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Synthesis and characterisation of organometallic imidazolium compounds that include a new organometallic ionic liquid†

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New imidazolium salts, 1-(prop-2-ynyl)-3-vinyl-3*H*-imidazol-1-ium bromide, **1a**, the tetraphenylborate, **1b**, and hexafluorophosphate, **1c**, salts of **1a** and 3-allyl-1-(prop-2-ynyl)-3*H*-imidazol-1-ium bromide, **2a**, containing alkene and alkyne groups for derivatisation were prepared from commercially available starting materials and fully characterised. New organometallic imidazolium salts, $[\{\mu_2\text{-HCCCH}_2\overline{\text{N=C(H)N(CH=CH}_2\text{)CH=C}}\text{H}\}\text{Co}_2\text{(CO)}_6]\text{X}$ $[\text{X}^- = \text{BF}_4{}^-, \text{B(C}_6\text{H}_5)_4{}^-$ or $\text{PF}_6{}^-]$, **3a**, **3b** or **3c**, and $[\{\mu_2\text{-HCCCH}_2\overline{\text{N=C(H)N(CH}_2\text{CH=CH}_2\text{)CH=C}}\text{H}\}\text{Co}_2\text{(CO)}_6]\text{BF}_4$, **4a**, and a new organometallic ionic liquid, $[\{\mu_2\text{-HCCCH}_2\overline{\text{N=C(H)N(CH}_2\text{CH=CH}_2\text{)CH=C}}\text{H}\}\text{Co}_2\text{(CO)}_6]\text{PF}_6$, **4b**, were isolated by reacting **1a**–**c** or **2a** with $\text{Co}_2\text{(CO)}_8$. The compound **4b**, the first ionic liquid bearing an organometallic moiety covalently attached to the cation, melts reversibly at 75–77 °C without decomposition. The imidazolium protons in **1b** and **3b** are shielded in the ^{1}H NMR as a result of π-interaction with the phenyl rings of the tetraphenylborate anion. The cation–anion contacts ($\text{C–H} \cdots \pi \sim 2.6$ Å) observed in the molecular structure of **3b** in the solid state are also maintained in solution, as evidenced in NOE NMR experiments. The molecular structures of **3b** and **3c** show an alkyne unit bonded to a $\text{Co}_2\text{(CO)}_6$ fragment with the C≡C bond perpendicular to the Co–Co bond.

Introduction

The replacement of volatile organic compounds as solvents in organic synthetic processes by recyclable environmentally friendly ionic liquids[1] together with their reaction modifying effects (activity and selectivity) and the possibility of multiphase reaction procedures with simple product separation and homogeneous catalyst recovery have rendered this new class of solvents extremely popular.[2,3]

A myriad of homogeneously catalysed reactions have been studied and promise clean synthetic methodologies for the future.[1] Generally, salts of organic cations *e.g.* tetraalkylammonium, tetraalkylphosphonium, *N*-alkylpyridinium, 1,3-dialkylimidazolium and trialkylsulfonium cations, are room-temperature ionic liquids.[1] Meticulous selection of the cations and anions in the ionic liquid can tailor the required solvent properties of the ionic liquid to the requirements of the target reactions.[1–3] The derivatisation of the cations and anions places an infinite set of designer solvents at the disposal of the synthetic chemist.[4] The functionalisation of the N-substituents in the imidazolium based ionic liquids with exocyclic alkene and alkyne groups creates many new opportunities for the extension of the pool of designer solvents, as well as functionality-tailored solute targets, *e.g.* 1-imidazolethynylphosphines.[5] By grafting the substrate benzaldehyde onto an ionic liquid through the N-substituent in the imidazolium salt, Fraga-Dubreuil and Bazureau have been able to perform Knoevenagel and 1,3-dipolar cycloaddition reactions on the substrate in a "solvent free environment".[6] Increased possibilities for functionalisation of the N-substituents in imidazolium cations would enable the use of bioactive molecules for the development of many more ionic liquids. This is demonstrated by an ionic liquid derived from the antifungal drug miconazole, which exhibits lyotropic liquid crystalline behaviour and induces the gelation of benzene.[7]

The protection of alkynes by reaction with $\text{Co}_2\text{(CO)}_8$ to form $(\mu\text{-alkyne})\text{Co}_2\text{(CO)}_6$ complexes, the generation of [2 + 2 + 2]-cycloadditions *via* an intramolecular Heck reaction, the formation of cyclopentenones with an alkyne, alkene and CO (Pauson–Khand reaction) and the stereo-controlled C–C bond formation using propargyl cations with α-carbons activated to nucleophilic substitution through stabilisation of the intermediate carbocation (Nicholas reaction), are well established in synthetic procedures[8–18] and can be used to extend the derivatisation of suitably N-substituted imidazolium salts. Several $(\mu\text{-alkyne})\text{Co}_2\text{(CO)}_6$ compounds have been structurally studied.[9–18] Organometallic imidazolium salts which act as anion receptors and Lewis acid catalysts are known. ^{1}H NMR studies of ferrocenyl imidazolium salts in CDCl_3 have indicated the existence of $\text{C–H} \cdots \text{X}^-$ hydrogen bonding at NC(H)N.[19]

Organic ligands with delocalised π-systems, joined by metal centres to form organometallic polymers, are suitable precursors for solid state materials of technological interest.[18] The synthesis and characterisation of metallopolymers, consisting of poly(phenylene diacetylenes) that contain Pt and Co coordinated to the triple bonds of the diacetylene moieties, and their conversion upon thermal treatment as thin films to conductive, metal-doped, hetero-glassy carbon (HGC), has important implications for fuel cell electrode development.[20]

Organometallic ionic liquids are rare[21] and the first catalytically active example $[\text{bmim}][\text{Co(CO)}_4]$ (bmim = 1-butyl-3-methylimidazolium) was recently described.[22] Analysis of $[\text{Rh(CO)}_2\text{I}_2][\text{bmim}]$ by ESI-MS combined with quadropole ion trap methods showed the Monsanto catalyst parent anion and fragments indicating sequential CO ligand loss.[23]

Other ionic liquids with transition metal containing anions $[\text{bmim}][\text{AuCl}_4]$, $[\text{emim}][\text{AuCl}_4]$[24] (emim = 1-ethyl-3-methylimid-

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† This paper is based on work presented at OMCOS 8 held at Santa Barbara, USA, 6–10 August 1995. Electronic supplementary information (ESI) available: Table of ionic liquids and melting points. See http://www.rsc.org/suppdata/dt/b3/b308252k/

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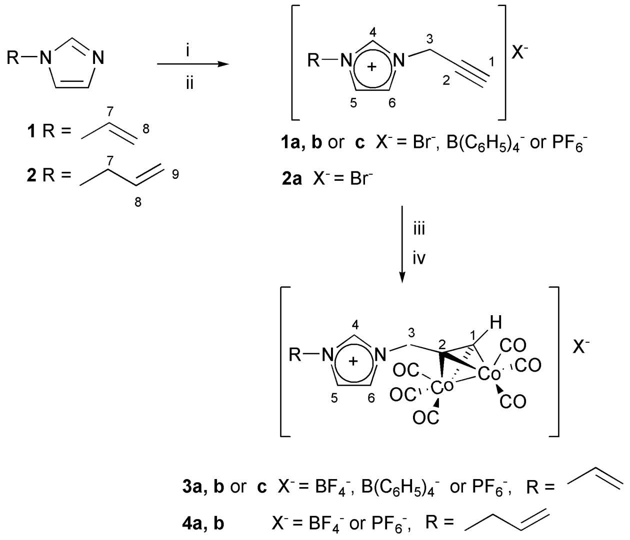
azolium), [BMTz][AuCl$_4$][25] (BMTz = 3-butyl-4-methylthiazolium), [dmim][CoCl$_4$] (dmim = 1-dodecyl-3-methylimidazolium), [omim][CoCl$_4$] (omim = 1-octadecyl-3-methylimidazolium), [dmim]$_2$[NiCl$_4$] and [omim]$_2$[NiCl$_4$][26] have been synthesised and characterised, and the latter Ni- and Co-containing compounds display liquid crystal behaviour over extended temperature ranges. Addition of 1,1′-bis(diphenylphosphino)cobaltocenium hexafluorophosphate to [Rh(CO)$_2$(acac)] in [bimim][PF$_6$] improved the hydroformylation of 1-octene substantially and prevented leaching of the catalyst into the substrate.[27]

We now report the straight forward synthesis of new imidazolium salts, [HC≡CCH$_2$N=C(H)N(CH=CH$_2$)CH=CH]X (X$^-$ = Br$^-$, B(C$_6$H$_5$)$_4$$^-$ or PF$_6$$^-$), **1a–c** and [HC≡CCH$_2$N=C(H)N(CH$_2$CH=CH$_2$)CH=CH]Br, **2a**, with two functional groups available for derivatisation, the synthesis of the new organometallic imidazolium salts, [{μ$_2$-HCCCH$_2$-N=C(H)N(CH=CH$_2$)CH=CH}Co$_2$(CO)$_6$]X [X$^-$ = BF$_4$$^-$, B(C$_6H_5$)$_4$$^-$ or PF$_6$$^-$], **3a–c** and [{μ$_2$-HCCCH$_2$-N=C(H)N(CH$_2$CH=CH$_2$)CH=CH}Co$_2(CO)_6$]BF$_4$, **4a** and a new organometallic ionic liquid, [{μ$_2$-HCCCH$_2$-N=C(H)N(CH$_2$CH=CH$_2$)CH=CH}Co$_2$(CO)$_6$]PF$_6$, **4b** (Scheme 1).‡



Scheme 1 Reagents and conditions: i, HC≡CCH$_2$Br; ii, NH$_4$B(C$_6$H$_5$)$_4$ for **1b**, NH$_4$PF$_6$ for **1c**; iii, Co$_2$(CO)$_8$; iv, NH$_4$BF$_4$ for **4a** and NH$_4$PF$_6$ for **4b**.‡

Results and discussion

Synthesis and characterisation

The treatment of 1-vinyl-1*H*-imidazole or 1-allyl-1*H*-imidazole with a commercially available stock solution of BrCH$_2$C≡CH in toluene produced **1a** and **2a**. Compound **2a** has a very low solubility in organic solvents but both **1a** and **2a** are soluble in water. The addition of NH$_4$BF$_4$ or NH$_4$B(C$_6$H$_5$)$_4$ to solutions of **1a** in water, precipitated **1b** and **1c** thus providing an efficient process for product purification. The difference in solubility of the compounds was also exploited in the purification of the new orange organometallic imidazolium salts **3a**, **3b**, **3c**, **4a** and **4b** formed by reacting Co$_2$(CO)$_8$ with equimolar amounts of **1a–c**, or **2a** in CH$_2$Cl$_2$ and counteranion exchange (when the anion is Br$^-$) with NH$_4$BF$_4$ or NH$_4$PF$_6$. Unreacted Co$_2$(CO)$_8$ was extracted with diethyl ether from the crude product mixture suspended in water, while the organometallic imidazolium salt remained in the aqueous phase. After counteranion exchange where necessary, the products **3a–c**, **4a** and **4b** were extracted from the aqueous phase with CH$_2$Cl$_2$. The cobalt compounds are stable in air and deoxygenated water and decompose slowly in CH$_2$Cl$_2$ – quite unusual for (μ-alkyne)Co$_2$(CO)$_6$-type compounds.[10,11,13–16,18]

The molecular ion, anion and fragments thereof of **1b** and the molecular ion and imidazolium fragment of **2a** were observed in the electron impact mass spectra of these compounds, while only the imidazolium cations were present in the spectra of **1a** and **1c**. The cations of **3a–c**, **4a** and **4b** were observed in the FAB mass spectra of these compounds.

The organic imidazolium salts **1c** and **2a** melt at temperatures below 100 °C and are ionic liquids, whereas **1a** and **1b** melt at temperatures above 100 °C and do not meet this requirement. Compound **4b** melts reversibly at 75–77 °C and thus qualifies as an organometallic ionic liquid that is not easy to crystallise. The other organometallic imidazolium salts **3a**, **3b**, **3c** and **4a** all decompose before melting.

Molecules of the type (μ-HCCR)Co$_2$(CO)$_6$ may possess at most, C_s symmetry and all six terminal C–O stretching modes are IR active.[12,14,28] As in reported results, three strong C–O frequencies [$\nu_1(a_1)$ at *ca.* 2092 cm^{-1}, $\nu_4(b_1)$ at *ca.* 2052 cm^{-1}, $\nu_2(a_1)$ at *ca.* 2021 cm^{-1}][9–18] are observed in the IR spectra of **3a-c**, **4a** and **4b** (*ca.* 2110, 2060 and 2020 cm^{-1}). The C–O frequencies that are not observed [$\nu_6(b_2)$ at *ca.* 2029s cm^{-1}, $\nu_5(b_1)$ at *ca.* 2011w cm^{-1} and $\nu_3(a_2)$ at *ca.* 2008vw cm^{-1}] are obscured by broad neighbouring bands [$\nu_6(b_2)$] or extremely weak.

The H–C stretch in the infrared spectrum of the imidazolium salts are observed at *ca.* 3200 cm^{-1} for the H–C≡C unit and at *ca.* 3100 cm^{-1} for the H–C=C unit. Upon coordination of the alkyne to Co$_2$(CO)$_6$, the H–C stretch for the H–C≡C unit moves to lower wavenumbers (*ca.* 3150 cm^{-1}). An even larger shift to lower wavenumbers is observed in the C≡C stretching frequencies: from *ca.* 2120 to *ca.* 1560 cm^{-1}. Similar changes in the H–C and C≡C stretching frequencies were observed for other alkyne ligands after coordination to Co$_2$(CO)$_6$.[9,10,14,18]

When comparing the ^{1}H NMR spectrum of **1b** to those of **1a** and **1c**, shielding of the NC(H)N proton (4 ppm) and the NCH=CHN protons (1 ppm) of the imidazolium ring are obvious. This can be ascribed to the influence of the B(C$_6$H$_5$)$_4$$^-$ anion which maintains a contact ion pair structure in solution and exerts CH $\cdots$ π interation on the protons of the imidazolium ring *via* its phenyl rings. Similar results were reported for 1-butyl-3-methyl-2,3-dihydro-1*H*-imidazolium tetraphenylborate.[29,30]

The strongest evidence for coordination of the alkynes to Co$_2$(CO)$_6$ is the downfield shift (from *ca.* δ 3 to *ca.* δ 6.4) of the terminal alkyne protons in the ^{1}H NMR spectra. The other largest change in chemical shift (0.5 ppm downfield) is observed for the CH$_2$ group of the alkyne substituent. These changes are also reflected in the ^{13}C NMR spectra of **3a–c**, **4a** and **4b** where the terminal alkyne carbon experiences a deshielding effect (8 ppm) and the CH$_2$ carbons of the alkyne substituent experience a similar downfield shift (10 ppm) upon co-ordination. These changes in chemical shift reflect the reduction in triple bond character of the coordinated alkyne.

In the ^{1}H NMR spectrum of **3b** a slight downfield shift of 0.5 ppm is observed for the imidazolium NC(H)N proton when compared to its shift in **1b** but this value is still significantly upfield (4 ppm) from the NC(H)N protons in **3a**, **3c**, **4a** and **4b**. The chemical shifts of the NCH=CHN protons of the imidazolium ring in **3b** are also shifted slightly upfield (1 ppm) when compared to those in **3a**, **3c**, **4a** and **4b**. In the molecular structure of **3b** (*vide infra*) the proton in question is seen to be lying in close proximity to one of the phenyl rings of the B(C$_6$H$_5$)$_4$$^-$ anion when in the solid state [distance H(4) to B-phenyl C(21)–C(26) centroid = 2.58 Å]. By carrying out 1D NOE experiments it was shown that this is also the situation in solution as excitation of selected protons [H(5), H(6) and H(7)] on the cation of **3b** resulted in enhancements of phenyl proton

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‡ The numbering of the ligands in Scheme 1, Fig. 1 and Fig. 2 is arbitrary.

Table 1 Selected bond lengths (Å) and angles (°) of complexes **3b** and **3c**

	3b	**3b** (B)	**3c**		**3b**	**3b** (B)	**3c**
Co(1)–Co(2)	2.4726(7)	2.4562(7)	2.4644(9)	C(1)–Co(1)–C(2)	39.28(14)	39.54(14)	39.80(12)
Co(1)–C(1)	1.949(4)	1.952(4)	1.963(3)	C(1)–Co(2)–C(2)	39.50(14)	39.59(15)	39.94(12)
Co(1)–C(2)	1.957(3)	1.955(4)	1.957(3)	Co(1)–C(1)–Co(2)	78.78(15)	78.02(14)	78.14(12)
Co(2)–C(1)	1.948(4)	1.950(4)	1.947(3)	Co(1)–C(2)–Co(2)	78.83(13)	77.91(13)	77.97(10)
Co(2)–C(2)	1.937(3)	1.951(3)	1.960(3)	Co(2)–Co(1)–C(10)	150.66(12)	149.63(17)	149.80(13)
Co(1)–C(10)	1.789(4)	1.747(5)	1.792(4)	C(1)–Co(1)–C(20)	141.56(17)	143.65(17)	140.62(14)
Co(1)–C(20)	1.806(4)	1.813(4)	1.824(4)	C(2)–Co(1)–C(30)	140.20(16)	139.25(17)	141.27(14)
Co(1)–C(30)	1.824(4)	1.809(5)	1.815(4)	Co(1)–Co(2)–C(40)	150.64(14)	145.61(13)	148.67(10)
Co(2)–C(40)	1.796(4)	1.790(4)	1.791(4)	C(1)–Co(2)–C(50)	141.2(2)	138.19(16)	144.34(14)
Co(2)–C(50)	1.803(6)	1.807(4)	1.820(4)	C(2)–Co(2)–C(60)	139.9(2)	144.65(17)	138.73(15)
Co(2)–C(60)	1.790(6)	1.817(4)	1.822(4)	Co–C–O (av.)	178.2(5)	177.2(4)	178.2(4)
C–O (av.)	1.129(5)	1.137(5)	1.131(4)	H(1)–C(1)–C(2)	143(2)	142(2)	143(2)
N(1)–C(4)	1.319(4)	1.325(4)	1.324(4)	C(1)–C(2)–C(3)	140.8(3)	141.0(3)	140.5(3)
N(1)–C(6)	1.378(4)	1.377(5)	1.374(4)	C(4)–N(1)–C(6)	107.9(3)	107.9(3)	107.7(2)
N(1)–C(3)	1.472(5)	1.471(5)	1.472(3)	C(4)–N(2)–C(5)	108.0(3)	108.3(3)	108.4(2)
N(2)–C(4)	1.332(5)	1.315(5)	1.325(4)	N(1)–C(4)–N(2)	109.0(3)	109.2(3)	108.8(3)
N(2)–C(5)	1.380(4)	1.374(5)	1.362(4)	C(6)–C(5)–N(2)	107.1(3)	107.3(3)	107.5(3)
N(2)–C(7)	1.420(5)	1.446(5)	1.435(6)	C(5)–C(6)–N(1)	108.0(3)	107.2(3)	107.6(3)
N(2)–C(7A)			1.534(18)	C(8)–C(7)–N(2)	124.9(4)	122.8(4)	122.0(6)
C(1)–C(2)	1.313(5)	1.321(5)	1.334(4)	C(8A)–C(7A)–N(2)			111.5(18)
C(2)–C(3)	1.492(5)	1.496(5)	1.488(4)				
C(5)–C(6)	1.328(5)	1.335(6)	1.331(4)				
C(7)–C(8)	1.284(6)	1.254(6)	1.280(8)				
C(7A)–C(8A)			1.23(2)				

signals of the anion. Thus, the cation and anion of **3b** as in **1b** remain close to each other even in solution and the shielding effect of one of the phenyl rings on the NC(H)C proton is cleary seen in the ^{1}H NMR spectrum.

All other signals are consistent with the proposed structures and do not experience large changes when compared to the signals of the uncoordinated imidazolium salts. The imidazolium carbons and alkyne carbons were unambigiously assigned using Gradient Heteronuclear Single Quantum Coherence (GHSQC) experiments and Gradient Heteronuclear Multiple Quantum Coherence (GHMQC) experiments.

One broad signal at δ 199 is observed for the carbonyl carbons suggesting that they are rapidly exchanging. The NMR data are typical of (μ-HCCR)Co$_2$(CO)$_6$ compounds.[9–11,13,14,18]

The septet for the P atom in the PF$_6^-$ ions is observed at δ −144 ($^1J_{PF}$ = 711 Hz) in the ^{31}P NMR spectra of **1c**, **3c** and **4b**. The *ipso* (quartet at δ 164, $^1J_{BC}$ = 49 Hz) and *meta* (quartet at δ 126, $^3J_{BC}$ = 3 Hz) phenyl carbon atoms of the tetraphenylborate anion in **1b** and **3b** experience boron coupling.

Molecular structures

The molecular structures of **3b** and **3c** are shown in Fig. 1 and Fig. 2. Selected bond parameters are listed in Table 1. The unit cell of compound **3b** contains two cation and anion pairs in the asymetric unit. The cations consists of a 'Co$_2$C$_2$' core with pseudo-tetrahedral geometry. The C(1)–C(2) alkyne bonds are arranged perpendicular to the Co(1)–Co(2) bonds. The coordination geometry about the Co atoms is pseudo-octahedral. The Co(1)–Co(2) bond length found in **3b** and **3c** lies within the range, 2.46–2.48 Å [not influenced by the groups attached to the C(1)–C(2) unit] observed for other dicobalt systems that are bridged by perpendicular alkyne ligands,[10,13–16,18] but is shorter than the value reported for the Co–Co distance in Co$_2$(CO)$_8$.[14] As widely reported, coordination of the ethynyl group C(1)–C(2) to the Co$_2$(CO)$_6$ unit leads to an expansion of the triple bond to 1.313(5) and 1.321(5) Å in **3b** and 1.334(4) Å in **3c**. This is consistent with the loss of C≡C bond character as a result of delocalisation of the electron density onto the Co$_2$(CO)$_6$ unit. The same bond distance in similar compounds ranges from 1.33 to 1.36 Å.[13–16,18] Deviation from sp-hybridisation at C(1) and C(2) is evident in the pivotal angles H(1)–C(1)–C(2) and C(1)–C(2)–C(3), similar values have been reported.[13,14,18] The four Co–C(alkyne) distances in **3b** and **3c** are similar to

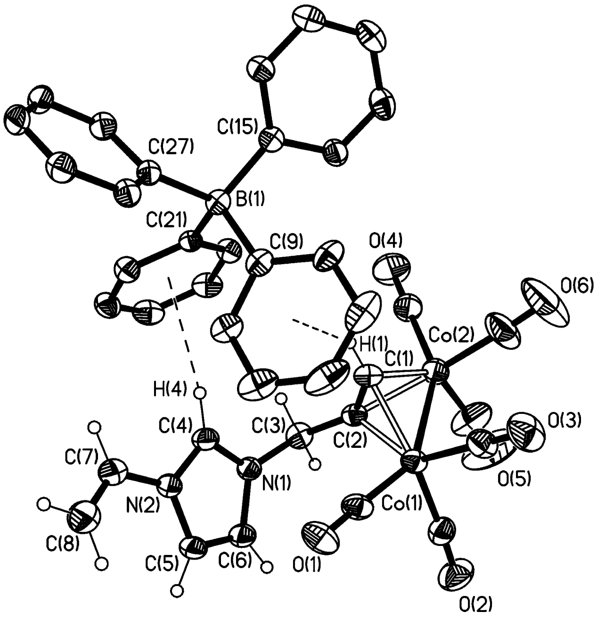

Fig. 1 Molecular structure of **3b** showing only one of the two ion pairs per asymmetric unit and the numbering scheme. Ellipsoids are shown at 30% probability level. ‡

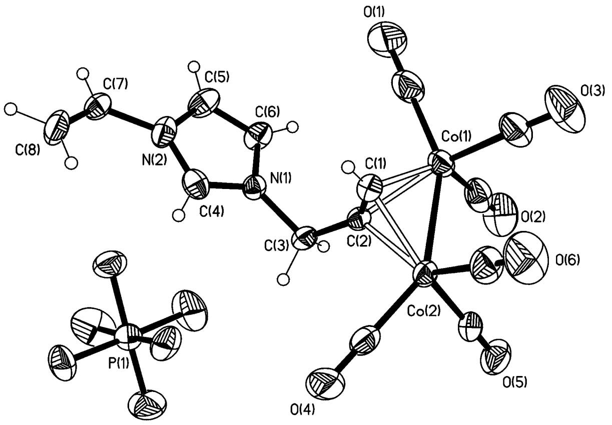

Fig. 2 Molecular structure of **3c** showing the numbering scheme. Ellipsoids are shown at 40% probability level. ‡

reported values.[13,16–18] These distances do not show the assymmetric pattern observed in [{Co$_2$(CO)$_6$}$_2$(HC$_2$C$_6$H$_4$C$_2$H)][14] [{Co$_2$(CO)$_6$]$_2${(CH$_3$)$_3$SiC$_2$C$_6$H$_4$C$_2$H)][13] and [{Co$_2$(CO)$_6$}-{(CH$_3$)$_3$SiCCSi[CCSi(CH$_3$)$_3$]$_3$}][15] in which the nature of the substituents on the ethynyl group are reflected in the Co–C bond lengths.

The C=N bond is more delocalised than the C=C bond in the imdazolium ring when compared to the neutral imidazole system,[31] whereas the single and double bonds of the N–C=N part are in the range of 1.349 and 1.313 Å and the C=C double bond is lengthened to 1.360 Å. The vinyl group in **3b** and in **3c** is nearly coplanar to the imidazolium plane, whereas the ethenyl group is twisted out of the plane with torsion angles N1–C3–C2–C4 of −61.6(6)° and N1B–C3B–C2B–C4B of 68.6(6)° for **3b** and 42.9(5)° for **3c**. Conformational disorder was observed for the vinyl substituent in **3c** (ratio 3 : 1), but the bond distance of the ethenyl group [C(7)–C(8)] in **3b** and **3c** is in the normal range of a double bond.[31] The angles in the ring vary between 107.1(3) and 109.0(3)°. The bond parameters for the imidazolium ring are similar to reported values.[32,33]

Bond angles and lengths of the tetrahedral tetraphenylborate anion in **3b** agree with values described for 1-butyl-3-methyl-2,3-dihydro-1*H*-imidazolium tetraphenylborate.[29] The average B–C bond distance is 1.651(5) Å.

Similarly, the bond parameters of the PF_6^- anion in **3c** are comparable to other reported examples.[33] The average P–F bond distance is 1.586(2) Å and the F–P–F(*cis*) and F–P–F(*trans*) angles deviate only slightly from 90 and 180°.

Packing in **3b** and **3c** consists of an interconnecting network of cations and anions. The crystallographic asymmetric unit in **3b** contains two ionic pairs, each with two C–H ··· π contacts [H(4) ··· C(21)–C(26) centroid 2.58, H(1) ··· C(9)–C(14) centroid 2.71 and H(4B) ··· C(45)–C(50) centroid 2.44, H(1B) ··· C(39)–C(44) centroid 2.62 Å]. These pairs are interconnected by further C–H ··· π contacts building a column along the *b*-axis [H(5) ··· C(33)–C(38) centroid 2.45, H(8Ba) ··· C(21)–C(26) centroid 2.74 Å]. In **3c** the imidazolium units are arranged in layers and face each other with PF_6^- anions sandwiched between these layers. The $Co_2(CO)_6$ units face each other in the alternate layers, and C–H ··· F [F(2) ··· H(4) 2.47, F(3) ··· H(3A) 2.60, F(4) ··· H(5) 2.37, F(6) ··· H(4) 2.45 Å] and O ··· H [O(4) ··· H(5) 2.50 Å] interactions dominate lattice arrangement.

Conclusions

The imidazolium salts **1a**–**c** and **2a** prepared from commercially available starting materials have the advantage that the N substituents carry alkene and alkyne groups which are available for derivatisation creating possibilities for a multitude of new imidazolium salts and ionic liquids.

Cobalt complexes of the imidazolium salts, **3a**–**c**, **4a** and **4b** were purified and isolated by exploiting differences in solubility upon variation of the counteranion. Compound **4b** melting at 75 °C qualifies as an ionic liquid.

The imidazolium protons, NC(H)N and NCH=CHN, in compounds **1b** and **3b** containing the tetraphenylborate anion experience π-interaction with the phenyl rings of the anion both in solution and in the solid state.

Experimental

General

Reactions were carried out under argon using standard Schlenk and vacuum-line techniques. Tetrahydrofuran and diethyl ether were distilled under N_2 from sodium diphenylketyl, CH_2Cl_2 from CaH_2 and hexane from sodium. All starting materials are commercially available and were used without further purification. Melting points were determined on a Kofler hot-stage or an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on an AMD 604, Varian CH-7 (EI, 70eV) or a MAT 95 (FAB in glycerin) instrument, the infrared spectra on a Perkin-Elmer 1600 Series FTIR or a Nicolet 510FT-IR spectrometer and NMR spectra on a Bruker AC 200, Varian 300 FT or INOVA 600 MHz spectrometer (^{1}H NMR at 200/300/600 MHz, ^{13}C{^{1}H} NMR at 75/150 MHz and ^{31}P{^{1}H} NMR at 121/243 MHz, δ reported relative to the solvent resonance, TMS or external reference 85% H_3PO_4). Elemental analyses were carried out by the Analytical Department of Lenzing AG, A-4840 Lenzing, Austria or the Department of Chemistry, University of Cape Town, South Africa.

Preparation of [HC≡CCH$_2$N=C(H)N(CH=CH$_2$)CH=CH]Br, 1a. Dichloromethane (30 cm^3), 80% HC≡CCH$_2$Br in toluene (16.9 cm^3, 151.7 mmol) and 1-vinyl-1*H*-imidazole (10.0 cm^3, 110.4 mmol) were stirred for 2.5 h at room temperature. The mixture was reduced to dryness *in vacuo*. After the addition of diethyl ether (40 cm^3) to the residue, trituration, filtration and thorough washing with diethyl ether (3 × 50 cm^3) the beige product (15.34 g, 65%) was dried *in vacuo*, mp 157–158 °C (Found: C, 44.90; H, 3.95; N, 13.07, $C_8H_9BrN_2$ requires C, 45.09; H, 4.26; N, 13.15%); selected ν_{max}/cm^{-1} (C_4Cl_6, NaCl) 3154w [H–C≡CCH$_2$N], 3077w, 3047w (H–C=C), 2115m (C≡C); δ_H (CD$_3$CN, 600 MHz) 9.53 [1H, s, NCHN], 7.80 [1H, t, $^3J(Z)$ = 1.9 Hz, NC*H*=CHNCH=CH$_2$], 7.64 [1H, t, $^3J(Z)$ = 1.9 Hz, NCH=C*H*NCH=CH$_2$], 7.25 [1H, dd, $^3J(E)$ = 15.5 Hz, $^3J(Z)$ = 8.6 Hz, NCH=CHNC*H*=CH$_2$], 5.89 [1H, dd, $^2J_{gem}$ = 15.5 Hz, $^3J(Z)$ = 2.8 Hz, NCH=CHNCH=C(H$_{trans}$)*H*$_{cis}$], 5.43 [1H, dd, $^2J_{gem}$ = 8.6 Hz, $^3J(Z)$ = 2.8 Hz, NCH=CHNCH=C-(*H*$_{trans}$)H$_{cis}$], 5.17 [2H, d, $^2J_{gem}$ = 2.5 Hz, HCCC*H*$_2$NCHN], 3.08 [1H, t,^4J = 2.7 Hz, *H*CCCH$_2$NCHN]; δ_C (CD$_3$CN, 151 MHz) 136.1 (s, NCHN), 129.5 (s, NCH=CHN*C*H=CH$_2$), 123.7 (s, N*C*H=CHNCH=CH$_2$), 120.8 (s, NCH=*C*HNCH=CH$_2$), 110.6 (s, NCH=CHNCH=*C*H$_2$), 78.8 (s, HC*C*CH$_2$NCHN), 75.2 (s, H*C*CCH$_2$NCHN), 40.4 (s, HCC*C*H$_2$NCHN); *m*/*z* (EI, 70 eV) 133 (M − Br, 11%), 94 (M–Br–CH$_2$C≡CH, 100%), 39 (CH$_2$C≡CH, 92%).

Preparation of [HC≡CCH$_2$N=C(H)N(CH=CH$_2$)CH=CH]B-(C$_6$H$_5$)$_4$, 1b. The addition NH$_4$B(C$_6$H$_5$)$_4$ (6.43 g, 18.8 mmol) to a solution of **1a** (2.0 g, 9.4 mmol) in H$_2$O (40 cm^3) and stirring for 5 min., yielded a colourless precipitate (4.11 g, 97%) of **1b** after extraction with CH$_2$Cl$_2$ (3 × 50 cm^3), washing of the extract with H$_2$O (2 × 100 cm^3), drying with MgSO$_4$ and removal of the solvent *in vacuo*; mp 170–171 °C (Found: C, 84.82; H, 6.64; N, 6.31, $C_{32}H_{29}BN_2$ requires C, 84.96; H, 6.46; N, 6.19%); selected ν_{max}/cm^{-1} (KBr) 3249w [H–CCCH$_2$N], 3098w, 3052w (H–C=C), 2134m (C≡C); δ_H (CD$_2$Cl$_2$, 600 MHz) 7.53 [8H, m, C$_6$H$_5$-*ortho*], 7.02 [8H, t, ^3J = 7.4 Hz, C$_6$H$_5$-*meta*], 6.79 [4H, m, ^3J = 7.4 Hz, C$_6$H$_5$-*para*], 6.66 [1H, m, ^3J = 1.7 Hz, NC*H*=CHNCH=CH$_2$], 6.62 [1H, m, ^3J = 1.7 Hz, NCH=C*H*NCH=CH$_2$], 6.15 [1H, dd, $^3J(E)$ = 15.6 Hz, $^3J(Z)$ = 8.5 Hz, NCH=CHNC*H*=CH$_2$], 5.26 [1H, dd, $^2J_{gem}$ = 15.6 Hz, ^3J(Z) = 3.2 Hz, NCH=CHNCH=C(H$_{trans}$)*H*$_{cis}$], 5.18 [1H, dd, $^2J_{gem}$ = 8.8 Hz, ^3J(Z) = 3.2 Hz, NCH=CHNCH=C(*H*$_{trans}$)H$_{cis}$], 4.81 [1H, br s, NCHN], 3.98 [2H, d, $^2J_{gem}$ = 2.4 Hz, HCCC*H*$_2$NCHN], 2.65 [1H, t, ^4J = 2.7 Hz, *H*CCCH$_2$NCHN]; δ_C (CD$_2$Cl$_2$, 151 MHz) 164.6 (q, $^1J_{BC}$ = 48 Hz, C$_6$H$_5$-*ipso*), 135.8 (s, C$_6$H$_5$-*ortho*), 134.3 (s, NCHN), 128.0 (s, NCH=CHN*C*H=CH$_2$), 126.5 (q, $^3J_{BC}$ = 2.9 Hz, C$_6$H$_5$-*meta*), 122.5 (s, C$_6$H$_5$-*para*), 121.6 (s, N*C*H=CHNCH=CH$_2$), 118.0 (s, NCH=*C*HNCH=CH$_2$), 109.8 (s, NCH=CHNCH=*C*H$_2$), 78.1 (s, HC*C*CH$_2$NCHN), 73.2 (s, H*C*CCH$_2$NCHN), 39.6 (s, HCC*C*H$_2$NCHN); *m*/*z* (EI, 70 eV) 452 [M$^+$, 0.2%], 242 [B(C$_6$H$_5$)$_3$, 54%], 164 [B(C$_6$H$_5$)$_2$, 100%].

Preparation of [HC≡CCH$_2$N=C(H)N(CH=CH$_2$)CH=CH]-PF$_6$, 1c. Compound **1c** was prepared in the same fashion as **1b**

from **1a** (1.0 g, 4.7 mmol) and NH_4PF_6 (1.53 g, 9.39 mmol) to yield a colourless precipitate (0.63 g, 48%); mp 86–88 °C (Found: C, 34.77; H, 3.08; N, 9.66, $C_8H_9F_6N_2P$ requires C, 34.55; H, 3.26; N, 10.07%); selected ν_{max}/cm^{-1} (KBr) 3292m [H–CCCH$_2$N], 3163m (H–C=C), 2141m (C≡C); δ_H (CD_2Cl_2, 600 MHz) 8.89 [1H, s, NCHN], 7.60 [1H, m, NC*H*=CHNCH=CH$_2$], 7.58 [1H, m, NCH=C*H*NCH=CH$_2$], 7.08 [1H, dd, $^3J(E)$ = 15.5 Hz, ^3J(Z) = 8.4 Hz, NCH=CHNC*H*=CH$_2$], 5.83 [1H, dd, $^2J_{gem}$ = 15.5 Hz, ^3J(Z) = 3.1 Hz, NCH=CHNCH=C(H$_{trans}$)*H*$_{cis}$], 5.54 [1H, dd, $^2J_{gem}$ = 8.4 Hz, $^3J(Z)$ = 3.1 Hz, NCH=CHNCH=C(*H*$_{trans}$)H$_{cis}$], 5.09 [2H, d, $^2J_{gem}$ = 2.7 Hz, HCCC*H*$_2$NCHN], 2.85 [1H, t, ^4J = 2.5 Hz, *H*CCCH$_2$NCHN]; δ_C (CD_2Cl_2, 151 MHz) 134.5 (s, NCHN), 128.1 (s, NCH=CHN*C*H=CH$_2$), 123.0 (s, N*C*H=CHNCH=CH$_2$), 120.1 (s, NCH=*C*HNCH=CH$_2$), 111.7 (s, NCH=CHNCH=*C*H$_2$), 78.8 (s, HC*C*CH$_2$NCHN), 73.1 (s, H*C*CCH$_2$NCHN), 40.4 (s, HCC*C*H$_2$NCHN), δ_P (CH_2Cl_2, 243 MHz) −143.3 (sp, $^1J_{PF}$ = 711.6 Hz, PF_6^-); *m*/*z* (EI, 70 eV) 131 (M − PF_6^-, 35%), 107 (M − PF_6^- − CHCH$_2$, 100%), 94 (M − PF_6^- − CH$_2$CCH, 53%).

Preparation of [HC≡CCH$_2$N=C(H)N(CH$_2$CH=CH$_2$)CH=CH]Br, 2a. Compound **2a** was prepared in the same way as **1a** from 1-allyl-1*H*-imidazole (5.0 cm^3, 44.0 mmol) and 80% HC≡CCH$_2$Br in toluene (7.2 cm^3, 65 mmol) and colourless, hygroscopic crystals of **2a** (10.8 g, 98%) were obtained, mp 65–66 °C (Found: C, 47.23; H, 5.50; N, 11.98, $C_9H_{11}BrN_2$ requires C, 47.60; H, 4.88; N, 12.34%); selected ν_{max}/cm^{-1} (KBr) 3186w, 3120w [H–C≡CCH$_2$N], 3087w, 3045w (H–C=C), 2116m (C≡C); δ_H (CD_3CN, 600 MHz) 9.48 [1H, s, NCHN], 7.67 [1H, t, ^3J = 1.7 Hz, NC*H*=CHNCH$_2$CH=CH$_2$], 7.56 [1H, t, ^3J = 1.7 Hz, NCH=C*H*NCH$_2$CH=CH$_2$], 6.05 [1H, m, $^3J(E)$ = 17.0 Hz, $^3J(Z)$ = 10.4 Hz, ^3J = 6.3 Hz, NCH=CHNCH$_2$C*H*=CH$_2$], 5.40 [2H, m, NCH=CHNCH$_2$CH=C(*H*$_{trans}$)*H*$_{cis}$], 5.25 [2H, d, ^2J = 2.7 Hz, HCCC*H*$_2$NCHN], 4.90 [2H, dt, ^4J = 1.3 Hz, ^3J = 6.3 Hz, NCH=CHNC*H*$_a$(*H*$_e$)CH=C(H$_{trans}$)H$_{cis}$], 3.13 [1H, t, ^4J = 2.7 Hz, *H*CCCH$_2$NCHN]; δ_C (CD_3CN, 151 MHz) 137.1 (s, NCHN), 131.1 (s, NCH=CHNCH$_2$*C*H=CH$_2$), 123.7 (s, NCH=CHNCH$_2$CH=*C*H$_2$), 123.2 (s, N*C*H=CHNCH$_2$CH=CH$_2$), 121.9 (s, NCH=*C*HNCH$_2$CH=CH$_2$), 78.4 (s, HC*C*CH$_2$NCHN), 75.6 (s, H*C*CCH$_2$NCHN), 52.6 (s, NCH=CHN*C*H$_2$CH=CH$_2$), 40.2 (s, HCC*C*H$_2$NCHN); *m*/*z* (EI, 70 eV) 227 (M$^+$, 10%), 147 (M − Br, 30%).

Preparation of [{μ$_2$-HCCCH$_2$N=C(H)N(CH=CH$_2$)CH=CH}Co$_2$(CO)$_6$]BF$_4$, 3a. The addition of $Co_2(CO)_8$ (4.62 g, 13.51 mmol) to a solution of **1a** (1.73 g, 8.11 mmol) in CH_2Cl_2 (80 cm^3) and THF (20 cm^3) and stirring for 3 days at room temperature produced an orange–brown precipitate. After removal of the solvent the residue was treated with water (1000 cm^3) and the unreacted $Co_2(CO)_8$ was extracted with diethyl ether (100 cm^3). After addition of NH_4BF_4 (1.30 g, 12.40 mmol) and stirring for 5 min., the orange mixture was extracted with CH_2Cl_2 (3 × 150 and 1 × 50 cm^3). The combined organic layers were washed with water (3 × 250 cm^3), dried with anhydrous $MgSO_4$ and evaporated to dryness *in vacuo* after filtration, to yield orange microcrystalline material (0.67 g, 16%), mp 129 °C (decomp.) (Found: C, 32.91; H, 2.10; N, 5.93, $C_{14}H_9BCo_2F_4N_2O_6$ requires C, 33.24; H, 1.79; N, 5.53%); selected ν_{max}/cm^{-1} (KBr) 3182w, 3150w [H–CCCo$_2$(CO)$_6$], 3108w (H–C=C), 2101vs (C–O), 2049vs (C–O), 2022vs (C–O), 1573m [CCCo$_2$(CO)$_6$]; δ_H (CD_3CN, 200 MHz) 8.99 [1H, s, NCHN], 7.79 [1H, m, NC*H*=CHNCH=CH$_2$], 7.69 [1H, m, NCH=C*H*NCH=CH$_2$], 7.19 [1H, dd, $^3J(E)$ = 15.8 Hz, $^3J(Z)$ = 8.8 Hz, NCH=CHNC*H*=CH$_2$], 6.51 [1H, s, *H*CCCH$_2$NCHN] 5.85 [1H, dd, $^3J(E)$ = 15.6 Hz, $^2J(Z)$ = 3.0 Hz, NCH=CHNCH=C(H$_{trans}$)*H*$_{cis}$], 5.55 [2H, s, HCCC*H*$_2$NCHN], 5.46 [1H, dd, $^3J(E)$ = 8.6 Hz, $^2J(Z)$ = 2.8 Hz, NCH=CHNCH=C(*H*$_{trans}$)H$_{cis}$]; δ_C (CD_2Cl_2, 75 MHz) 199.4 (s, CO), 136.1 (s, NCHN), 128.6 (s, NCH=CHN*C*H=CH$_2$), 123.6 (s, N*C*H=CHNCH=CH$_2$), 120.0 (s, NCH=*C*HNCH=CH$_2$), 111.6 (s, NCH=CHNCH=*C*H$_2$), 87.2 (s, HC*C*CH$_2$NCHN), 74.9 (s, H*C*CCH$_2$NCHN), 53.3 (s, HCC*C*H$_2$NCHN); *m*/*z* (FAB, positive ion) 418.83 ($C_{14}H_9Co_2N_2O_6^+$, 100%).

Preparation of [{μ$_2$-HCCCH$_2$N=C(H)N(CH=CH$_2$)CH=CH}Co$_2$(CO)$_6$]B(C$_6$H$_5$)$_4$, 3b. The addition of $Co_2(CO)_8$ (0.83 g, 2.43 mmol) to a solution of **1b** (1.00 g, 2.2 mmol) in CH_2Cl_2 (80 cm^3) and stirring for 1h at room temperature produced an orange–brown solution. After reducing the solvent *in vacuo* the residue was washed with diethyl ether (2 × 50 cm^3) to extract the unreacted $Co_2(CO)_8$. The product was extracted with a H_2O/CH_2Cl_2 (200/150 cm^3) mixture. The organic layer was washed with water (100 cm^3), dried with anhydrous Na_2SO_4 and evaporated to dryness *in vacuo* after filtration, to yield red microcrystalline material (0.81 g, 50%), mp 75 °C (decomp.) (Found: C, 61.82; H, 3.86; N, 3.68, $C_{38}H_{29}BCo_2N_2O_6$ requires C, 61.82; H, 3.96; N, 3.79%); selected ν_{max}/cm^{-1} (KBr) 3136w [H–CCCo$_2$(CO)$_6$], 3066w (H–C=C), 2114vs (C–O), 2068vs (C–O), 2045vs (C–O), 2017vs (C–O), 1542m [CCCo$_2$(CO)$_6$]; δ_H (CD_2Cl_2, 300 MHz) 7.48 [8H, br s, C$_6$H$_5$-*ortho*], 7.04 [8H, t, ^3J = 7.3 Hz, C$_6$H$_5$-*meta*], 6.93–6.85 [5H, m, NCH=C*H*NCH=CH$_2$, C$_6$H$_5$-*para*], 6.71 [1H, s, NC*H*=CHNCH=CH$_2$], 6.26 [1H, dd, $^3J(E)$ = 15.5 Hz, $^3J(Z)$ = 8.8 Hz, NCH=CHNC*H*=CH$_2$], 6.06 [1H, s, *H*CCCH$_2$NCHN] 5.38–5.21 [3H, m, $^3J(Z)$ = 8.8 Hz, $^2J_{gem}$ = 3.2 Hz, NCHN, NCH=CHNCH=C(*H*$_{trans}$)*H*$_{cis}$], 4.53 [2H, s, HCCC*H*$_2$NCHN]; δ_C (CD_2Cl_2, 75 MHz) 198.7 (s, CO), 164.7 (q, $^1J_{BC}$ = 48.8 Hz, C$_6$H$_5$-*ipso*), 136.2 (s, C$_6$H$_5$-*ortho*), 134.3 (s, NCHN), 128.1 (s, NCH=CHN*C*H=CH$_2$), 126.6 (q, $^3J_{BC}$ = 1.9 Hz, C$_6$H$_5$-*meta*), 122.7 (s, C$_6$H$_5$-*para*), 122.4 (s, N*C*H=CHNCH=CH$_2$), 118.9 (s, NCH=*C*HNCH=CH$_2$), 110.6 (s, NCH=CHNCH=*C*H$_2$), 84.9 (s, HC*C*CH$_2$NCHN), 74.5 (s, H*C*CCH$_2$NCHN), 52.2 (s, HCC*C*H$_2$NCHN); *m*/*z* (FAB, positive ion) 418.9 ($C_{14}H_9Co_2N_2O_6^+$, 26%).

Preparation of [{μ$_2$-HCCCH$_2$N=C(H)N(CH=CH$_2$)CH=CH}Co$_2$(CO)$_6$]PF$_6$, 3c. Compound **3c** was prepared in the same way as **3b** from **1c** (0.21 g, 0.77 mmol) and $Co_2(CO)_8$ (0.27 g, 0.79 mmol). Orange, microcrystalline material (0.15 g, 34%) was obtained, mp 132 °C (decomp.) (Found: C, 29.61; H, 1.82; N, 5.04, $C_{14}H_9Co_2F_6N_2O_6P$ requires C, 29.81; H, 1.61; N, 4.97%); selected ν_{max}/cm^{-1} (KBr) 3161w, 3114w [H–CCCo$_2$(CO)$_6$], 3053w (H–C=C), 2102vs (C–O), 2061vs (C–O), 2030vs (C–O), 1554m [CCCo$_2$(CO)$_6$]; δ_H (CD_2Cl_2, 600MHz) 9.01 [1H, s, NCHN], 7.61 [1H, m, NCH=C*H*NCH=CH$_2$], 7.52 [1H, m, NC*H*=CHNCH=CH$_2$], 7.11 [1H, dd, $^3J(E)$ = 15.1 Hz, $^3J(Z)$ = 8.5 Hz, NCH=CHNC*H*=CH$_2$], 6.36 [1H, s, *H*CCCH$_2$NCHN], 5.82 [1H, d, $^3J(E)$ = 15.1 Hz, NCH=CHNCH=C(H$_{trans}$)*H*$_{cis}$], 5.55–5.50 [3H, m, HCCC*H*$_2$NCHN, NCH=CHNCH=C(*H*$_{trans}$)H$_{cis}$]; δ_C (CD_2Cl_2, 151 MHz) 198.5 (s, *C*O), 134.9 (s, NCHN), 128.1 (s, NCH=CHN*C*H=CH$_2$), 123.6 (s, N*C*H=CHNCH=CH$_2$), 120.0 (s, NCH=*C*HNCH=CH$_2$), 111.8 (s, NCH=CHNCH=*C*H$_2$), 86.5 (s, HC*C*CH$_2$NCHN), 74.7 (s, H*C*CCH$_2$NCHN), 53.4 (s, HCC*C*H$_2$NCHN), δ_P (CH_2Cl_2, 243 MHz) −143.7 (sp, $^1J_{PF}$ = 711.6 Hz, PF_6^-); *m*/*z* (FAB, positive ion) 418.9 ($C_{14}H_9Co_2N_2O_6^+$, 100%).

Preparation of [{μ$_2$-HCCCH$_2$N=C(H)N(CH$_2$CH=CH$_2$)CH=CH}Co$_2$(CO)$_6$]BF$_4$, 4a. Complex **4a** was prepared in the fashion as **3a** from **2a** (1.60 g, 7.05 mmol), $Co_2(CO)_8$ (2.53 g, 7.40 mmol), and NH_4BF_4 (0.96 g, 9.16 mmol) (used in the water extraction). Dark red, microcrystalline material (1.05 g, 29%) was obtained, mp 76 °C (decomp.) (Found: C, 34.38; H, 2.08; N, 5.19, $C_{15}H_{11}BCo_2F_4N_2O_6$ requires C, 34.65; H, 2.13; N, 5.39%); selected ν_{max}/cm^{-1} (KBr) 3139w [H–CCCo$_2$(CO)$_6$], 3101w, (H–C=C), 2102vs (C–O), 2060vs (C–O), 2010vs (C–O), 1557m [CCCo$_2$(CO)$_6$]; δ_H (CH_2Cl_2, 300 MHz) 9.10 [1H, s, NCHN], 7.50 [1H, m, NC*H*=CHNCH$_2$CH=CH$_2$], 7.38 [1H, m, NCH=

Table 2 Crystal data and structure refinement for **3b** and **3c**

	3b	**3c**
Molecular formula	$C_{38}H_{29}BCo_2N_2O_6$	$C_{14}H_9Co_2F_6N_2O_6P$
M_r	738.30	564.06
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
Unit cell dimensions		
a/Å	9.4434(2)	8.089(2)
b/Å	17.5931(5)	9.378(2)
c/Å	21.6424(7)	14.739(4)
α/°	99.918(2)	85.89(2)
β/°	98.869(2)	87.19(2)
γ/°	91.452(2)	66.28(2)
V/Å^3	3494.58(17)	1020.7(4)
Z	4	2
T/K	233(3)	203(2)
D_c/g cm^{-3}	1.403	1.835
μ/mm^{-1}	0.998	1.791
F(000)	1512	556
Color, habit	Red prism	Orange prism
Crystal size/mm	0.3 × 0.14 × 0.09	0.7 × 0.3 × 0.25
θ-Range for data collection/°	1.65–23.00	4.09–25.00
Index ranges, hkl	0 to 10; −19 to 19; −23 to 23	−1 to 9; −11 to 11; −17 to 17
No. of reflections collected	17646	4392
No. of independent reflections (R_{int})	9694 (0.0252)	3578 (0.0191)
No. of reflections with $I > 2\sigma(I)$	7664	3006
Absorption correction	None	ψ-Scans
Max., min. transmission		0.842, 0.671
Refinement method	Full-matrix least squares on F^2	Full-matrix least squares on F^2
Data, restraints, parameters	9694, 0, 892	3578, 0, 303
Goodness-of-fit on F^2	1.051	1.036
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0419$; $wR2 = 0.1016$	$R1 = 0.0331$; $wR2 = 0.0815$
R indices (all data)	$R1 = 0.0588$; $wR2 = 0.1019$	$R1 = 0.0432$; $wR2 = 0.0854$
Extinction coefficient	0.0006(2)	0.0001(10)
Largest diff. peak and hole/e nm^{-3}	1267 and −813	459 and −268

C*H*NCH$_2$CH=CH$_2$], 6.38 [1H, s, *H*CCCH$_2$NCHN], 5.98 [1H, m, NCH=CHNCH$_2$C*H*=CH$_2$], 5.53 [2H, s, HCCC*H*$_2$NCHN], 5.50 [1H, m, NCH=CHNCH$_2$CH=C(H$_{trans}$)H_{cis}], 5.47 [1H, m, NCH=CHNCH$_2$CH=C(H_{trans})H$_{cis}$], 4.83 [2H, dm, ^2J = 6.5 Hz, NCH=CHNCH_a(H_e)CH=C(H$_{trans}$)H$_{cis}$]; δ_C (CH$_2$Cl$_2$, 75 MHz) 198.9 (s, *C*O), 136.8 (s, NCHN), 129.8 (s, NCH=CHNCH$_2$*C*H=CH$_2$), 123.4 (s, NCH=CHNCH$_2$CH=*C*H$_2$), 123.2 (s, N*C*H=CHNCH$_2$CH=CH$_2$), 122.7 (s, NCH=*C*HNCH$_2$CH=CH$_2$), 87.6 (s, HC*C*CH$_2$NCHN), 74.8 (s, H*C*CCH$_2$NCHN), 52.9 (s, HCC*C*H$_2$NCHN), 52.8 (s, NCH=CHN*C*H$_2$CH=CH$_2$); *m*/*z* (FAB, positive ion) 432.9 ($C_{15}H_{11}Co_2N_2O_6^+$, 100%).

Preparation of [{μ_2-HCCCH$_2$$\overline{\text{N=C(H)N(CH}_2\text{CH=CH}_2\text{)CH=C}}$-H}Co$_2(CO)_6$]PF$_6$, 4b. The salt **4b** was obtained in a similar fashion to **3a** from **2a** (2.00 g, 8.81 mmol), Co$_2$(CO)$_8$ (3.16 g, 9.24 mmol), and NH$_4$PF$_6$ (1.58 g, 9.69 mmol) (used in the water extraction). Red microcrystalline material (1.09 g, 21%) was obtained, mp 75–77 °C (reversible) (Found: C, 31.11; H, 1.90; N, 4.92, $C_{15}H_{11}Co_2F_6N_2O_6P$ requires C, 31.17; H, 1.92; N, 4.85%); selected ν_{max}/cm^{-1} (KBr) 3154w [H–CCCo$_2$(CO)$_6$], 3090w, (H–C=C), 2119vs (C–O), 2059vs (C–O), 1989vs (C–O), 1560m [CCCo$_2$(CO)$_6$]; δ_H (CD$_2$Cl$_2$, 300 MHz) 8.80 [1H, s, NCHN], 7.45 [1H, m, NC*H*=CHNCH$_2$CH=CH$_2$], 7.36 [1H, m, NCH=C*H*NCH$_2$CH=CH$_2$], 6.37 [1H, s, *H*CCCH$_2$NCHN], 5.97 [1H, m, NCH=CHNCH$_2$C*H*=CH$_2$], 5.54 [1H, br s, HCCC*H*$_2$NCHN], 5.49 [3H, br s, HCCC*H*$_2$NCHN and NCH=CHNCH$_2$CH=C(H_{trans})H_{cis}], 4.82 [2H, d, ^2J = 6.3 Hz, NCH=CHNCH_a(H_e)CH=C(H$_{trans}$)H$_{cis}$]; δ_C (CD$_2$Cl$_2$, 75 MHz) 198.7 (s, CO), 136.2 (s, NCHN), 129.4 (s, NCH=CHNCH$_2$*C*H=CH$_2$), 123.9 (s, NCH=CHNCH$_2$CH=*C*H$_2$), 123.2 (s, N*C*H=CHNCH$_2$CH=CH$_2$), 122.8 (s, NCH=*C*HNCH$_2$CH=CH$_2$), 87.0 (s, HC*C*CH$_2$NCHN), 74.8 (s, H*C*CCH$_2$NCHN), 53.1 (s, HCC*C*H$_2$NCHN), 53.0 (s, NCH=CHN*C*H$_2$CH=CH$_2$), δ_P (CH$_2$Cl$_2$, 121 MHz) −143.4 (sp, $^1J_{PF}$ = 710.3 Hz, PF$_6^-$); *m*/*z* (FAB, positive ion) 432.9 ($C_{15}H_{11}Co_2N_2O_6^+$, 100%).

X-Ray crystal structure determinations

Crystal structure determination of 3b and 3c. Single crystals of **3b** or **3c** suitable for X-ray analysis, were obtained by slow crystallisation from dichloromethane or dichloromethane/diethyl ether.

For compound **3b** a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-Kα radiation was used and the raw data were processed with the program DENZO-SMN[34] to obtain the conventional data. For compound **3c** a Bruker P4 diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) was used for data collection. Intensities were measured *via* ω-scans and corrected for Lorentz and polarisation effects. The structure was solved by direct methods (SHELXS-86)[35] and refined by full-matrix least squares against F^2 (SHELXL-97).[36] The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms at the ethynyl groups of **3b** and **3c** were refined isotropically; all others were placed on calculated positions. The atoms of the ethenyl group in **3c** were split in two positions by a 3 : 1 disorder of C(7)=C(8) and C(7A)=C(8A), leading to more inexact bond distances and angles around this group by correlation effects. Further crystallographic data are collected in Table 2.

CCDC reference numbers 215682 and 215683.

See http://www.rsc.org/suppdata/dt/b3/b308252k/ for crystallographic data in CIF or other electronic format.

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