

Cyanoacetylenes and cyanoacetylides: versatile ligands in organometallic chemistry

Richard L. Cordiner, Deborah Corcoran, Dmitri S. Yufit, Andrés E. Goeta,
Judith A. K. Howard and Paul J. Low*

Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE.
E-mail: p.j.low@durham.ac.uk

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The nitrile like lone pair of the cyanoacetylene $\text{PhC}\equiv\text{CC}\equiv\text{N}$ (**1**) has been found to coordinate readily to the $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment, to give $[\text{Ru}(\text{N}\equiv\text{CC}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ (**2**) which may be considered as an “extended” derivative of the more common benzonitrile complex $[\text{Ru}(\text{N}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ (**3**). Reaction of **1** with $[\text{Co}_2(\text{CO})_6(\text{dppm})]$ readily forms the μ, η^2 complex $[\text{Co}_2(\mu, \eta^2\text{-PhC}_2\text{C}\equiv\text{N})(\text{CO})_4(\text{dppm})]$ (**4**), which reacts with $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ to give the mixed metal species $[\{\text{Co}_2(\mu, \eta^2\text{-PhC}_2\text{C}\equiv\text{N})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}(\text{CO})_4(\mu\text{-dppm})\}]\text{PF}_6$ (**5**). The $\eta^1(\text{N})$ bonded $\text{PhC}\equiv\text{CC}\equiv\text{N}$ ligand is labile, being displaced by NCMe at ambient temperature to afford $[\text{Ru}(\text{NCMe})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$, or by tcne to give *trans*- $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-tcne})]\text{PF}_6$ (**9**). The metallocyanoacetylide $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$ (**6**) was prepared by lithiation (BuLi) of $[\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}]$ followed by treatment with PhOCN . Coordination of the metal fragments $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ or $\text{Fe}(\text{dppe})\text{Cp}$ to the N terminus in **6** occurs readily to give the homo- or hetero-bimetallic cations $[\{\text{Cp}(\text{PPh}_3)_2\text{Ru}\}(\mu\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{ML}_2\text{Cp}\}]^+$, which were isolated as the PF_6^- salts $[\text{ML}_2\text{Cp} = \text{Ru}(\text{PPh}_3)_2\text{Cp}$ (**7**); $\text{Fe}(\text{dppe})\text{Cp}$ (**8**)]. The crystal structures of **2–5**, **7** and **9** are reported. The electrochemical response of these complexes suggests there are considerable electronic interactions between the heterometallic end-caps in **8** through the polarised C_3N bridge.

Introduction

Cyanoacetylenes $\text{RC}\equiv\text{CC}\equiv\text{N}$ offer both an alkyne- π system and a nitrile-like lone pair for bonding to metal centres and should be useful in the assembly of multi-metallic complexes. The cyanoacetylene moiety, $\text{RC}\equiv\text{CC}\equiv\text{N}$, also bears a number of close structural and electronic relationships with nitriles, $\text{RC}\equiv\text{N}$, and the diyne anion, $[\text{RC}\equiv\text{CC}\equiv\text{C}]^-$ and comparisons of the chemistry of the cyanoacetylide anion $[\text{C}\equiv\text{CC}\equiv\text{N}]^-$ with that of the ubiquitous cyanide ligand would be interesting. However, somewhat surprisingly, the coordination chemistry of cyanoacetylenes and the cyanoacetylide ligand has not been thoroughly developed.

In very early work, the alkyne moiety in cyanoacetylene was found to coordinate in η^2 -fashion following reaction with $[\text{IrCl}(\text{CO})(\text{PPh}_3)_2]$ and nickelocene,¹ while related η^2 -complexes of $\text{RC}\equiv\text{CC}\equiv\text{N}$ systems ($\text{R} = \text{H}$, CN , $\text{Fe}(\text{CO})_2\text{Cp}$) were prepared in complimentary studies.² The formation of σ -vinyl complexes *via* insertion of cyanoacetylene into metal-hydride or metal-sulfur bonds has also been described.³

Simple $\eta^1(\text{C})$ - and $\eta^1(\text{N})$ -bonded cyanoacetylide complexes are rare. Oxidative addition of dicyanoacetylene to $[\text{Pt}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2]$ afforded $[\text{Pt}(\text{CN})(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2]$,⁴ while $[\text{Fe}(\text{SMe})(\text{CO})_2\text{Cp}]$ reacts with $\text{HC}\equiv\text{CC}\equiv\text{N}$ to afford $[\text{Fe}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{CO})_2\text{Cp}]$ together with various products derived from insertion of the cyanocarbon into the Fe-S bond.⁵ Complexes containing multiple $\eta^1\text{-C}\equiv\text{CC}\equiv\text{N}$ ligands have been prepared from the reaction of $[\text{Co}(\text{PPh}_3)_2\text{Cp}]$ with $\text{HC}\equiv\text{CC}\equiv\text{N}$, which afforded the bis(acetylide) $[\text{Co}(\text{C}\equiv\text{CC}\equiv\text{N})_2(\text{PPh}_3)_2\text{Cp}]$ together with the vinylacetylide $[\text{Co}(\text{C}\equiv\text{CC}\equiv\text{N})\{\text{CH}=\text{CH}(\text{CN})\}(\text{PPh}_3)_2\text{Cp}]$,⁶ and from $[\text{NiEt}_4][\text{MCl}_4]$ ($\text{M} = \text{Ni}$, Pd , Pt) with $\text{Me}_3\text{SnC}\equiv\text{CC}\equiv\text{N}$, which afforded $[\text{NiEt}_4][\text{M}(\text{C}\equiv\text{CC}\equiv\text{N})_4]$.⁷ The coordinating ability of the nitrogen lone-pair from the cyanoacetylide ligand is relatively unexplored. The coordination complexes $[\text{Ru}(\text{N}\equiv\text{CC}\equiv\text{CR})(\text{tpy})(\text{bpy})]\text{PF}_6$ ($\text{tpy} = 1,2,4\text{-tripyridine}$, $\text{bpy} = 2,2'\text{-bipyridine}$), which were characterised on the basis of elemental analysis, electronic spectroscopy and electrochemical (cyclic voltammetry) methods, contain the only examples of $\eta^1(\text{N})$ bonded cyanoacetylene ligands reported to date.⁸

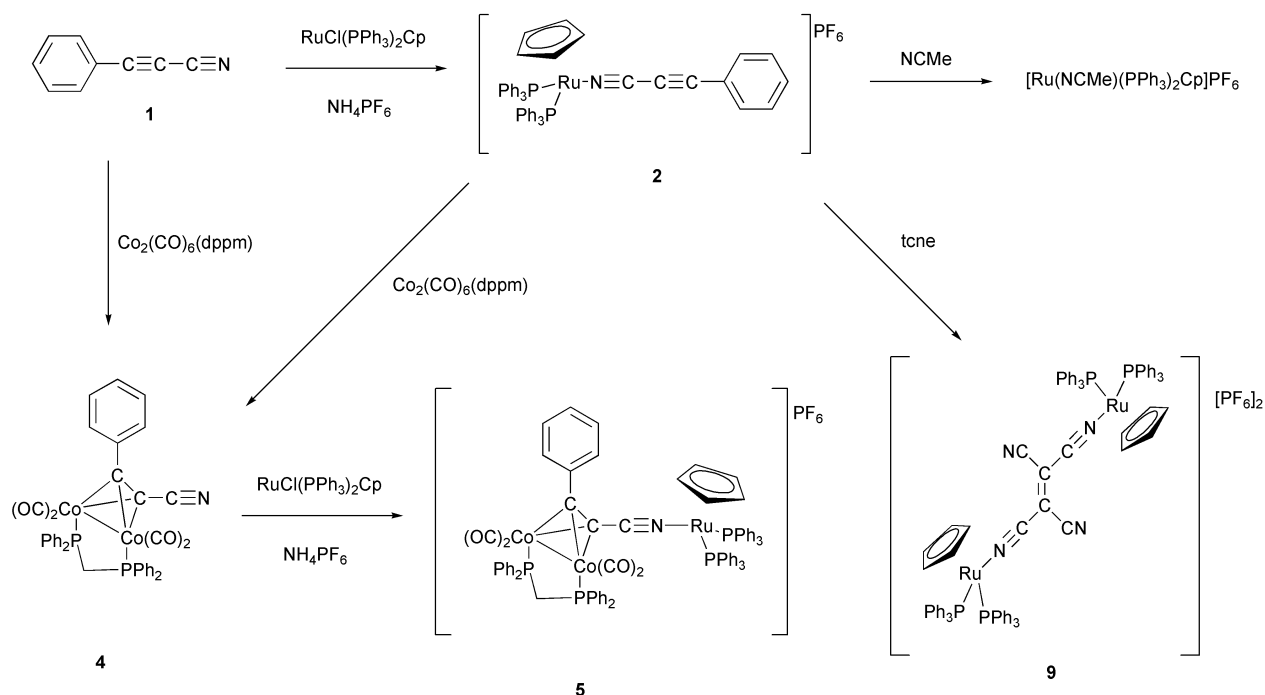
As part of our interest in the preparation and properties of metal complexes containing unsaturated ligands,⁹ we have undertaken a study of the coordination chemistry of the simple cyanoacetylene $\text{PhC}\equiv\text{CC}\equiv\text{N}$, and the metallocyanoacetylide $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$. We now report the synthesis and molecular structures of a series of cyanoacetylene and cyanoacetylide complexes *via* simple reaction schemes, and preliminary reactivity and electrochemical studies.

Results and discussion

Synthesis

Treatment of a solution of $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ in methanol with $\text{PhC}\equiv\text{CC}\equiv\text{N}$ (**1**) and the halide abstracting agent NH_4PF_6 resulted in the formation of a bright yellow solution, from which $[\text{Ru}(\text{NCC}\equiv\text{CPh})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ (**2**) could be isolated as bright yellow crystals in good yield (Scheme 1). The complex salt, which has the obvious chemical and structural analogies with the benzonitrile complex $[\text{Ru}(\text{NCPh})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ (**3**),¹⁰ was characterised by the usual spectroscopic data, which included sharp resonances in the NMR spectra at δ 4.52 (^1H) and 84.90 (^{13}C) from the cyclopentadienyl ligand. The acetylenic carbons of the cyanoacetylene ligand were observed as singlets at δ 115.88 and 116.63 in the ^{13}C NMR spectrum. In the ^{31}P NMR spectrum, resonances at δ 41.86 and -143.02 ($J_{\text{PF}} = 713$ Hz) were assigned to the phosphine ligands of the complex and the PF_6^- counter ion, respectively. The complex gave rise to an intense isotopic envelope from the complex cation at m/z 818 and the $[\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$ fragment ion was observed at m/z 691 in the positive ion electrospray mass spectrum (ES(+)-MS). The IR spectrum contained a relatively strong $\nu(\text{C}\equiv\text{C})$ absorption band at 2141 cm^{-1} , which may be compared with that of the free ligand at 2145 cm^{-1} , but no absorption arising from the coordinated nitrile moiety was detected.

Coordination to the alkyne-like π -system in $\text{PhC}\equiv\text{CC}\equiv\text{N}$ occurred readily upon reaction with the known alkyne sequestering agent $[\text{Co}_2(\text{CO})_6(\text{dppm})]$ to give the dark red complex $[\text{Co}_2(\mu, \eta^2\text{-PhC}_2\text{C}\equiv\text{N})(\text{CO})_4(\text{dppm})]$ (**4**) (Scheme 1). In addition to the NMR resonances arising from the aromatic groups, the



Scheme 1

complex exhibited the usual doublet of triplet resonances for the CH_2 group of the dppm ligand at δ 3.15 and 3.49 in the ^1H NMR spectrum. The ^{13}C NMR spectrum was characterised by a triplet resonance from the dppm methylene carbon at δ 36.58 ($J_{\text{CP}} = 21$ Hz). The carbon nuclei of the Co_2C_2 cluster core were found as triplets at 97.96 ($J_{\text{CP}} = 18$ Hz) and 123.55 ($J_{\text{CP}} = 3$ Hz). The IR spectrum was dominated by the strong $\nu(\text{CO})$ bands between 1960–2037 cm^{-1} , with a weaker $\nu(\text{CN})$ band at 2156 cm^{-1} . The ES(+)-MS contained ions at m/z 1504 ($[2\text{M} + \text{Na}]^+$) and 764 ($[\text{M} + \text{Na}]^+$).

With examples of cyanoacetylene ligands in both the $\eta^1(\text{N})$ and $\eta^2(\text{alkyne})$ motifs established, we attempted to construct a multi-metallic complex which featured both bonding modes. The reaction of **2** with $[\text{Co}_2(\text{CO})_8(\text{dppm})]$ resulted in the formation of a dark red solution from which only **4** could be isolated. However, when **4** was allowed to react with $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ in the presence of NH_4PF_6 , a bright red solution was obtained, from which $[\text{Co}_2(\mu\text{-}\eta^2\text{-PhC}_2\text{C}\equiv\text{N}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\})(\text{CO})_4(\text{dppm})]\text{PF}_6$ (**5**) was isolated as a brick-red powder (Scheme 1). The composition of the complex was established spectroscopically while careful recrystallisation at low temperature afforded red cube-shaped crystals of **5**.

The ^1H and ^{13}C NMR spectra of **5** clearly indicated the formation of the heterometallic species, with sharp singlets at δ 4.30 (^1H) and 84.34 (^{13}C) together with unresolved multiplet resonances centred at 3.28 (^1H), and 35.84 (^{13}C) confirming the presence of both Cp and dppm ligands. The IR spectrum contained the signature pattern from the carbonyl ligands but the $\nu(\text{CN})$ band was not observed. The mass spectrum was consistent with the suspected bimetallic composition, and the complex cation was observed as an isotopic envelope centred at m/z 1431.

As a $\mu\text{-}\eta^1(\text{C}),\eta^1(\text{N})$ ligand, the cyanoacetylide anion could be expected to transmit electronic information between metal centres located at the C and N termini in much the same way as the $\mu\text{-CN}$ ligand.¹¹ However, the synthetic procedures for the preparation of transition metal cyanoacetylide complexes reported to date require the use of cyanoacetylene or dicyanoacetylene, both of which are volatile compounds prone to rapid polymerisation, or trialkyltin substituted cyanoacetylenes. The limited availability of $\text{M}(\text{C}\equiv\text{CC}\equiv\text{N})\text{L}_n$ complexes has precluded a detailed examination of this chemistry to date. We chose to explore the possibility of cyanating a terminal acetylide ligand directly as a simple synthetic route to these complexes.

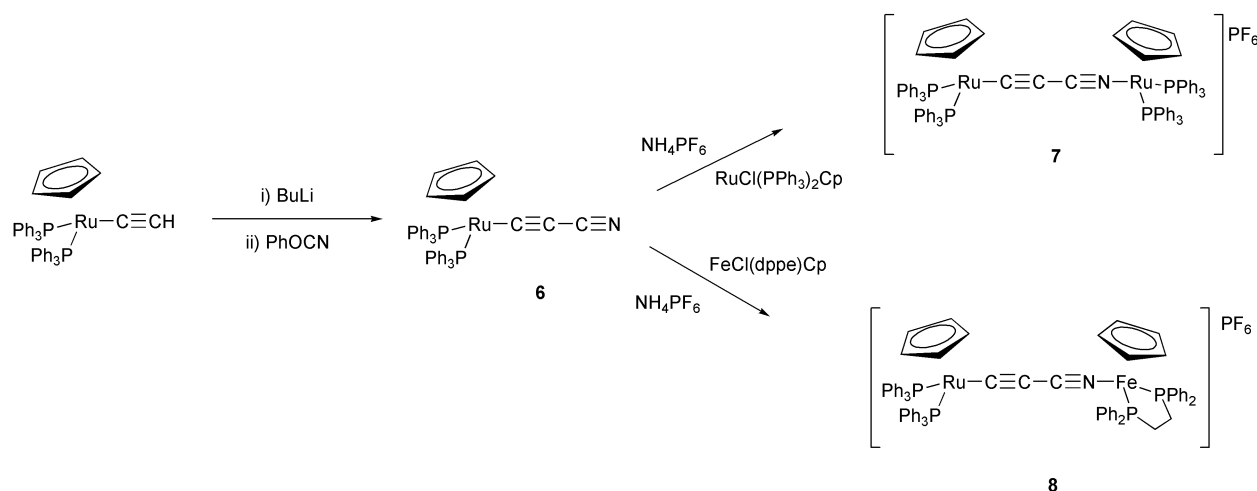
Sequential treatment of $[\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}]$ with BuLi, to generate the intermediate lithiated species $[\text{Ru}(\text{C}\equiv\text{CLi})(\text{PPh}_3)_2\text{Cp}]$, and phenylcyanate (PhOCN) afforded $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$ (**6**) in good yield (65%) (Scheme 2). In addition to the molecular ion in the ES(+)-MS (m/z 764) and Cp resonances in the ^1H and ^{13}C NMR spectra (δ_{H} 4.37, δ_{C} 86.68), three ^{13}C resonances at 121.64, 107.75 and 83.08 ppm were observed, and assigned to the carbons of the C_3N ligand. In the IR spectrum (Nujol), strong $\nu(\text{C}\equiv\text{C})$ (2000 cm^{-1}) and $\nu(\text{C}\equiv\text{N})$ (2180 cm^{-1}) bands were observed. The product decomposes slowly in solution, but was found to be stable for several months if kept as a solid in a freezer.

Reaction of **6** with $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ and NH_4PF_6 in methanol resulted in a smooth conversion to the binuclear species $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-}\eta^1(\text{C}),\eta^1(\text{N})\text{-C}\equiv\text{CC}\equiv\text{N})]\text{PF}_6$ (**7**), which precipitated from the reaction mixture as a bright yellow powder (Scheme 2). The spectroscopic data were in agreement with the proposed formulation, and included an ion in the ES(+)-MS arising from the complex cation (m/z 1432), two Cp resonances in each of ^1H (4.47 and 4.35 ppm) and ^{13}C (87.55 and 83.64 ppm) NMR, two phosphine resonances in the ^{31}P NMR, in addition to the septet expected from the PF_6^- counter ion and the characteristic $\nu(\text{C}\equiv\text{C})$ (1985 cm^{-1}) and $\nu(\text{C}\equiv\text{N})$ (2196 cm^{-1}) bands in the IR spectrum.

An analogous procedure with $[\text{FeCl}(\text{dppe})\text{Cp}]$ led to the formation of the heterobimetallic species $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}(\mu\text{-}\eta^1(\text{C}),\eta^1(\text{N})\text{-C}\equiv\text{CC}\equiv\text{N})\{\text{Fe}(\text{dppe})\text{Cp}\}](\text{PF}_6)$ (**8**) as a pale, reddish-brown powder (Scheme 2). ES(+)-MS confirmed the presence of the complex cation (m/z 1261) and two Cp resonances were visible in both the ^1H and ^{13}C NMR spectra (4.24 and 4.20 ppm, and 87.22 and 79.16 ppm respectively). Both $\nu(\text{C}\equiv\text{C})$ (1986 cm^{-1}) and $\nu(\text{C}\equiv\text{N})$ (2194 cm^{-1}) bands were clearly visible in the IR spectrum. The relative differences in the IR spectra of the mononuclear complex **6** and binuclear **7** and **8** are complicated by kinematic effects, as commonly observed in $\mu\text{-CN}$ systems,¹² making qualitative judgements about the underlying electronic structure based upon this data alone difficult.

Reactivity

By way of assessing the stability of the metal– NC_3R linkage, a sample of **2** was treated with one equivalent of NCMe in



CDCl_3 . Over the course of 24 h, the Cp signal due to **2** slowly diminished, whilst a new resonance from $[\text{Ru}(\text{NCMe})(\text{PPh}_3)_2\text{Cp}]^+$ grew, the assignment of which was verified by comparison with an authentic sample (Scheme 1). The metallocyanoacetylide “ligand” $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$ was more difficult to displace and there was no evidence of reaction between **7** and NCMe (in CDCl_3) at room temperature after 72 h.

Metal acetylide, diynyl and polyynediyl complexes are known to react readily with tetracyanoethylene (tcne) under mild conditions to afford $[2 + 2]$ cyclisation products, which ring open to afford highly conjugated cyanocarbon ligands.¹³ The tcne ligand has also been used as a $\eta^1(\text{N})$ bonding ligand, and reactions with oxidisable metal fragments often give products derived from charge transfer processes with the ligand best formulated as a tcne radical or dianion.¹⁴ Reaction of **2** with tcne at ambient temperature resulted in a rapid change in the colour of the solution from yellow to dark blue, and after work-up the dark blue complex $\text{trans}-[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-tcne})][\text{PF}_6]_2$ (**9**) was obtained (64%) (Scheme 1). The spectroscopic data were inconclusive with regards the formation of the mononuclear species $[\text{Ru}(\text{tcne})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$, or the *cis* or *trans* forms of the binuclear species **9**. Recrystallisation from CHCl_3 afforded sapphire blue crystals suitable for a single-crystal X-ray diffraction study, which served to conclusively identify the compound and the results of which are described in more detail below. The IR spectrum of **9** showed the expected $\nu(\text{C}\equiv\text{N})$ (2139 cm^{-1}) with a shoulder at 2164 cm^{-1} . The deep blue colour of this compound ($\lambda_{\text{max}}\ 650\text{ nm}$, $\epsilon\ 2900\text{ M}^{-1}\text{ cm}^{-1}$) can be attributed to a charge transfer transition. The ground state molecular structure (see below) is consistent with a description of this compound in terms of a simple dicationic tcne coordination product containing a neutral tcne ligand and the poorly oxidisable $\text{Ru}(\text{PPh}_3)_2\text{Cp}^+$ fragment.

Molecular structures

The molecular structures of **2**, the closely related benzonitrile complex **3**,¹⁰ the cobalt clusters **4** and **5**, and the binuclear complexes **7** and **9** have been determined. Crystallographic details are summarised in Table 1, and selected bond lengths and angles are given in Tables 2 and 3.

Complexes $[\text{Ru}\{\text{NC}(\text{C}\equiv\text{C})_n\text{Ph}\}(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ [$n = 0$ (**3**), **1** (**2**)]

The complex cations are illustrated in Fig. 1 (**2**) and Fig. 2 (**3**). The $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragment is similar in each case, and while the Ru–P bond lengths [$2.352(1)$ and $2.355(1)\text{ Å}$ in **2**; $2.334(1)$ and $2.335(1)\text{ Å}$ in **3**] are at the long end of the range usually encountered, the geometry is generally unremarkable. The differences in the N(1)–C(2) bond lengths in **2** and **3** fall within the limits of precision, while the Ru(1)–N(1) separation in **2** is

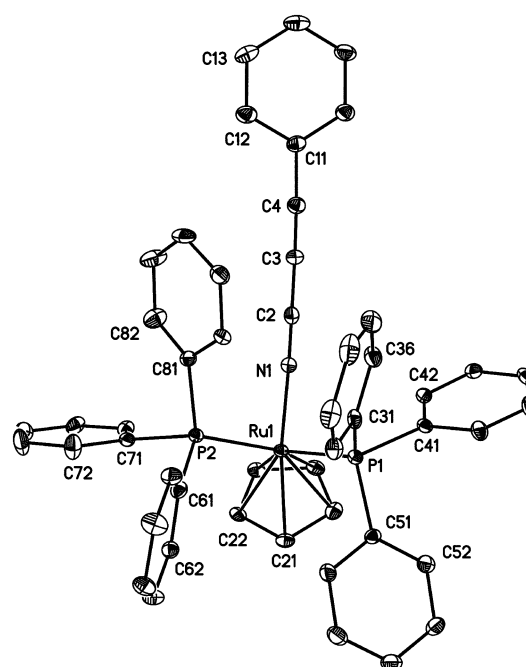


Fig. 1 Molecular structure of the cation of **2**, showing the atom labelling scheme. In this and subsequent Figures, H-atoms have been omitted for clarity.

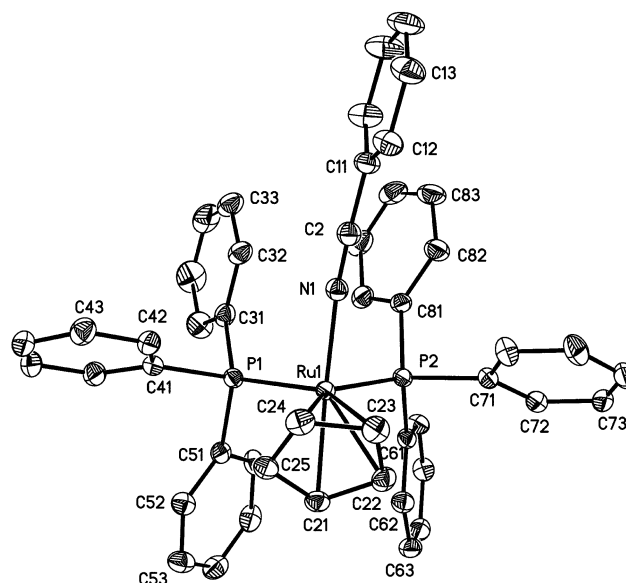
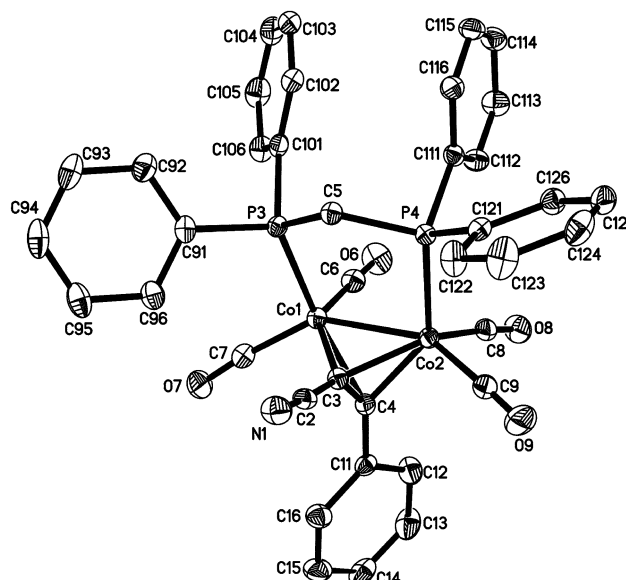
significantly shorter than that in **3** [$2.002(4)$; $2.037(1)\text{ Å}$]. Some other subtle variations arising from the differing steric properties of the cyanocarbon ligands are apparent. For example, while the Ru–N(1)–C(2)–C(3)–C(4) fragment in **2** is essentially linear, the Ru(1)–N(1)–C(2) angle in **3** is $171.7(1)^\circ$, no doubt a consequence of steric interactions between the phenyl rings of the benzonitrile and phosphine ligands. The relative orientation of the C(11)–C(16) phenyl group in **3**, which appears to be dictated by the constraints of the phenyl groups on the PPh_3 ligands, is approximately orthogonal to that found in the solid state structure of **2**.

Complexes $[\text{Co}_2(\mu\text{-}\eta^2\text{-PhC}_2\text{C}\equiv\text{N})(\text{CO})_4(\text{dppm})]$ (**4**) and $[\text{Co}_2(\mu\text{-}\eta^2\text{-PhC}_2\text{C}\equiv\text{N}\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\})(\text{CO})_4(\text{dppm})]\text{PF}_6$ (**5**)

The structures of **4** (Fig. 3) and **5** (Fig. 4) indicate the coordination of the cyanacetylene ligand to the dicobalt fragment *via* the alkyne moiety in the usual μ, η^2 fashion. In addition, Fig. 4 clearly demonstrates the capacity for the nitrile and alkyne moieties to simultaneously coordinate different metal fragments. The structural parameters are not unusual, although we note that the Co(1)–Co(2) [$2.4651(3)\text{ Å}$] and C(3)–C(4) [$1.370(2)\text{ Å}$] bond lengths in **4** are respectively at the shorter and

Table 1 Crystallographic details for the structures of **2–5**, **7** and **9**

	2	3	4	5	7	9
Formula	$C_{50}H_{40}NP_3F_6Ru_0.7CH_2Cl_2$	$C_{48}H_{40}NP_3F_6Ru$	$C_{38}H_{27}NO_4P_2Co_2$	$C_{39}H_{42}NO_4P_3F_6Co_2Ru_2.2CH_2Cl_2$	$C_{85}H_{70}NP_3F_6Ru_2.3CH_2Cl_2$	$C_{44}H_{35}N_2P_3F_6Ru_2CHCl_3$
M_r	1022.26	938.79	741.41	1746.93	1831.19	1019.09
$a/\text{\AA}$	10.3647(5)	15.6383(4)	16.5859(8)	11.7464(7)	13.1761(5)	10.0332(4)
$b/\text{\AA}$	35.1128(16)	13.9146(3)	10.8413(5)	17.3929(10)	45.8822(17)	20.3162(9)
$c/\text{\AA}$	12.9836(6)	20.1345(5)	18.4223(9)	20.18925(13)	14.4799(6)	20.6003(9)
α°	90	90	90	71.121(3)	90	90
β°	104.145(2)	108.921(1)	95.558(1)	76.244(2)	112.92(1)	101.213(2)
γ°	90	90	90	73.405(2)	90	90
$V/\text{\AA}^3$	4581.9(4)	4144.5(2)	3297.0(3)	4003.4(4)	8062.9(5)	4118.9(3)
$D_c/\text{Mg m}^{-3}$	1.482	1.505	1.494	1.449	1.509	1.643
T/K	120(2)	120(2)	110(2)	120(2)	120(2)	120(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
Z	4	4	4	2	4	4
μ/mm^{-1}	0.590	0.557	1.146	0.892	0.734	0.757
Reflections collected	24223	44123	25776	46232	61477	35233
Independent reflections (R_{int})	9181 (0.0465)	10287 (0.0171)	9562 (0.0373)	19669 (0.0386)	16576 (0.0379)	10935 (0.0709)
Final R indices (all data)	$R_1 = 0.0898$, $wR_2 = 0.1395$	$R_1 = 0.0260$, $wR_2 = 0.0602$	$R_1 = 0.0449$, $wR_2 = 0.0814$	$R_1 = 0.0706$, $wR_2 = 0.1486$	$R_1 = 0.0582$, $wR_2 = 0.1029$	$R_1 = 0.1195$, $wR_2 = 0.2672$

**Fig. 2** Molecular structure of the cation in **3**, showing the atom labelling scheme.**Fig. 3** The structure and numbering scheme of compound **4**.

longer ends of the range of bond lengths normally associated with $[\text{Co}_2(\mu, \eta^2\text{-alkyne})(\text{CO})_4(\text{dppm})]$ complexes. The bond lengths along the $\text{Ph-C}_2\text{CN}$ chains in **4** and **5** are identical, and there are no differences in bond angles of significance. The bonds between C(2), C(3) and C(4) in the cobalt complexes **4** and **5** are elongated in comparison to those in **2**, a fact which is attributed to the difference in hybridisation at C(3) and C(4).

More interesting are the torsion angles C(6)–Co(1)–Co(2)–C(8) $[-17.86(7)^\circ]$, C(7)–Co(1)–Co(2)–C(9) $[-36.1(1)^\circ]$ and P(3)–Co(1)–Co(2)–P(4) $[-11.13(2)^\circ]$ in **4**, which are unusually large when compared against a series of closely related structures $[\text{Co}_2(\mu, \eta^2\text{-RC}_2\text{C}_6\text{H}_4\text{X-4})(\text{CO})_4(\text{dppm})]$ (X = H, NO_2 , CN, NMe_2).¹⁵ The ligand arrangement about the cobalt centres is not as heavily distorted in **5**, but shows some deviation from the norm [C(7)–Co(1)–Co(2)–C(8) $5.0(2)^\circ$; C(6)–Co(1)–Co(2)–C(9) $25.6(3)^\circ$; P(3)–Co(1)–Co(2)–P(4) $8.85(4)^\circ$].

The cyanoacetylide bridged complex $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2-(\mu: \eta^1(\text{C}):\eta^1(\text{N})-\text{C}\equiv\text{CC}\equiv\text{N})]\text{PF}_6$ (**7**)

The complex cation is illustrated in Fig. 5. The metal centres lie in an approximately *cis* arrangement, but there is no crystallographically imposed symmetry element relating these moieties.

Table 2 Selected bond lengths (Å) for **2–5**, **7** and **9**

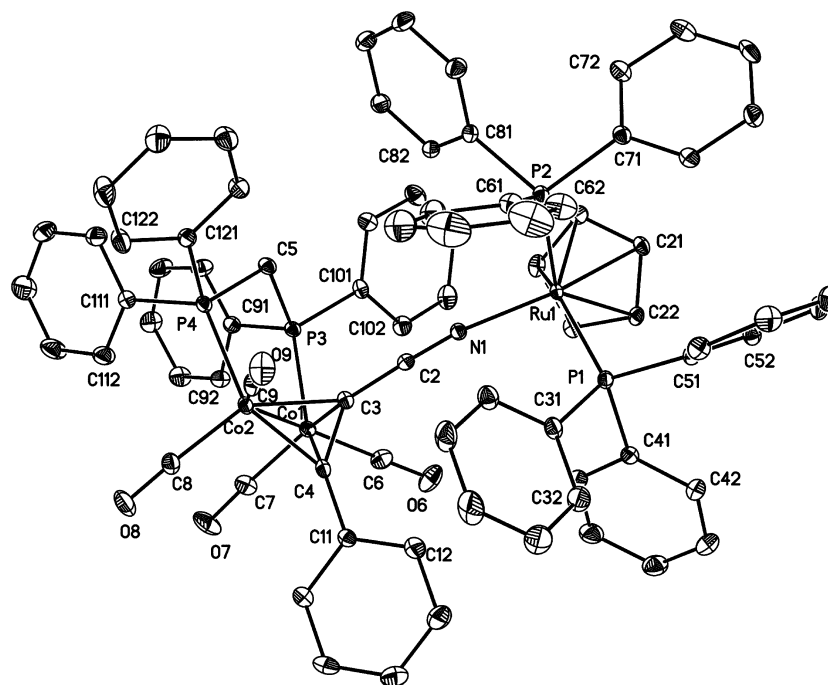
	2	3	4	5	7	9^c
Ru(1)–N(1)	2.002(4)	2.037(1)	–	2.036(3)	1.999(3)/2.011(3)	1.976(5)
Ru(1)–P(1)	2.3547(14)	2.3338(3)	–	2.3420(9)	2.3213(9)/2.3262(9)	2.342(2)
Ru(1)–P(2)	2.3521(14)	2.3348(3)	–	2.3343(9)	2.3225(9)/2.3250(9)	2.360(2)
N(1)–C(2)	1.162(7)	1.145(2)	1.153(2)	1.162(4)	1.198(5)	1.151(7) ^b
C(2)–C(3)	1.365(8)		1.412(2)	1.393(5)	1.359(5)	1.411(7) ^c
C(3)–C(4)	1.208(8)		1.370(2)	1.382(5)	1.192(5)	1.393(11) ^d
C(4)–C(11)	1.430(8)	1.440(2) ^a	1.465(2)	1.460(5)		
Co(1)–Co(2)			2.4651(3)	2.4846(7)		

^a C(2)–C(11). ^b N(1)–C(1). ^c C(1)–C(2). ^d C(2)–C(2A). ^e Also C(2)–C(3) 1.432(8) Å, C(3)–N(2) 1.135(8) Å.

Table 3 Selected bond angles (°) for **2–5**, **7** and **9**

	2	3	4	5	7	9^c
P(1)–Ru(1)–P(2)	101.25(5)	97.46(1)		101.61(3)	99.20(3)/100.73(3)	95.56(6)
Ru(1)–N(1)–C(2)	177.4(4)	171.7(1)		166.8(3)	166.9(3)/169.8(3)	169.7(4) ^b
N(1)–C(2)–C(3)	177.6(6)	177.8(2) ^a	174.5(2)	175.0(4)	176.1(4)/176.4(4)	177.3(6) ^c
C(2)–C(3)–C(4)	175.9(7)		143.0(1)	137.4(3)		121.3(6) ^d
C(3)–C(4)–C(11)	176.5(6)		141.3(1)	140.4(3)		

^a N(1)–C(2)–C(11). ^b Ru(1)–N(1)–C(1). ^c N(1)–C(1)–C(2). ^d N(1)–C(2)–C(2A). ^e Also C(1)–C(2)–C(3) 119.3(5)°, C(2)–C(3)–N(2) 175.3(6)°.



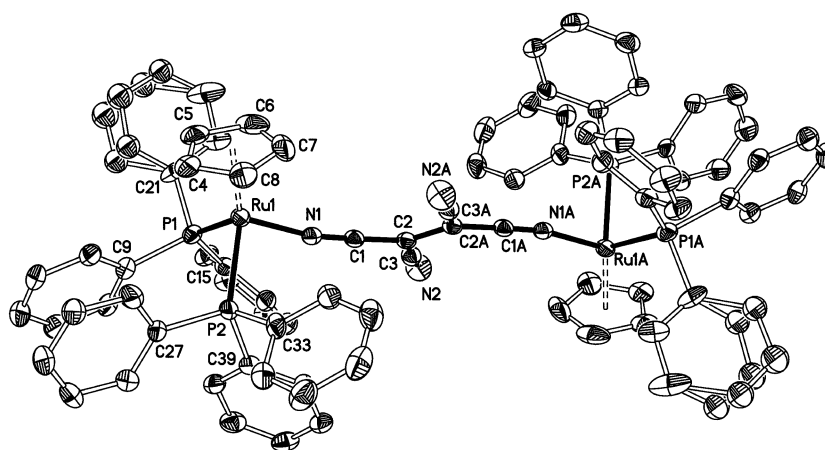


Fig. 6 A plot of the dication **9** illustrating the atom labelling scheme.

The structure is therefore comparable with the thf solvate of the *cis* form of the diyndiyl complex $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-C}\equiv\text{CC}\equiv\text{C})]$,¹⁶ although a detailed discussion is hampered by the crystallographic difficulties in resolving N(1) and C(4). The best result of the refinement were obtained with 50 : 50 C : N occupancy of the terminal atoms in the C_3N chain, as described in the Experimental section. The $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragments display the same general trends noted in the other complexes in this work and elsewhere, with Ru–P bond lengths spanning a narrow range in the range 2.313(9)–2.3263(9) Å and P–Ru–P' bond angles of *ca.* 100° (Table 2). The bridging ligand itself is quite linear, although there is a more pronounced bend at the termini of the RuC_3NRu chain, probably due to the steric influence of the PPh_3 ligands (Table 2).

The tene bridged complex *trans*- $[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-tcne})][\text{PF}_6]_2$ (**9**)

The dication in **9** (Fig. 6) rests on a crystallographic centre of inversion at the mid-point of the tene $\text{C}(2)=\text{C}(2\text{A})$ double bond. The P(1)–Ru–P(2) bond angles are relatively small [95.56(5)°], but the other parameters associated with the $\text{Ru}(\text{PPh}_3)_2\text{Cp}$ fragments are not unusual. Of somewhat greater interest is the geometry adopted by the formally charge neutral tene ligand. The general geometry of the tene fragment is very similar to that of the parent organic molecule,¹⁷ with no evident twisting of the two halves of the tene fragment [$\text{C}(1)\text{--C}(2)\text{--C}(2\text{A})\text{--C}(3\text{A})$ 1.6°]. The $\text{C}(1)\text{--C}(2)\text{--C}(3)$ bond angle in **9** [119.3(5)°] is comparable with that in tene (*ca.* 116°). Similarly, the bond lengths of the non-coordinated $\text{C}(3)\text{--N}(2)$ [1.135(8) Å] and $\text{C}(2)\text{--C}(3)$ [1.432(8) Å] groups fall within the range of values displayed by tene in the solid state. The central $\text{C}(2)\text{--C}(2\text{A})$ bond length [1.393(11) Å] is marginally longer than in tene, for which a value of about 1.35 Å is common. Coordination of the metal fragment results in elongation of $\text{N}(1)\text{--C}(1)$ [1.151(7) Å] and a contraction of $\text{C}(1)\text{--C}(2)$ [1.411(7) Å], which may arguably be taken as evidence of an extended $\text{Ru}\text{--NC}\text{--CC}\text{--CN}\text{--Ru}$ conjugation pathway.

Electrochemistry

Cyclic voltammetry studies were carried out on the complexes **2–9** as described in the Experimental section, with electrode potentials quoted against an internal ferrocene (Fc/Fc^+ 0.46 V *vs.* SCE) or decamethylferrocene ($\text{Fc}^*/\text{Fc}^{*+}$ –0.13 V *vs.* SCE) standard.¹⁸ The electrochemical response of **2** and **3** were characterised by a single oxidation wave (**2**, E_{pa} +1.47 V; **3**, E° +1.30 V), which in the case of **3** was as reversible as the internal ferrocene standard. The carbon-bonded monometallic species **6** showed a single, reversible oxidation at +0.92 V.

The CV response of **4** at a glassy carbon electrode was characterised by a reduction (E_{red}° –1.40 V) as well as an oxidation

(E_{ox}° +0.98 V) wave, the chemical reversibility of each wave improving at lower temperatures. The electron withdrawing influence of the CN moiety is evident when these redox potentials are compared with the electrochemical response of the closely related species $[\text{Co}_2(\mu\text{-HC}_2\text{Ph})(\text{CO})_4(\text{dppm})]$ [E_{red}° –1.73 V; E_{ox}° +0.79 V]. Coordination of the cationic ruthenium fragment to the pendent CN moiety in **5** results in a shift in the reduction potential to –1.23 V, and an increase in the chemical stability of the reduction product. Oxidation of **5** occurred at +1.06 V, but this wave was almost totally chemically irreversible. The tene bridged bimetallic dication **9** underwent a single irreversible oxidation (E_{pa} +1.42 V). Evidently, there is little electronic interaction between the formally $\text{Ru}(\text{II})$ centres through the tene bridge.

The homobimetallic cyanoacetylide bridged species **7** gave rise to two oxidation waves, which became reversible at –30 °C. By comparison with **2** and **6**, these waves can be confidently assigned to the sequential oxidation of the metal centres at the C (+0.91 V) and N (+1.43 V) termini. The similarity of the oxidation potentials to those of the model complexes **2** and **6**, implies little electronic communication between the two ruthenium centres through the C_3N ligand.

However, the heterometallic complex **8** displayed more interesting electrochemical response with two reversible oxidation waves at surprisingly low potentials (+0.47, +1.11 V). These may be compared with the oxidation potentials of **7**, and the mono-nuclear species **6** (+0.92 V) and $[\text{Fe}(\text{NCMe})(\text{dppe})\text{Cp}][\text{PF}_6]$ (**10**),¹⁹ which is reversibly oxidised at +0.75 V, provided we make the assumption that the relative solvation energies of the various oxidation states of **6**, **7**, **8** and **10** are similar. The trend in E° values requires a significant interaction between the heterometallic end-groups *via* the polarised C_3N bridge. The simplest interpretation of the results would consider the electrode potentials in **8** in terms of metal-centred electrochemical events. The greater electron donating ability of the $\text{Cp}(\text{PPh}_3)_2\text{RuC}\equiv\text{CCN}$ “ligand” *vs.* NCMe results in a more favourable oxidation potential of the $\text{Fe}(\text{dppe})\text{Cp}$ fragment. However, the second oxidation, which is presumably more heavily ruthenium centred, is some 0.4 V more favourable than the corresponding process in the homometallic complex **7**. This indicates that the mono-oxidised form of the $\text{Fe}(\text{dppe})\text{Cp}$ fragment can behave as an electron donating group and facilitate oxidation of the remote ruthenium centre.²⁰ An alternate interpretation would consider the electrochemical results in terms of the depopulation of a high lying HOMO derived from the anti-bonding combination of the $\pi(\text{RuC}\equiv\text{CCN})$ and $d(\text{Fe})$ based fragment orbitals similar to that found in isoelectronic butadienyldiyl systems.²¹ A more detailed study of the electronic and magnetic properties of cyanoacetylide bridged complexes in the various electrochemically detected oxidation states is necessary to determine the extent to which either of these

interpretations are valid. Work in this direction, which falls outside of the scope of this manuscript, is underway.

Conclusion

We have shown that simple cyanoacetylenes are capable of simultaneously acting as $\eta^1(\text{N})$ and $\eta^2(\text{C}_2)$ ligands to give stable mixed-metal species. Cyanoacetylide complexes $\text{M}(\text{C}\equiv\text{CCN})\text{L}_n$ are readily prepared *via* cyanation of $\text{M}(\text{C}\equiv\text{CH})\text{L}_n$, and are in turn capable of acting as ligands in their own right to form μ - η^1, η^1 bridged bimetallic species. The inherently polarised cyanoacetylide bridge is apparently capable of promoting electronic interactions between different metal centres. The reversible redox behaviour and polarised electronic structures of these species prompt interesting questions about the potential of this class of compound to find application as organometallic components in molecular electronics and in the construction of metal-containing assemblies.

Experimental

General conditions

The reagents $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$,²² $\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$,²³ $[\text{Ru}(\text{NCPh})(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ (3),¹⁰ $[\text{Co}_2(\text{CO})_6(\text{dppm})]$,²⁴ PhOCN ,²⁵ and $\text{PhC}\equiv\text{CC}\equiv\text{N}$ (1)²⁵ were prepared according to the literature methods. Other reagents were purchased and used as received. NMR spectra were recorded using solutions in CDCl_3 on Varian Mercury 200 (^1H , $^{31}\text{P}\{\text{H}\}$) or 400 ($^{13}\text{C}\{\text{H}\}$) spectrometers. IR spectra were collected using a Nicolet Avatar spectrometer from samples mounted as Nujol mulls (NaCl) or cyclohexane or CH_2Cl_2 solutions in a 0.5 mm pathlength solution cell fitted with CsF windows. Electronic spectra were recorded using a Varian Cary 5 spectrophotometer. Elemental analyses were performed in house. Electrochemical measurements were recorded from solutions in CH_2Cl_2 containing 0.1 M NBu_4BF_4 as supporting electrolyte using Pt working, counter and pseudo-reference electrodes and an EcoChemie PGSTAT30. Potentials are referenced such that internal ferrocene and decamethylferrocene standards have half-wave potentials of 0.46 and -0.13 V, respectively.

$[\text{Ru}(\text{N}\equiv\text{CC}\equiv\text{CC}_6\text{H}_5)(\text{PPh}_3)_2\text{Cp}]\text{PF}_6$ (2)

An oven-dried, two-necked Schlenk flask was charged with $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ (247 mg, 0.341 mmol), $\text{PhC}\equiv\text{CC}\equiv\text{N}$ (122 mg, 0.961 mmol), and NH_4PF_6 (212 mg, 1.30 mmol). The solids were suspended in MeOH (20 ml) and heated at reflux under a nitrogen atmosphere. After 30 min the yellow solution which formed was allowed to cool to room temperature and then further cooled using an ice-water bath. The resulting yellow precipitate was collected to give **2** as a yellow solid (0.211 g, 63%). Found: C, 61.90; H, 4.13; N, 1.50. $\text{RuC}_{50}\text{H}_{40}\text{P}_3\text{F}_6\text{N}$ requires: C, 62.37; H, 4.19; N, 1.45%. ^1H NMR: δ 4.52 (s, 5H, Cp), 6.98–7.57 (m, 40H, Ph). ^{13}C NMR: δ 135.20–128.43 (m, Ph), 116.63, 115.88 (2 \times s, $\text{C}\equiv\text{C}$), 84.90 (s, Cp). ^{31}P NMR: δ 41.86 (s, PPh_3), -143.02 (septet, $J_{\text{PF}} = 713$ Hz, $[\text{PF}_6]^-$). ES(+)-MS (m/z): 818 $[\text{Ru}(\text{NCC}\equiv\text{CC}_6\text{H}_5)(\text{PPh}_3)_2\text{Cp}]^+$, 691 $[\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$. IR (Nujol): $\nu(\text{C}\equiv\text{C})$ 2141 cm^{-1} .

$[\text{Co}_2(\mu, \eta^2\text{-PhC}_2\text{C}\equiv\text{N})(\text{CO})_4(\mu\text{-dppm})]$ (4)

A solution of $[\text{Co}_2(\text{CO})_6(\text{dppm})]$ (100 mg, 0.150 mmol) and $\text{PhC}\equiv\text{CC}\equiv\text{N}$ (18.9 mg, 0.147 mmol) in benzene (10 ml) was heated at reflux point under a nitrogen atmosphere. After 2 h the dark red solution was allowed to cool to room temperature. The solvent was removed and the residue recrystallised (CH_2Cl_2 –MeOH) to give dark red–black crystals of **4** (50 mg, 45%). Found: C, 60.17; H, 3.75; N, 2.08. $\text{C}_{38}\text{H}_{22}\text{Co}_2\text{O}_4\text{P}_2\text{N}$ ·MeOH requires: C, 60.56; H, 3.67; N, 1.89%. IR (Nujol): $\nu(\text{CN})$ 2156w; $\nu(\text{CO})$ 2036m, 2009s, 1983s, 1960m cm^{-1} . ^1H NMR:

δ 3.15 (dt, 1H, CHP_2), 3.49 (dt, 1H, CHP_2), 7.06–7.70 (m, 24H, Ph). ^{13}C NMR: δ 205.89, 199.21 (2 \times br, CO), 141.32–127.36 (m, Ph), 123.55 (t, $J_{\text{CP}} = 3$ Hz, Co_2C_2), 97.96 (t, $J_{\text{CP}} = 18$ Hz, Co_2C_2), 36.58 (t, $J_{\text{CP}} = 21$ Hz, PCH_2P). ^{31}P NMR: δ 39.92 (s, dppm). ES(+)-MS (m/z): 1504 $[2\text{M} + \text{Na}]^+$; 764 $[\text{M} + \text{Na}]^+$. IR (cyclohexane): $\nu(\text{C}\equiv\text{N})$ 2167 cm^{-1} , $\nu(\text{CO})$ 2040s, 2017s, 1990sh cm^{-1} .

$[\{\text{Co}_2(\mu, \eta^2\text{-PhC}_2\text{C}\equiv\text{N})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}(\text{CO})_4(\mu\text{-dppm})\}]\text{PF}_6$ (5)

A suspension of $[\text{Co}_2(\mu, \eta^2\text{-PhC}_2\text{C}\equiv\text{N})(\text{CO})_4(\mu\text{-dppm})]$ (**4**) (100 mg, 0.135 mmol), $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ (97 mg, 0.135 mmol) and NH_4PF_6 (22 mg, 0.135 mmol) in MeOH (20 ml) was heated at reflux point for 2 h. After this time, the resulting dark red solution was allowed to cool, the solvent removed and the residue taken up in the minimum volume of CH_2Cl_2 . Filtration of the extract into hexane precipitated the product **5** as a brick-red powder (160 mg, 75%). Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane in a CH_2Cl_2 solution at -20 °C. Found: C, 60.13; H, 4.07; N, 0.99. $\text{C}_{79}\text{H}_{62}\text{P}_5\text{F}_6\text{O}_4\text{-Co}_2\text{NRu}$ requires: C, 60.16; H, 3.96; N, 0.89%. ^1H NMR: δ 3.28 (m, 2H, PCH_2P), 4.30 (s, 5H, Cp), 7.12–7.25 (m, 62H, Ph). ^{13}C NMR: δ 205.89, 199.21 (2 \times br, 2 \times CO), 141.31–128.36 (m, Ph), 123.56 (t, $J_{\text{CP}} = 3$ Hz, Co_2C_2), 100.01 (s, Cp), 97.96 (t, $J_{\text{CP}} = 19$ Hz, Co_2C_2), 36.58 (t, $J_{\text{CP}} = 21$ Hz, PCH_2P). ^{31}P NMR: δ 42.00 (s, PPh_3), 37.67 (s, dppm), -142.96 (septet, $J_{\text{PF}} = 711$ Hz, $[\text{PF}_6]^-$). ES(+)-MS (m/z): 1431 $[\text{Co}_2(\mu, \eta^2\text{-C}_6\text{H}_5\text{C}_2\text{CN})\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}(\text{CO})_4(\text{dppm})]^+$, 691 $[\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$. IR (cyclohexane): $\nu(\text{CO})$ 2040s, 2017s, 1990sh cm^{-1} . IR (Nujol): $\nu(\text{CO})$ 2037m, 2011s, 1985s, 1967sh.

$[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$ (6)

An oven-dried, two-necked Schlenk flask was cooled under nitrogen and fitted with a stirrer bar and a low-temperature thermometer. The flask was charged with $\text{Ru}(\text{C}\equiv\text{CH})(\text{PPh}_3)_2\text{Cp}$ (390 mg, 0.55 mmol) in 30 ml dry, distilled THF and cooled to -70 °C. To this solution $\text{Bu}^\text{t}\text{Li}$ (0.4 ml of a 1.6 M solution in hexane). This was added at such a rate as to prevent the temperature from exceeding -60 °C. The solution was stirred for 10 min at this temperature, brought to -20 °C for 10 min to ensure complete reaction, and cooled back to -70 °C. Neat PhOCN (0.4 ml, 3.5 mmol) was added to the cooled solution and the solution stirred for a further 30 min at -70 °C before being allowed to come to room temperature. The solvent was removed using a rotary evaporator to leave a dark-green residue which was dissolved in the minimum amount of dichloromethane and micro-filtered into hexane. The resulting yellow–green solid was collected and dried *in vacuo* to give the crude product (400 mg, 0.54 mmol, 98%), which was sufficiently pure for further reaction and electrochemical measurements. Solutions of the complex slowly decomposed, which made attempts to purify the material by recrystallisation difficult, and an accurate microanalysis was not obtained. ^1H NMR (CDCl_3): δ 4.37 (s, 5H, Cp), 7.11–7.51 (m, 35H, Ph). $^{31}\text{P}\{\text{H}\}$ NMR (CDCl_3): δ 49.77 (s, PPh_3). $^{13}\text{C}\{-\text{H}\}$ NMR (CDCl_3): δ 137.86–137.36 (m, C_{ipso} , PPh_3), 133.79 (t, $J_{\text{CC}} = 5.09$ Hz, C_{ortho} , PPh_3), 129.33 (s, C_{para} , PPh_3), 127.87 (t, $J_{\text{CC}} = 4.84$ Hz, C_{meta} , PPh_3), 121.64 (s, C_a), 107.75 (s, $\text{C}\equiv\text{N}$), 86.68 (s, Cp), 83.08 (s, C_β). ES(+)-MS (m/z): 764.1 $[\text{M} + \text{Na}]^+$; 742.1 $[\text{M} + \text{H}]^+$; 691 $[\text{Ru}(\text{PPh}_3)_2\text{Cp}]^+$. IR (CH_2Cl_2): $\nu(\text{C}\equiv\text{N})$ 2180 cm^{-1} , $\nu(\text{C}\equiv\text{C})$ 2000 cm^{-1} .

$[\{\text{Ru}(\text{PPh}_3)_2\text{Cp}\}_2(\mu\text{-}\eta^1(\text{C}), \eta^1(\text{N})\text{-C}\equiv\text{CC}\equiv\text{N})](\text{PF}_6)$ (7)

An oven-dried, two-necked Schlenk flask was cooled under nitrogen and fitted with condenser and stirrer bar and charged with $[\text{RuCl}(\text{PPh}_3)_2\text{Cp}]$ (100 mg, 0.138 mmol), $[\text{Ru}(\text{C}\equiv\text{CC}\equiv\text{N})(\text{PPh}_3)_2\text{Cp}]$ (102 mg, 0.138 mmol) and NH_4PF_6 (90 mg, 0.55 mmol). The solids were suspended in methanol (20 ml) and heated at reflux. During the reflux the suspension became a pale

yellow/green colour. After 90 min the reaction mixture was allowed to cool to room temperature and then cooled further in an ice-water bath. The pale yellow–green solid produced was collected by filtration and dried *in vacuo* (141 mg, 0.090 mmol, 65%). Recrystallisation (CH₂Cl₂–MeOH) afforded the product as bright yellow blocks of a tri-CH₂Cl₂ solvate. Found: C, 63.93; H, 4.58; N, 1.08. C₈₅H₇₀P₅F₆NRu₂·0.5CH₂Cl₂ requires: C, 63.37; H, 4.38; N, 0.86%. ¹H NMR (CDCl₃): δ 4.36 (s, 5H, Cp), 4.48 (s, 5H, Cp), 7.08–7.29 (m, 67H, Ph). ³¹P{¹H} NMR (CDCl₃): 48.92 (s, PPh₃), 42.16 (s, PPh₃), –143.05 (ht, J_{PF} = 712 Hz, PF₆). ¹³C{¹H} NMR (CDCl₃): δ 137.69–137.09 (m, C_{ipso}, PPh₃), 136.83–136.17 (m, C_{ipso}, PPh₃), 133.69 (t, J_{CC} = 5.03 Hz, C_{ortho}, PPh₃), 133.42 (t, J_{CC} = 5.03 Hz, C_{ortho}, PPh₃), 130.02 (s, C_{para}, PPh₃), 129.66 (s, C_{para}, PPh₃), 128.39 (t, J_{CC} = 4.78 Hz, C_{meta}, PPh₃), 127.96 (t, J_{CC} = 4.78 Hz, C_{meta}, PPh₃), 117.07 (s, C≡N), 87.55 (s, Cp), 83.64 (s, Cp), 83.49 (s, C_β). ES(+)-MS (*m/z*) 1432 [{Ru(PPh₃)₂Cp}₂(C≡CC≡N)]⁺; 691 [Ru(PPh₃)₂Cp]⁺. IR (CH₂Cl₂): ν(C≡N) 2197 cm^{–1}, ν(C≡C) 1986 cm^{–1}.

[{Ru(PPh₃)₂Cp}(μ-η¹(C),η¹(N)–C≡CC≡N){Fe(dppe)Cp}](PF₆) (8)

An oven-dried, two-necked Schlenk flask was cooled under nitrogen and fitted with a condenser and stirrer bar and charged with [FeCl(dppe)Cp] (75 mg, 0.135 mmol), [Ru(C≡CC≡N)-(PPh₃)₂Cp] (100 mg, 0.135 mmol) and NH₄PF₆ (88 mg, 0.54 mmol). The solids were suspended in methanol (20 ml) and the reaction mixture heated at reflux point for 1 h. A pale orange/brown precipitate rapidly formed in a dark solution. The solution was allowed to cool and the brick-red precipitate collected by filtration and purified by precipitation of a concentrated dichloromethane solution into hexane (84 mg, 0.0598 mmol, 44%). ¹H NMR (CDCl₃): δ 7.31–7.00 (m, 52H, Ph), 4.24 + 4.20 (unresolved, 10H, Cp). ³¹P{¹H} NMR (CDCl₃): 98.02 (s, PPh₃), 48.76 (s, PPh₃), –143.06 (ht, J_{PF} = 712 Hz, PF₆). ¹³C{¹H} NMR (CDCl₃): δ 137.45–137.09 (m, C_{ipso}, PPh₃), 133.69 (t, J_{CC} = 5.28 Hz, C_{ortho}, PPh₃), 133.12 (t, unresolved, C_{ortho}, dppe), 131.84 (t, unresolved, C_{ortho}, dppe), 130.80 (s, C_{para}, dppe), 130.60 (s, C_{para}, dppe), 129.67 (s, C_{para}, PPh₃), 129.12 (t, unresolved, C_{meta}, dppe), 128.96 (t, unresolved, C_{meta}, dppe), 127.92 (t, J_{CC} = 4.78 Hz, C_{meta}, PPh₃), 121.60 (s, C_α), 87.22 (s, Cp), 79.16 (s, Cp), 83.08 (s, C_β), 28.02 (t, J_{CP} = 21.62 Hz, CH₂, dppe). ES(+)-MS (*m/z*): 1260 [{Ru(PPh₃)₂Cp}(C≡CC≡N){Fe(dppe)Cp}]⁺; 519 [Fe(dppe)Cp]⁺. IR (CH₂Cl₂): ν(C≡N) 2194 cm^{–1}, ν(C≡C) 1986 cm^{–1}.

[{Ru(PPh₃)₂Cp}₂(μ-tcne)](PF₆)₂ (9)

A solution of [Ru(N≡CC≡CPh)(PPh₃)₂Cp]PF₆ (150 mg, 0.156 mmol) in THF (10 ml) was treated with tetracyanoethylene (tcne) (20 mg, 0.156 mmol) and the solution stirred at room temperature for 15 min. The solution rapidly darkened and after 15 min the solvent was removed. The resulting dark green residue was dissolved in DCM and precipitated into diethyl ether to give [{Ru(PPh₃)₂Cp}₂(μ-tcne)](PF₆)₂ as a grey–green solid which was recrystallised (CHCl₃) to give the product as sapphire-blue crystals (90 mg, 77%). ¹H NMR (CDCl₃): δ 7.66–7.05 (m, Ph); 4.58 (s, 5H, Cp). ³¹P{¹H} NMR (CDCl₃): δ 41.87 (s, PPh₃), –142.45 (ht, J_{PF} = 713 Hz, PF₆). ES(+)-MS (*m/z*): 818.2 [{Ru(PPh₃)₂Cp}₂(μ-tcne)]⁺; 691 [Ru(PPh₃)₂Cp]⁺. IR (CH₂Cl₂): ν(C≡C) 2139, 2164sh cm^{–1}.

Crystallography

Diffraction data were collected on a Bruker SMART-CCD detector diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collections were carried out at 120 K (2, 3, 5, 7, 9) and 110 K (4) using an Oxford Cryosystems N₂ open-flow gas cryostat.²⁶ Cell parameters were determined and refined using the SMART software²⁷ and raw frame data were integrated using the SAINT program.²⁸ Data were cor-

rected for absorption by numerical integration based on measurements and indexing of the crystal faces using SHELXTL software²⁹ (2, 4, 9) and by the multi-scan method based on multiple scans of identical and Laue equivalent reflections using the SADABS program.³⁰ (3, 7). No absorption correction was applied to data of 5. All structures were solved using Direct Methods and refined by full-matrix least squares on *F*² using SHELXTL.²⁹

Hydrogen atoms were geometrically placed and allowed to ride on their parent C atom with *U*_{iso}(H) = 1.2*U*_{eq}(C). Idealised C–H distances were fixed at 0.95 Å for carbon atoms in six-membered rings of 2, 3, 7 and 9 (0.93 Å in 5), 1.00 Å for the C–H in the five-membered rings of 2, 3, 7 and 9 (0.98 Å in 5), 0.99 Å for the C–H's in partially occupied and disordered dichloromethane molecules in 2 and 7, 0.97 Å for a CH₂ unit and C–H's of a dichloromethane molecule in 5 and 1.00 Å for the C–H in a chloroform molecule of 9. Hydrogen atoms for 4 were located from difference Fourier maps and their positions and isotropic atomic displacements parameters were refined. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters.

The four-atomic bridge between metal atoms in 7 is disordered over two positions. The terminal atoms of this bridge were refined using mixed (1 : 1) atomic scattering factors of C and N. The PF₆ anion in 9 is severely disordered. One of the Ph groups of 9 is also disordered over two positions which were refined with equal occupation factors.

CCDC reference numbers 188693–188696, 211648 and 211649.

See <http://www.rsc.org/suppdata/dt/b3/b306089f/> for crystallographic data in CIF or other electronic format.

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