (MH^+). ^1H NMR (δ): 1.61 [t ($J = 2$ Hz), 15H, –C_5Me_5), 2.2, 2.7 [2 × (br m, 2H, C_2H_4)], 3.52 (s, 3H, N–Me), 6.80 [d ($J = 8$ Hz), naphth. *H3*], 7.17 [dd ($J = 8$, 7 Hz), naphth. *H6*], 7.2–7.4 (m, 16H, phenyl-*H*), 7.77 [dd ($J = 8$, 1 Hz), naphth. *H5*], 7.93 (m, 4H, phenyl-*H*), 8.23 [d ($J = 8$ Hz), naphth. *H2*], 8.41 [dd ($J = 7$, 1 Hz), naphth. *H7*]. ^{31}P NMR (δ): 81.7. IR (KBr): $\nu_{C\equiv C}$ 2035, 2024, ν_{CO} 1688, 1651 cm^{-1}. UV–Vis (CH_2Cl_2): λ_{max} (ε) 344 (15000), 543 (16800). $E°$ 0.50 V, $I_c/I_a = 1.0$ (CH_2Cl_2 versus Fc* = 0.0 V).

2.6. X-ray data collection, reduction and structure solutions

Crystal data for **1**–**4** are given in Table 1. Crystals of **1** and **2** were obtained from CH_2Cl_2/hexane and CH_2Cl_2/pentane. Those of the ruthenium based compounds **3** and **4** were grown from ethyl acetate/pentane and Et_2O/pentane, respectively. Data were collected at low temperatures on a Bruker SMART CCD diffractometer, processed using SAINT, with empirical absorption corrections applied using SADABS [25]. The structures were solved by direct methods using SHELXS [26] and refined by full-matrix least squares on F^2 using TITAN2000 [27] and SHELXL-97 [28]. Non-hydrogen atoms were assigned anisotropic temperature factors, with hydrogen atoms included in calculated positions. A difference Fourier synthesis following location of all non-hydrogen atoms for **2** revealed a number of additional high peaks which could be assigned to positional disorder in the naphthalene fragment of the naphthalimide unit. The disorder can be described in terms of two, discrete orientations of the naphthalene rings, approximately related through rotation by 180° and a translation of approximately 1 Å in the naphthalimide ring plane, such that the discrete naphthalene fragments shared two common C atoms C3 and C5. The disorder was resolved by refining two unique positions for the remaining C atoms of the naphthalene moieties with their occupancy factors f and f' refined such that $f' = 1 - f$. The final value of f refined to 0.531(5). Following the resolution of the positional disorder, a further high peak remained in the difference Fourier map. This was assigned to the O atom of a water molecule and refinement of the occupancy factor for the atom converged at 0.5. In the final refinement cycles, this occupancy factor was fixed at 0.5 and the atom was refined anisotropically resulting in a significant improvement in R_1. No attempt was made to locate the H atoms of the water solvate.

Table 1
Crystal data and structure refinement for **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{38}H_{28}NO_2PNi$	$C_{46}H_{38}NO_{2.5}P_2Fe$	$C_{46}H_{37}NO_2P_2Ru$	$C_{51}H_{47}NO_2P_2Ru$
Formula weight	620.29	761.56	798.78	868.91
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell dimensions				
a (Å)	21.946(1)	11.7881(12)	10.8093(19)	8.7254(6)
b (Å)	11.825(5)	13.4064(14)	31.018(5)	22.5474(17)
c (Å)	23.43(1)	13.7534(14)	11.9809(19)	21.5817(16)
α (°)	90	116.561(1)	90	90
β (°)	105.324	107.461(1)	112.054(2)	90.470(1)
γ (°)	90	90.515(1)	90	90
V (Å^3)	5865(4)	1828.3(3)	3723.1(11)	4245.7(5)
Z	8	2	4	4
D_{calc} (Mg m^{-3})	1.405	1.383	1.425	1.359
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	0.753	0.543	0.548	0.486
$F(000)$	2576	792	1640	1800
Temperature (K)	168(2)	163(2)	164(2)	173(2)
Crystal size (mm)^3	0.35 × 0.20 × 0.15	0.45 × 0.26 × 0.15	0.24 × 0.19 × 0.01	0.85 × 0.39 × 0.30
θ Range (°)	1.92–26.40	1.76–26.48	1.95–26.49	1.81–26.44
Total reflections	37052	23680	45968	53998
Independent reflections	5991	7435	7547	8654
R_{int}	0.0880	0.0214	0.3417	0.0226
Number of parameters	359	552	470	520
Goodness-of-fit (F^2)	0.956	1.071	0.989	1.032
$R_1[I > 2\sigma(I)]$	0.0656	0.0463	0.0944	0.0377
wR_2 (all data)	0.1799	0.1214	0.1805	0.1058
Residuals (e Å^{-3})	1.555 and −0.708	0.792 and −0.740	1.252 and −0.463	1.959 and −0.463



1

Scheme 1.

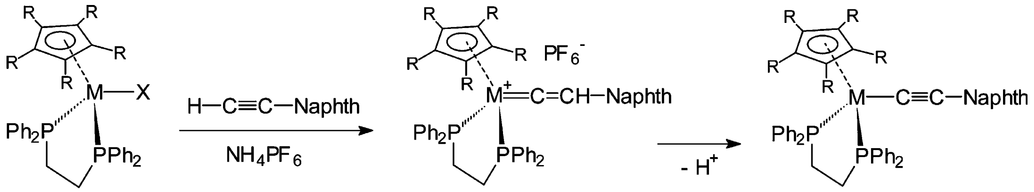
3. Results and discussion

1 was prepared in good yield by reaction of 4-ethynyl-*N*-Me-naphthalimide and $CpNi(PPh_3)Br$ in Et_3N at ambient temperature with a CuI catalyst following the methodology of Bruce et al. [29] (Scheme 1). The acetylide formed precipitates out of the Et_3N solvent, and unlike the parent nickel bromide proved stable to chromatographic work-up. Solutions of **1** were a rich red-orange in contrast to most simple aryl acetylides which are a pale green-yellow [30].

The general preparative route to Group 8 $CpML_2$ (= [M]) alkynes is via the vinylidene salt generated from the reaction of H–C≡C–R with [M]–X and NH_4PF_6 in MeOH. The vinylidene salt is converted to the alkyne by deprotonation, either on alumina [31], with $KOBu^t$ in THF [10], with NaOMe or proton sponge [32]. Thus reaction of CpFe(dppe)I with 4-ethynyl-*N*-Me-naphthalimide in the presence of NH_4PF_6 produced the brown vinylidene salt **2v** in high yield (Scheme 2). An intense purple solution of **2** was prepared by flash chromatography of **2v** on $^iPr_2NH$ deactivated Al_2O_3 with EtOAc eluent. Although the initial yield of crude material was high, significant losses occurred on the column, in solution and during recrystallisation attempts, particularly in chlorinated solvents, which resulted in low yields of pure product. Dark red and purple [Ru] derivatives **3** and **4** were prepared similarly by reaction of CpRu(dppe)Cl and Cp*Ru(dppe)Cl with 4-ethynyl-*N*-Me-naphthalimide in the presence of NH_4PF_6. As with **2**, there were problems attaining pure crystalline samples due to instability of the compounds during chromatography and recrystallisation.

Products **1**–**4** were characterised by microanalysis, NMR and spectroscopic techniques. Proton resonances of all the acetylides show the expected ordering and splitting patterns of a 4-(donor) substituted naphthalimide and confirm the stoichiometry of the compounds. The naphthalimide *H3* of **1**–**4** shows significant shielding when compared to alkyne naphthalimides previously reported [7]. This shielding effect has been previously noted for *ortho* protons of CpFe phenyl acetylides with increasing acceptor strength and is attributed to π-back donation between the metal orbitals and C≡C acetylide group [33]. Cyclopentadienyl ^1H and ^{13}C resonances for **1** fall into the narrow range typical of $CpNi(PPh_3)$-C_2-aryl compounds [13,16,34,35]. The ^{31}P NMR of the phosphine and alkyne $C_{(2)}$ are likewise unremarkable. The carbon shift of the alkyne $C_{(1)}$ varies significantly with acceptor properties of the alkyne substituent. For **1**, $^{13}C_{(1)}$ occurs at 108.9 ppm and compares with the benchmark *p*-nitrophenyl nickel acetylide $C_{(1)}$ of 103.5 ppm [13]. $^{13}C_{(1)}$ exhibits the typical coupling to phosphorus, $^3J_{PC} = 46$ Hz. For the Group 8 [M]–C≡C–naphthalimides, ^1H and ^{13}C NMR of Cp and Cp* rings and ^{31}P NMR resonances, although differing between **2**, **3** and **4** fall within the narrow ranges reported for other [M] acetylides [12,32,33]. The potentially most interesting resonances, the alkyne $C_{(1)}$ carbons, of inherently low intensity and further reduced in height by phosphorus coupling, could not be located. Similarly the alkyne $C_{(2)}$ which generally do not show the P–C coupling and occur in a much narrower range [10] could not be assigned.

$\nu_{C\equiv C}$ energies of **1**–**4** in CH_2Cl_2 solution are included in Table 2. In all cases the vibration occurs at lower energy than the equivalent *p*-NO_2-phenyl analogue indicating a weaker C≡C bond, and consistent with substantial electron delocalisation. This, and the shift to lower energy with increasing solvent polarity, suggest



2-4v

2 M = Fe, R = H
3 M = Ru, R = H
4 M = Ru, R = Me

Scheme 2.

Table 2
IR ($\nu_{C\equiv C}$) of R–C≡C–naphthalimides and related compounds (CH_2Cl_2 solution)

	$\nu_{C\equiv C}$ (cm^{-1})	ε ($mol^{-1}\ cm^{-1}\ L$)
Fc–C≡C–naphth [7]	2200	400
H–C≡C–naphth [7]	2101	6
$CpNi(PPh_3)$–C≡C–naphth (**1**)	2079	1100
$CpNi(PPh_3)$–C≡C–C_6H_4–NO_2 [13]	2091	
CpFe(dppe)–C≡C–naphth (**2**)	2037, 2023	900
CpFe(dppe)–C≡C–C_6H_4–NO_2 [12]	2044	
Cp*Fe(dppe)–C≡C–C_6H_4–NO_2 [10]	2036, 2008	
CpRu(dppe)–C≡C–naphth (**3**)	2047, 2032(sh)	1900
CpRu(dppe)–C≡C–C_6H_4–NO_2 [12]	2056	
Cp*Ru(dppe)–C≡C–naphth (**4**)	2039, 2028	2000

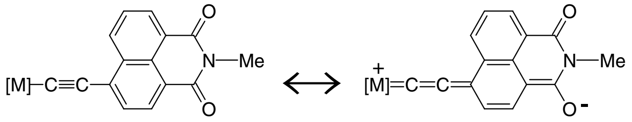


Fig. 1. Acetylide and cumulene configurations.

a contribution of a cumulene form to the ground state structure (Fig. 1). Of note are the twin peaks recorded for **2**–**4**. The splitting also occurs in the solid state (KBr) spectra and is attributed to Fermi coupling. Similar behaviour has been reported for Cp*Fe acetylides in the IR [10] and Raman [20] spectra. Extinction coefficients were calculated for the alkyne stretching vibration and are also shown in Table 2. The high values for compounds **1**–**4** reflect a large change in dipole moment associated with the vibration and are not simply a function of oscillator mass [30].

3.1. Crystal structure *1–4*

The X-ray structures of **1**–**4** were determined and are shown in Figs. 2–5. These representations define the atom numbering schemes used in the following discussion. Selected bond length and angle data are given in Table 3. The naphthalimide fragment in each case is unremarkable. Of more interest is the geometry at the respective metal centre. The Ni atom of 1 has a distorted square pyramidal coordination sphere with the alkyne–naphthalimide residue and the phosphine ligand *cis* to one another. C(15)–Ni(1)–P(1) at 90.21(17)° and distances and angles within the cyclopentadienyl ring and phosphine fragment fall into the expected ranges. The CpFe and CpRu derivatives **2**, **3** and Cp*Ru acetylide **4** are sufficiently similar to be discussed together. A familial resemblance and similarity to $CpNi(PPh_3)$–C≡C–naphthalimide is clear from Figs. 3–5. However, the Fe Group metallocenes **2**–**4** each require an additional pair of electrons in comparison to the Ni complex. These are provided by the additional phosphorus atoms of the bidentate, chelate dppe ligands giving a distorted octahedral coordination geometry at the Fe and Ru atoms with the ligated alkyne C atom and both P atoms of the diphosphine mutually *cis*. As with **1**, the bond length and angle data within the naphthalimide ring systems of **2**–**4** are unremarkable although disorder in the naphthalimide rings of **2** means that data for this system should be treated with caution.

Acetylides **1**–**4** all show an extended C(14)–C(4) distance in comparison with other [M]–C≡C–aryl compounds. This probably reflects the greater steric

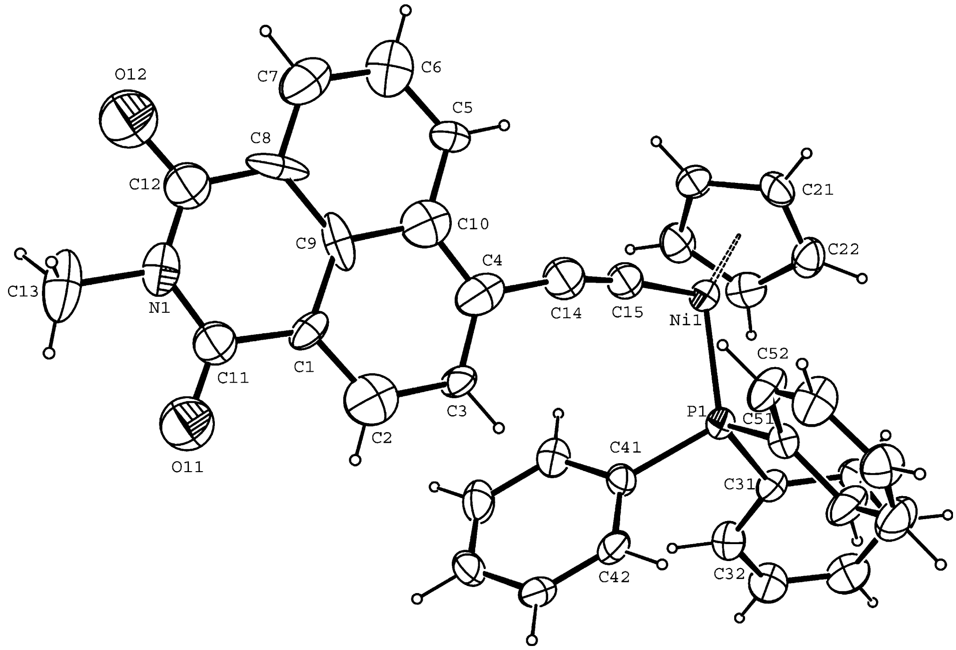


Fig. 2. Perspective view of **1** showing the atom numbering scheme.

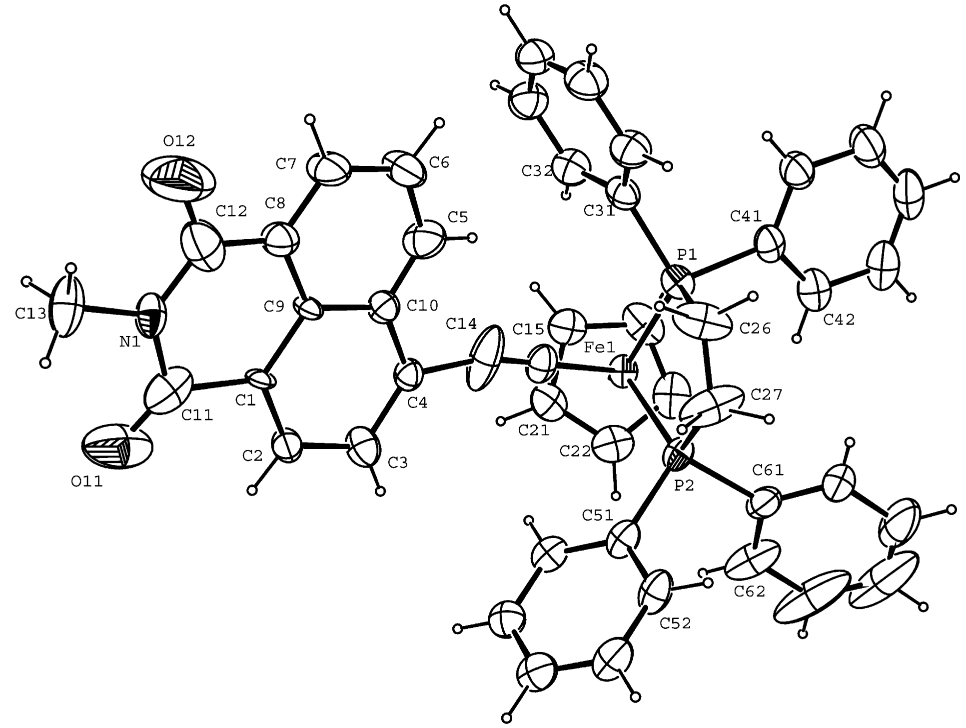


Fig. 3. Perspective view of **2** showing the atom numbering scheme. Only one set of atoms of the disordered naphthalimide unit (occupancy 0.53, see Section 2) are shown.

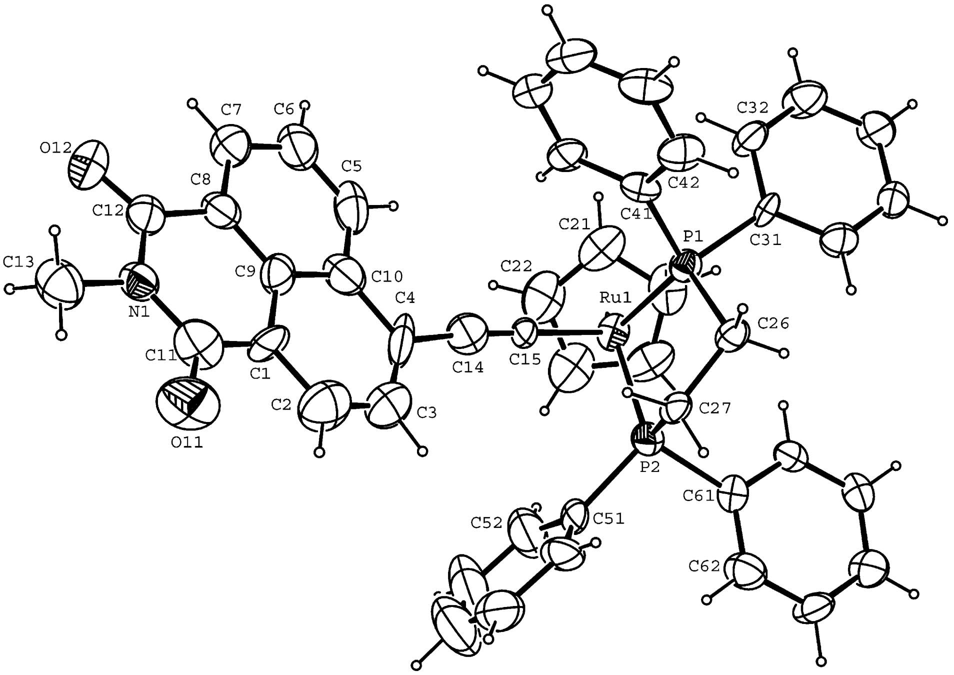


Fig. 4. Perspective view of **3** showing the atom numbering scheme.

demands of the naphthalimide system. The Ni(1)–C(15) bond is short, 1.834(5) Å and C(14)≡C(15) relatively long, 1.220(7) as was observed for CpNi(PPh_3)–C≡C–CHO [16] and CpNi(PPh_3)–C≡C–*p*-NO_2-phenyl [15].

For **2**, Fe(1)–C(15) and C(15)–C(14) at 1.888(3) and 1.208(4) Å are similar to other CpFe(dppe) compounds with electron withdrawing acetylide substituents [33]. **3** shows Ru(1)–C(15) distance at 2.055(9) Å and C(15)–C(14) at 1.085(12) Å similar to the [Ru]–C≡C–*p*-NO_2-phenyl analogue [12] and Cp*RuL_2–C≡C–phenyl [L_2 = dppe, $(PPh_3)_2$] [36,37]. In contrast the Ru(1)–C(15) bond in **4** is significantly shorter and the corre-

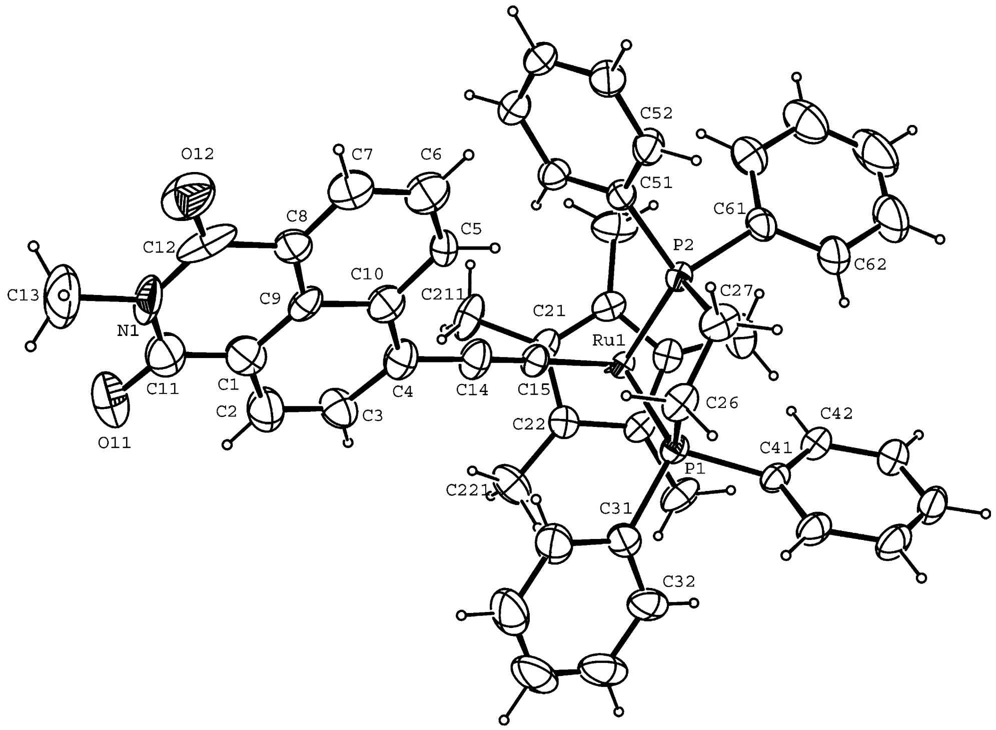


Fig. 5. Perspective view of **4** showing the atom numbering scheme. In all figures for clarity only the first two C atoms of the consecutively numbered cyclopentadiene and phenyl rings and the methyl substituents on the pentamethyl cyclopentadiene ring have been labelled.

Table 3
Selected bond lengths (Å) and angles (°) for **1**–**4**

	1	**2**	**3**	**4**
M(1)–C(15)	1.834(5)	1.888(3)	2.055(9)	1.992(3)
C(15)–C(14)	1.220(7)	1.208(4)	1.085(12)	1.208(4)
C(14)–C(4)	1.532(8)	1.488(7), 1.533(8)[a]	1.496(14)	1.427(4)
M(1)–P(1)	2.1362(16)	2.1827(8)	2.285(3)	2.2636(7)
M(1)–P(2)	–	2.1734(8)	2.282(3)	2.2786(7)
M(1)–C(21)	2.144(5)	2.098(3)	2.249(10)	2.251(3)
M(1)–C(22)	2.134(5)	2.107(3)	2.258(10)	2.230(3)
M(1)–C(23)	2.107(5)	2.105(3)	2.262(9)	2.266(3)
M(1)–C(24)	2.125(5)	2.090(3)	2.230(11)	2.277(3)
M(1)–C(25)	2.079(5)	2.101(3)	2.205(10)	2.262(3)
M(1)–C(15)–C(14)	171.7(5)	177.2(3)	166.0(10)	173.3(3)
C(15)–C(14)–C(4)	167.6(6)	162.6(5), 158.9(5)[a]	162.4(13)	176.5(4)
C(15)–M(1)–P(1)	90.21(17)	85.09(9)	87.9(2)	85.40(8)
C(15)–M(1)–P(2)	–	88.69(8)	80.8(3)	86.08(9)
P(1)–M(1)–P(2)	–	86.50(3)	84.54(9)	83.02(3)

[a] Crystal contains disordered naphthalimide.

sponding C(15)–C(14) vector is longer than in these comparable molecules.

A common feature of all four alkynenaphthalimide systems is the significant deviation from linearity of the acetylide links between the metals and the naphthalimide units. Thus **1** shows significantly greater non-linearity than the eleven previously reported CpNi(PPh_3) acetylides [14–16,34,35] with Ni(1)–C(15)–C(14) at 171.7(5)° and C(15)–C(14)–C(4) at 167.6(6)°.

The Group 8 [M]–C≡C–naphthalimides **2**–**4** exhibit similar variations. The M–C≡C and C≡C–C angles for **4** at 173.3(3) and 176.5(4)° are comparable with the other Cp*Ru compounds reported by Bruce et al. [36,37]. However, the deviations shown by **2** and **3** are remarkably different from their [M]–C≡C–*p*-NO_2-phenyl analogues. Thus for **2**, while Fe(1)–C(15)–C(14) at 177.2(3)° is of similar magnitude to the Fe–C≡C angle of 178.7(8)° for CpFe(dppe)–C≡C–*p*-NO_2-phenyl [33], the C(15)–C(14)–C(4) angles of 162.6(5)° and 158.9(5)° of the disordered naphthalimide are significantly lower than those for the nitrophenyl compound, 173.2(9)°. For **3**, Ru(1)–C(15)–C(14) and C(15)–C(14)–C(4) angles of 166(1)° and 162.4(13)° compare with 177.4(3) and 176.7(3) for CpRu(dppe)–C≡C–*p*-NO_2-phenyl [12].

A common feature of the solid state chemistry of naphthalimide derivatives is the occurrence of offset π-stacking interactions involving the naphthalimide rings [7,38]. There is good evidence for comparable π-stacking interactions for both **1** and **2**, with interplanar separations in the range 3.44–3.48 Å for **1** and 3.37–3.41 Å for **2** [39] and displacement angles in the range 18.8–20.2° for **1** and 25.4–31.4° for **2** [40]. In sharp contrast, there is no evidence for any degree of stabilisation of the solid state structures of **3** or **4** by way of π-stacking interactions, despite the structural similarities between them. Indeed the only intermolecular contacts of note in these structures are weak non-classical H-bonding interactions involving the O atoms of the naphthalimide units.

3.2. Spectroelectrochemistry

1 undergoes a partially reversible one-electron oxidation process in CH_2Cl_2 associated with the Ni^{II}/Ni^{III} couple with $I_c/I_a \sim 0.7$. In acetonitrile, the nickel oxidation step becomes completely irreversible; the explanation for this is discussed in detail elsewhere [30]. E_{pa} 0.93 V (Fc* = 0.0 V) is consistent with a strongly electron withdrawing substituent on the CpNi alkyne [13,30]. The naphthalimide moiety undergoes an irreversible reduction ca. −1.0 V. The Group 8 metal acetylides **2**–**4** undergo a similar one-electron oxidation in CH_2Cl_2 associated with the $M^{II/III}$ couple; the ruthenium compounds **3** and **4** show an irreversible second anodic process at $E_{pa} \sim 1.3$ V. Ease of oxidation decreases on replacing Fe with Ru, but predictably becomes easier again for the methylated Cp derivative **4**. The [M]–C≡C–naphthalimides are consistently 0.16 V more difficult to oxidise than [M] phenylacetylides, but on a par with the stronger acceptor nitrophenylacetylides. The I_c/I_a ratios resemble those reported for other [M] acetylides [12,32,33].

UV–Visible data for **1**–**4** are given in Table 4 and a representative spectrum, that of **2** shown in Fig. 6. All show a high intensity band between 300 and 350 nm ($\varepsilon \sim 13000$) with vibrational structure characteristic of a naphthalimide π–π* transition. More significantly the group 8 [M]-acetylides exhibit another strong but lower energy band at ca. 500 nm ($\varepsilon \sim 15000$). This is close to the intensity of, but slightly lower in energy than the charge transfer band reported for enamine-donor naphthalimide-acceptor compounds [7]. The absorption, broad in ethanol solution, resolves into two λ_{max} in less polar solvents. The accompanying blue shift fits with an assignment to a MLCT transition. Why there should be two transitions is uncertain. The related Cp*Fe- and CpFe-*p*-nitrophenyl acetylides [10,33] are only reported as having one band, albeit broad, in the 400–800 nm region. The energy of the MLCT bands for **2**–**4** are the lowest reported for Group 8 [M] arylacetylides and diminish in the order **3** > **4** > **2**, a trend that matches the observed $[M]^{II/III}$ oxidation potential. Spectra of the CpNi acetylide **1** show evidence of two CT bands in CH_2Cl_2 at 409 ($\varepsilon = 11000$) and 484 nm ($\varepsilon = 14000$). Unlike the Group 8 metal compounds these remain clearly resolved in ethanol. These are the lowest energy transitions reported for a CpNi acetylide.

Table 4
Electronic spectra (charge transfer bands) for **1**–**4**

	CT bands (nm)	
	Hexane	Ethanol
1	400, 465	415, 489
2	496, 560	562
3	460, 491	501
4	482, 518	545

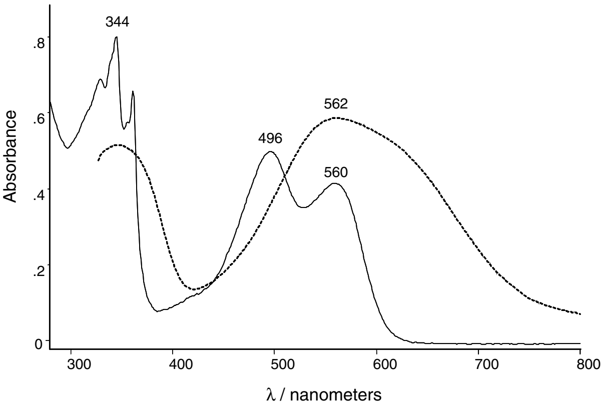


Fig. 6. Electronic spectra of **2**, (–) hexane, (· · ·) ethanol.

The electronic absorption of the oxidised CpFe acetylide **2** was obtained by performing an oxidation in an OTTLE cell. The resultant spectra (Fig. 7) showed clean isosbestic points and reversal of the cell potential regen-

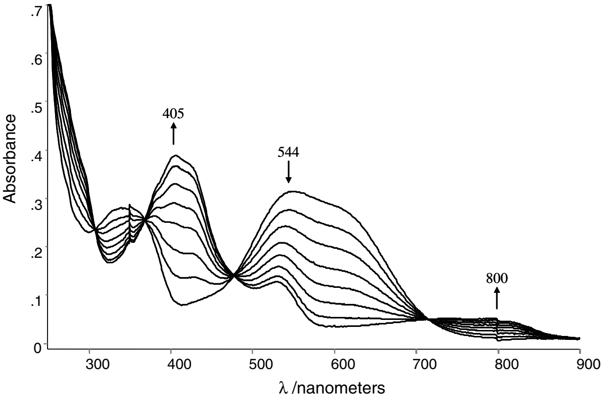


Fig. 7. OTTLE spectra of **2** (0–0.3 V, CH_2Cl_2, 0.1 M $TBAPF_6$).

erated the starting spectrum. Upon oxidation of Fe^{II} to Fe^{III} the MLCT transition/s at ~550 nm disappears, replaced by a band s at 405 nm and weak broad band in the NIR at 800 nm. This type of NIR absorption is characteristic of dyads where a Fc^+–C≡C or Fc^+–C=C group is linked to a π donor [41], including naphthalimide [7] and is ascribed to a $Fc^+ \leftarrow \pi$-donor LMCT. The oxidised dyad $\mathbf{2}^+$ provides the first example of a similar LMCT NIR bands for a [M]–C≡C complex with the naphthalimide acting as the π-donor in the excited state. The energy of the LMCT for $\mathbf{2}^+$ of 12 500 cm^{-1} is high compared to polyaromatic donors such as anthracene (8900 cm^{-1}) but identical to that in Fc–C≡C–naphthalimide [7]. A detailed analysis of the NIR LMCT are given elsewhere [42].

4. Conclusions

Compounds **1**–**4** provide further examples of donor–acceptor arrays in which the metal half-sandwich moiety is acting as the donor. In the dyads the naphthalimide is a strong acceptor on a par with the previously reported [M]–C≡C–*p*-NO_2-phenyl compounds. The latter possess interesting NLO properties and it is expected that this will also be the case for **1**–**4**. The intense $\nu_{C\equiv C}$ at low energy and significant non-linearity in the X-ray structures indicate some cumulene or vinylidene character to the acetylide link. All neutral dyads show an intense band in the visible spectrum due to a MLCT transition, and upon oxidation, the interesting NIR band due to a naphthalimide (π) → C≡C–[M] LMCT in the excited state. Absorption of NIR radiation is of technological significance [43] and it should be possible to tune the energy and intensity of the absorption in these acetylide dyads by appropriate substitution around the metal centre or naphthalimide component.

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