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Organometallic Complexes Derived from Alkyne-Functionalized Imidazolium Salts

Zhaofu Fei, Dongbin Zhao, Rosario Scopelliti, and Paul J. Dyson*

Institut de Chimie Moléculaire et Biologique, Ecole Polytechnique Fédérale de Lausanne, EPFL-BCH, CH-1015 Lausanne, Switzerland

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Two 1,3-dialkyne-functionalized imidazolium chlorides, 1,3-dipropynylimidazolium chloride and 1,3-dipentynylimidazolium chloride, have been prepared from the direct reaction between the appropriate chloroalkyne and (trimethylsilyl)imidazole. Replacement of the chloride counterion with BF_4^- or BPh_4^- gave four further imidazolium salts, three of which melt below 100 °C and one of which is a liquid at room temperature. Reactions of the BF_4^- and BPh_4^- salts with $Co_2(CO)_8$ afforded complexes in which both of the alkyne functionalities coordinated to a $Co_2(CO)_6$ unit. One of these organometallic derivatives, viz. 1,3-dipentynylimidazolium bis(hexacarbonyldicobalt) tetrafluoroborate, can be classified as an ionic liquid on the basis of its melting point. The solid-state structures of three of these new salts have been elucidated by single-crystal X-ray diffraction, revealing extensive networks of C···H···π and π···π interactions. Attempts to prepare carbene derivatives from the functionalized imidazolium salts have also been made.

Introduction

The application of ionic liquids to overcome a variety of problems in catalysis has caught the imagination of researchers across the world, and a number of excellent reviews on this topic have been published in the past few years.[1] Many catalysts immobilized in ionic liquids are organometallic species, are derived from organometallics, or involve organometallic intermediates at certain stages of the reaction cycle. However, in addition to these catalyst systems, classical organometallic reactions have been carried out in ionic liquids and ionic liquids containing organometallic components have also been prepared.[2]

The organometallic alkylchloroaluminates were among the first widely studied ionic liquids, and they were employed in the first transition-metal-catalyzed reactions to be conducted in ionic liquids. Chauvin and coworkers combined them with various nickel complexes to give solutions that catalyzed the dimerization of alkenes.[3] Around the same time, Carlin and Osteryoung showed that the Ziegler−Natta catalyst $Ti(\eta\text{-}C_5H_5)_2Cl_2$ dissolved in alkylchloroaluminates was able to polymerize ethylene.[4] In both processes, the transition-metal catalysts were only active when a Lewis acidic ionic liquid was used.

Following the pioneering work of Chauvin, Carlin, and Osteryoung, Lewis acidic chloroaluminate ionic liquids have found numerous applications in catalysis[5] and have also been exploited in the synthesis of organometallic compounds such as transition-metal−arene complexes. Lewis acidic [bmim]Cl−$AlCl_3$ (bmim = 1-butyl-3-methylimidazolium cation), combined with the Brønsted acid [bmim][HCl_2], aluminum powder, and an arene, is an excellent medium for cyclopentadienyl ring exchange reactions of ferrocene leading to compounds of the general formula $[Fe(\eta\text{-}C_5H_5)(\eta\text{-arene})]^+$.[6] In Lewis acidic [bmim]Cl−$AlCl_3$ ionic liquid, chromium(III) chloride may be reduced with aluminum in the presence of an arene to afford sandwich complexes of the formula $[Cr(\eta\text{-arene})_2]^+$, and $Mn(CO)_5Br$ reacts with arenes to afford the half-sandwich compounds $[Mn(CO)_3(\eta\text{-arene})]^+$.[7] In these reactions the intrinsically high concentration of the Lewis acid catalyst facilitates the reaction; unfortunately, isolation of the complexes from these reactions involves addition of an aqueous solution of HBF_4, resulting in the decomposition of the ionic liquid. The acylation of ferrocene may also be conducted in acidic choroaluminate ionic liquid. Ferrocene reacts with ethanoyl chloride in [bmim]Cl−$AlCl_3$ to afford 1-ethanoylferrocene as the main product and 1,1′-diethanoylferrocene and 1,2-diethanoylferrocene in somewhat lower yield.[8]

Organometallic compounds have also been prepared in basic ionic liquid; for example, [emim]Cl−$AlCl_3$ (emim

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* To whom correspondence should be addressed. E-mail: paul.dyson@epfl.ch.

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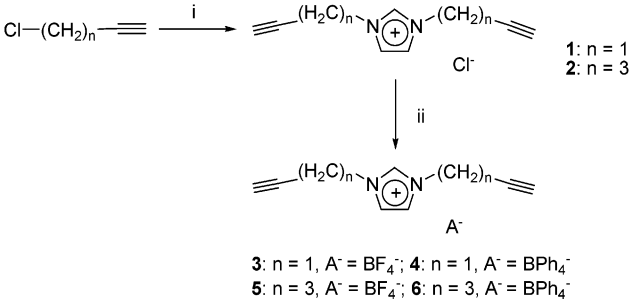
= the 1-ethyl-3-methylimidazolium cation) has been used as a medium to prepare a platinum carbene complex from $PtCl_2$, $PtCl_4$, and ethylene.[9] The reaction exploits the fact that the proton in the 2-position of imidazolium cations is acidic and may be removed under basic conditions. Since palladium−carbene complexes have been implicated as catalysts in C−C cross-coupling reactions conducted in ionic liquids, there have been some attempts to show under what conditions such species are likely to be generated, under conditions more characteristic of real catalytic systems; i.e., in the presence of a phosphine ligand and base, palladium−carbene complexes have been observed.[10]

In an interesting development, organometallic anions have been combined with imidazolium cations to give low-melting salts. For example, [bmim]Cl reacts with $Na[Co(CO)_4]$ in propanone to afford $[bmim][Co(CO)_4]$, and a similar approach has been used to prepare ionic liquids containing $[Mn(CO)_5]^-$ and $[HFe(CO)_4]^-$.[11] The cobalt-containing ionic liquid has also been shown to be catalytically active. The Monsanto catalyst has also been isolated in liquid form as $[bmim][Rh(CO)_2I_2]$, prepared from the direct reaction of $[Rh(CO)_2I]_2$ and 2 equiv of [bmim]I in methanol.[12] Since the submission of this paper related, but different, alkyne-functionalized imidazolium salts and their dicobalt hexacarbonyl derivatives have been reported.[13]

Inclusion of organometallic fragments as part of the cationic component of the ionic liquid has yet to be reported. However, a number of ionic liquids composed of cations that have been derivatized with functionalized groups that can complex to metal centers, albeit not necessarily affording organometallic species, have been reported. Functional groups that have been reported include thiourea, thioether, and urea employed for the extraction of metal ions from aqueous solutions,[14,15] amines,[13,14,16,17] amides,[18] phosphines,[19] and nitriles.[20] In this paper we describe the synthesis and characterization of alkyne-functionalized imidazolium salts (some of which are ionic liquids by virtue of their low melting points) and their subsequent organometallic (dicobalthexacarbonyl) derivatives. One of these organometallic ionic liquids has a melting point of 100 °C, which by definition[21] can be regarded as an ionic liquid.

Scheme 1. Synthesis of 1−6



[a] Reagents and conditions: (i) (trimethylsilyl)imidazole; (ii) $NaBF_4$ for **3** and **5**, $NaBPh_4$ for **4** and **6**.

Table 1. Melting Point Data for 1−10

compd	mp (°C)	compd	mp (°C)
1	142	**6**	135
2	65	**7**	110
3	67	**8**	115
4	185	**9**	100
5	−23	**10**	132

Results and Discussion

The reaction of the commercially available chloroalkynes with (trimethylsilyl)imidazole using a literature method[22] gave the alkyne-derivatized imidazolium salts **1** and **2** in a single step in high yield (see Scheme 1). Compounds **1** and **2** were isolated as white solids following washing with diethyl ether, but they were very hygroscopic and became pale yellow oils when exposed to air. Treatment of **1** and **2** with $NaBF_4$ or $NaBPh_4$ in acetone afforded **3**−**6**, which were isolated in pure form following washing with diethyl ether. Compounds **2**, **3**, and **5** melt below 100 °C (Table 1) and can be classified as ionic liquids, with **5** being a liquid at room temperature.

Characterization of **1**−**6** was achieved using a combination of electrospray ionization (ESI) mass spectrometry, IR, ^1H, and ^{13}C NMR spectroscopy, and elemental analysis. Two of the salts (**4** and **6**) were also characterized in the solid state by single-crystal X-ray diffraction.

The ESI mass spectra of **1**−**6** in water recorded in positive ion mode were dominated by a peak corresponding to the intact parent ion. Similarly, the negative ion spectra of **1**−**6** showed the presence of the anion.

The IR spectra of **1**, **3**, and **4** exhibit a sharp medium/strong vibration in the region 2125−2132 cm^{-1}, which corresponds to the $C\equiv C$ bonds. In **2** a weak $C\equiv C$ vibration at 2112 cm^{-1} is observed, and in **5** and **6** the $C\equiv C$ bond does not afford a distinct vibration; instead, weak split vibrations between 2120 and 1842 cm^{-1} are observed, presumably due to interactions between the $C\equiv C{-}H$ bond from the cation and the phenyl ring from the anion. The two $C\equiv C{-}H$ groups in **4** and **6** are not identical, as confirmed by a single-crystal X-ray diffraction analysis (see below). Compound **1** also contains a vibration at 2410 cm^{-1}, which could be due to an intramolecular and/or intermolecular hydrogen bond between the chloride anion and the hydrogen atoms from the cation (the H atoms in the ring $NCH{=}CHN$, $NCHN$, and the arms $CH_2C\equiv CH$ are all acidic). Related

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anion−cation interactions have been noted elsewhere.[23,24] This may explain the difference in solubility of the imidazolium salts; viz., compound **1** is soluble in water and only sparingly soluble in dichloromethane, chloroform, and acetonitrile, whereas **2**−**6** are soluble in all these solvents.

The ^{1}H NMR spectra of **1**−**6** in CD_3CN give rise to signals between 7.47 and 9.00 ppm, which correspond to the protons on the imidazolium ring. The exact frequency is dependent on the concentration of the solution, presumably due to the presence of hydrogen-bonding interactions in solution, as observed previously.[25] The CH_2 units of **1**, **3**, and **4** display a doublet at 5.00 ppm (^4J(HH) = 2.44 Hz), and no significant influence of the anion could be observed. The alkyne protons in **1**, **3**, and **4** are around 3 ppm and in **2**, **5**, and **6** are around 2 ppm, and in all cases the two alkyne groups attached to the imidazolium ring are equivalent.

Crystals of **4** and **6** suitable for X-ray diffraction analysis were obtained from acetone by slow evaporation at room temperature. The structures of **4** and **6** are illustrated in Figures 1 and 2, respectively, and key bond parameters are given in the captions. Both are monoclinic crystal systems, but in **4** the cation displays a *pseudo* S_4 symmetry, whereas in **6** no particular molecular symmetry is observed for the cation. The two alkyne arms in **4** are trans to the imidazolium plane, while in **6** they are cis. There are $\pi\cdots\pi$ interactions between the imidazolium ring and a phenyl ring from the BPh_4^- anion, the centroid distances being the same in both compounds (3.568(2) Å in **4** and 3.568(3) Å in **6**). The C≡C bonds in **4** and **6** are not involved in any $\pi\cdots\pi$ interactions, but there are several significant C−H$\cdots\pi$ interactions in the solid state of **4** and **6**; related C−H$\cdots\pi$ interactions have been observed in imidazolium salts containing the BPh_4^- anion.[26] In **4** and **6** the H atom from the C≡C−H groups forms a hydrogen bond with a phenyl ring from the anion. The C≡C−H$\cdots\pi$ distances are very different; they are 2.92 Å for H6$\cdots\pi$ and 2.46 Å for H9$\cdots\pi$ in **4** and 2.81 Å for H13$\cdots\pi$ and 2.52 Å for H8$\cdots\pi$ in **6**. In compound **4**, only H1 from the imidazolium ring is involved in the C−H$\cdots\pi$ interaction (H1$\cdots\pi$ = 2.60 Å), but in compound **6**, all three hydrogens from the imidazolium ring form a C−H$\cdots\pi$ bond, with the strongest being that involving H3 (2.35 Å); this is in accordance with the fact that the H3 is the most acidic. In compound **4**, the H atoms from the sidearms (the CH_2 groups) also form hydrogen bonds with the phenyl rings from the anions. In contrast, in **6** none of the H atoms from the CH_2 groups interact with the phenyl rings of the anion. Presumably, the acidity of the CH_2 unit in **4** is enhanced by both the imidazolium ring and the alkyne unit.

The C≡C bond lengths are nearly the same in **4** and **6**, ranging from 1.170(3) to 1.192(7) Å. The tetraphenylborate anions in **4** and **6** have slightly distorted tetrahedral configurations. The different sidearms seem to affect the geometry around the boron in the anion. The B−C distances in **4** (1.642(3)−1.649(3) Å) are slightly shorter than those in **6** (1.648(7)−1.669(6) Å). The *cis*-{HC≡C(CH_2)$_3$}N(CH)N{(CH_2)$_3$C≡CH} group in **6** forms a cavity into which a phenyl ring of the anion has inserted. The C−H$\cdots\pi$ interaction is the strongest; accordingly, the B1−C20 distance of 1.669(6) Å is the longest and the C20−B1−C32 angle of 101.9(3)° is the smallest. In comparison, the longest B−C distance in 1-butyl-3-methylimidazolium salts containing a tetraphenylborate anion substituted with the strongly electron-withdrawing CF_3 group at the para position is 1.647 Å, with the smallest C−B−C angle being 103.72°.[27]

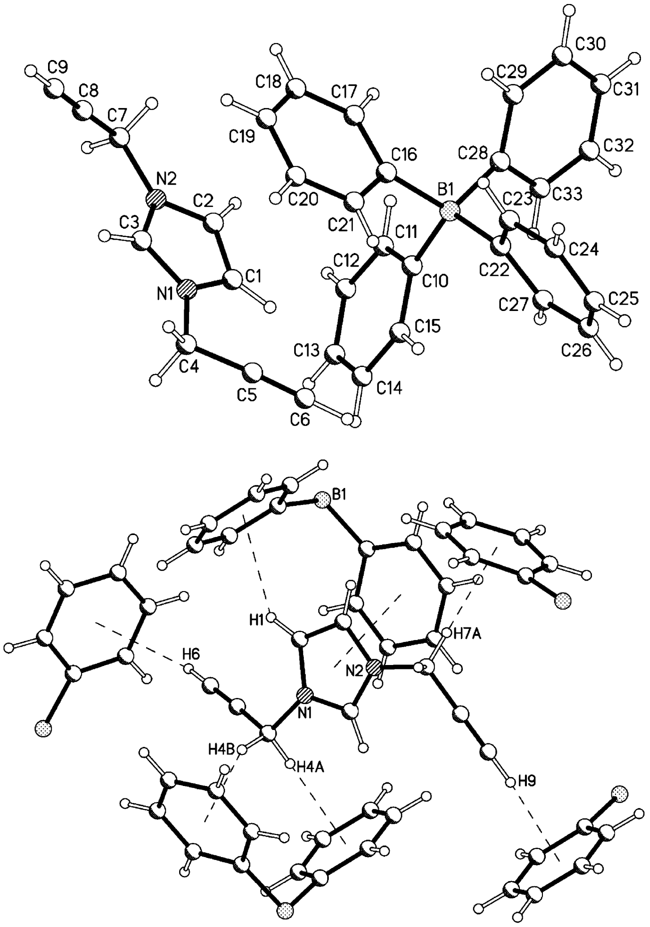

Figure 1. (top) Molecular structure of **4** in the solid state (showing the labeling scheme for the asymmetric unit). Key bond lengths (Å): N1−C3, 1.328(3); N1−C1, 1.379(3); N2−C3, 1.329(3); N2−C2, 1.384(3); C1−C2, 1.351(3); C5−C6, 1.170(3); C8−C9, 1.177(3). (bottom) $\pi\cdots\pi$ and C−H$\cdots\pi$ interactions around the imidazolium cation of **4**.

Reactions of 3−6 with $Co_2(CO)_8$. Hexacarbonyldicobalt−alkyne complexes have been known for many years and are most conveniently obtained by direct reaction of $Co_2(CO)_8$ with the alkyne, which acts as a four-electron donor.[28] Accordingly, reaction of the alkyne-

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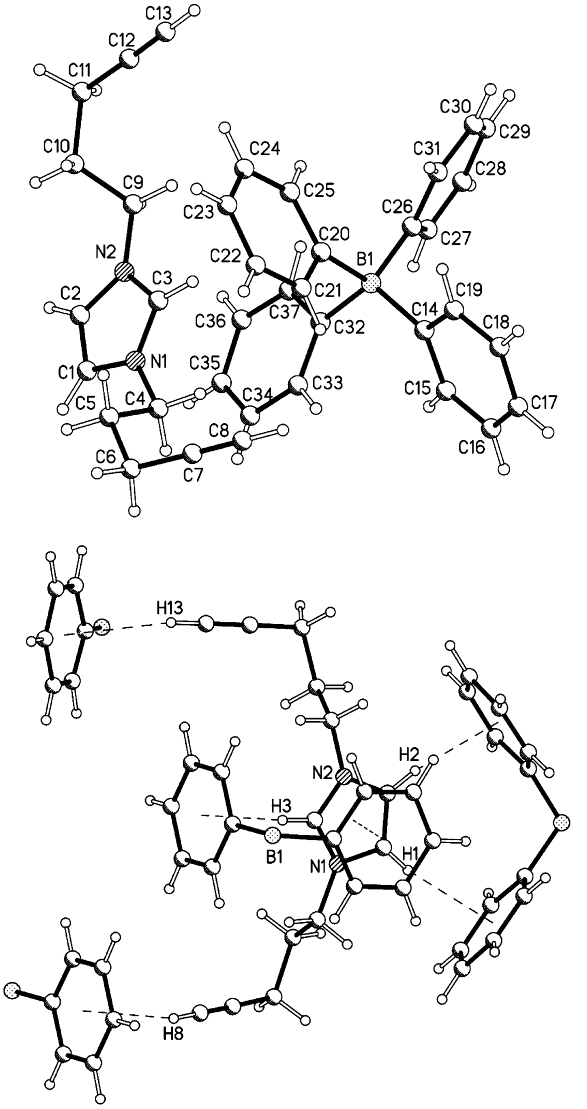
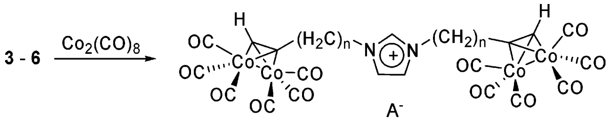


Figure 2. (top) Molecular structure of **6** in the solid state (showing the labeling scheme for the asymmetric unit). Key bond lengths (Å): N1−C3, 1.339(5); N1−C1, 1.376(5); N2−C3, 1.339(5); N2−C2, 1.376(5); C1−C2, 1.350(6); C7−C8, 1.169(6); C12−C13, 1.192(7). (bottom) $\pi\cdots\pi$ and C−H$\cdots\pi$ interactions around the imidazolium cation of **6**.

Scheme 2. Synthesis of 7−10



7: n = 1, $A^- = BF_4^-$; **8**: n = 1, $A^- = BPh_4^-$
9: n = 3, $A^- = BF_4^-$; **10**: n = 3, $A^- = BPh_4^-$

functionalized imidazolium salts **3**−**6** with 2.2 equiv of $Co_2(CO)_8$ in dichloromethane under ambient conditions gave the expected complexes **7**−**10** in high yield (see Scheme 2). The slight excess of $Co_2(CO)_8$ is essential to ensure complete derivatization of the alkyne functionalities. The organometallic products are obtained in high purity (as evidenced by elemental analysis) following washing with diethyl ether.

In keeping with related compounds, **7**−**10** are stable under an inert atmosphere but decompose slowly when exposed to air/moisture. They were characterized using the same methods outlined for compounds **1**−**6**. The positive ion ESI mass spectra of **7**−**10** exhibit parent peaks corresponding to the intact cation. The dominant feature in the IR spectra of **7**−**10** are the ν(CO) stretches, which exhibit the expected absorptions between 1990 and 2100 cm^{-1}. The wavenumber of the alkyne bond decreases to between 1600 and 1500 cm^{-1}, indicating the bond order to be more reminiscent of a C=C double bond. In comparison to the free imidazolium salts, the most notable changes in the cobalt carbonyl derivatized complexes **7**−**10** are observed in the ^{1}H NMR spectra, where the proton attached to the alkyne unit changes from ca. 3 ppm in **3** and **4** and 2 ppm in **5** and **6** to 6.31−6.50 ppm in the Co complexes **7**−**10**, reflecting the increased acidity induced by coordination of the electron-withdrawing organometallic fragment. The chemical shifts of the carbonyl carbon atoms come at 202−203 ppm, shifted slightly lower than for structurally similar compounds.[29]

Single crystals of **10** suitable for X-ray diffraction analysis were grown from a solution of dichloromethane and diethyl ether at 0 °C. The molecular structure of **10** is shown in Figure 3, and key bond lengths and angles are listed in the caption.

The length of the C≡C bonds in **10** (C7−C8 = 1.32(2) Å and C12−C13 = 1.31(1) Å) are longer than those observed in the precursor imidazolium salt **6** but somewhat shorter than in related compounds, where the C≡C bond lengths range from 1.33 to 1.36 Å.[30,31] In comparison to the structures of the free salts, where the 1,3-dialkyne arms extrude from the same face of the imidazolium ring, in **10** the arms adopt a trans conformation. The slightly different Co−Co distances (Co1−Co2 = 2.468(3) Å and Co3−Co4 = 2.474(3) Å) are shorter than that in the parent $Co_2(CO)_8$[32] but are in keeping with other dicobalt systems that are bridged by alkyne ligands.

The three different C−H$\cdots\pi$ interactions observed in the solid state of free imidazolium salts **6**, viz. NC*H*N$\cdots\pi$, NC*H*C*H*N$\cdots\pi$, and C≡C−H$\cdots\pi$, are present in the structure of **10**. In addition, one of the H atoms in the CH_2 group is also involved in a C−H$\cdots\pi$ interaction with the phenyl ring from the anion. However, the $\pi\cdots\pi$ interactions between the imidazolium ring and the phenyl ring in the anion are no longer present.

While imidazolium salts are currently attracting considerable attention as ionic liquids, at least those with low melting points, for many years they have been

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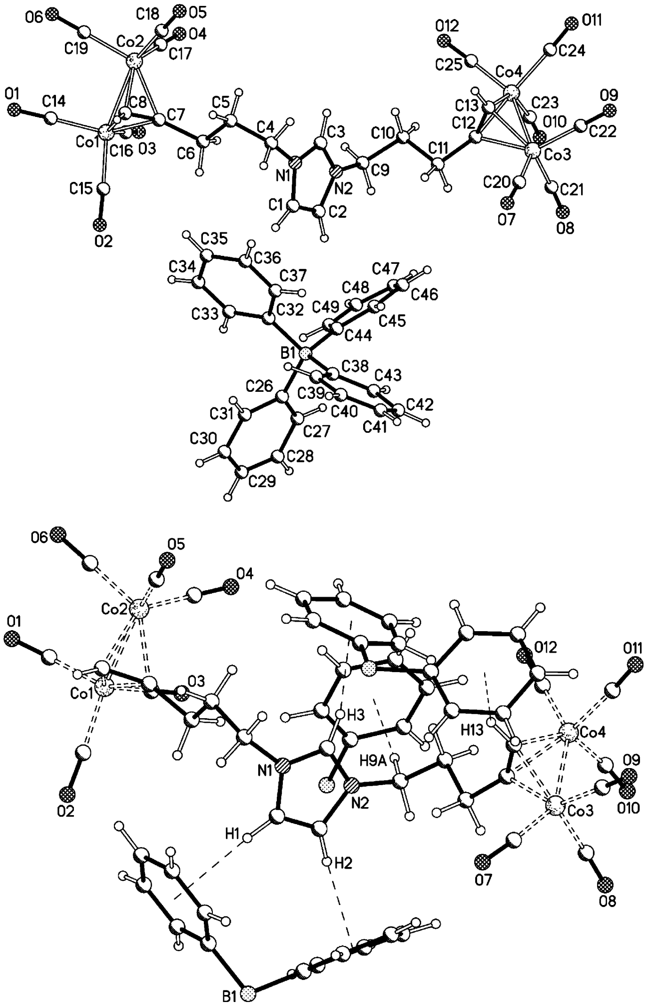
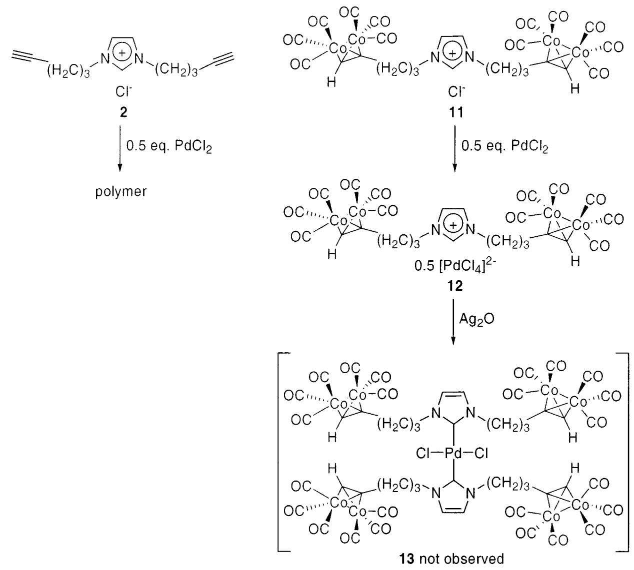


Figure 3. (top) Molecular structure of **10** in the solid state (showing the labeling scheme for the asymmetric unit; solvent molecules have been omitted for clarity). Key bond lengths (Å): Co1−C7, 1.938(12); Co1−C8, 1.946(12); Co1−Co2, 2.468(3); Co2−C8, 1.945(12); Co2−C7, 1.985(13); Co3−C13, 1.916(12); Co3−C12, 1.942(11); Co3−Co4, 2.474(3); Co4−C13, 1.952(11); Co4−C12, 1.972(10); N1−C3, 1.302(12); N1−C1, 1.390(11); N2−C3, 1.335(12); N2−C2, 1.385(11); C1−C2, 1.309(14); C7−C8, 1.318(16); C12−C13, 1.310(14). (bottom) C−H···π interactions around the imidazolium cation of **10**.

of interest as precursors to carbenes.[33] Attempts have also been made to convert the functionalized imidazolium chlorides **2** and [{μ_2-HCC(CH$_2$)$_3$N=C(H)N(μ_2-CCH(CH$_2$)$_3$CH=CH}{Co$_2$(CO)$_6$}$_2$]Cl (**11**) (obtained from **2** by reaction with Co$_2$(CO)$_8$ in dichloromethane for 2 h) to carbenes. In the first step salts **2** and **11** were treated with PdCl$_2$ in a 2:1 ratio to give a polymeric material (a clear plasticlike substance) and [{μ_2-HCC(CH$_2$)$_3$N=C(H)N(μ_2-CCH(CH$_2$)$_3$CH=CH}{Co$_2$(CO)$_6$}$_2$]$_2$[PdCl$_4$] (**12**), respectively (Scheme 3). Further reaction of **12** with Ag$_2$O does not afford the expected carbene complex [HCC(CH$_2$)$_3$N=CN(μ_2-CCH(CH$_2$)$_3$CH=CH}{Co$_2$(CO)$_6$}$_2$]$_2$PdCl$_2$] (**13**), although we have established a related chemistry for other functionalized imidazolium salts that will be reported in due course. The reaction of any of the dicobalt hexacarbonyl derivatized ionic liquids reported herein with base, not surprisingly, leads to reaction at the metal carbonyl site, resulting in decomposition; thus, carbenes have not as yet been identified.

Scheme 3. Attempts To Prepare Carbenes from 2 and 11



In conclusion, we have prepared a series of alkyne-functionalized imidazolium salts (including ionic liquids) and derivatized them with the dicobalt hexacarbonyl fragment to yield novel organometallic materials. Dicobalt hexacarbonyl alkyne complexes have previously been prepared in ionic liquids,[34] but this differs from our work, in which the alkyne is part of the ionic liquid. The spectroscopic and structural properties of the materials prepared in this study have been examined in some detail, and in the future we intend to explore their chemical properties.

Experimental Section

Starting materials were purchased from Acros and used as received without further purification. The reactions were performed under an inert atmosphere of dry nitrogen using standard Schlenk techniques, in solvents dried using appropriate reagents and distilled prior to use. IR spectra were recorded on a Perkin-Elmer FT-IR 2000 system. NMR spectra were measured on a Bruker DMX 400, using SiMe$_4$ for ^{1}H and ^{13}C as external standards at 20 °C. Electrospray ionization mass spectra (ESI-MS) were recorded on a ThermoFinnigan LCQ Deca XP Plus quadrupole ion trap instrument on samples dissolved in water (**1**−**6**) and dichloromethane (**7**−**10**) using a method described elsewhere.[35] Differential scanning calorimetry (DSC) used to determine the melting points of the room-temperature liquid salts was performed with a SETARAM DSC 131 instrument. Elemental analysis was carried out at the Institute of Molecular and Biological Chemistry at the EPFL.

Synthesis of [HC≡CCH$_2$N=C(H)N(CH$_2$C≡CH)CH=CH]Cl (1). A mixture of (trimethylsilyl)imidazole (14.026 g, 0.100

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(34) Becheanu, A.; Laschat, S. *Synlett* **2002**, *11*, 1865.

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mol) and $ClCH_2C\equiv CH$ (21.502 g, 0.202 mol, 70 wt % in toluene solution) was refluxed at 60 °C for 24 h. The resulting solid was filtered, washed with diethyl ether (3 × 30 mL), and dried under vacuum for 24 h. Yield: 28.5 g, 98%. Mp: 142 °C. ESI-MS (H_2O; *m/z*): positive ion, 145 $[HC\equiv CCH_2N{=}C(H)N(CH_2C\equiv CH)CH{=}CH]^+$; negative ion, 35, 37 $[Cl]^-$. ^1H NMR (D_2O): δ 9.00 (s, 1H, NC*H*N), 7.56 (s, 2H, NC*H*=C*H*N), 4.93 (d, ^4J(HH) = 2.44 Hz, 4H, 2 × $C\mathit{H}_2C\equiv CH$), 2.98 (t, ^4J(HH) = 2.44 Hz, 2H, 2 × $CH_2C\equiv C\mathit{H}$). ^{13}C NMR (D_2O): δ 138.91 (s, N*C*HN), 125.77 (s, NCH=*C*HN), 81.16 (s, $CH_2\mathit{C}\equiv CH$), 74.82 (s, $CH_2C\equiv \mathit{C}H$), 42.55 (s, $N\mathit{C}H_2C\equiv CH$). IR (cm^{-1}): 3394 (s, $H{-}C\equiv CCH_2N$), 3208, 3086, 3010 (m, H−C=C), 2125 (m, C≡C). Anal. Calcd for $C_9H_9ClN_2$: C, 59.84; H, 5.02; N, 15.51. Found: C, 60.01; H, 5.08; N, 15.65.

Synthesis of $[HC\equiv C(CH_2)_3N{=}C(H)N\{(CH_2)_3C\equiv CH\}CH{=}CH]Cl$ (2). 2 was prepared in a manner similar to that for **1** from (trimethylsilyl)imidazole (1.403 g, 0.010 mol) and $ClCH_2CH_2CH_2C\equiv CH$ (2.0718 g, 0.0202 mol) in toluene (10 mL). Yield: 3.23 g, 94%. Mp: 65 °C. ESI-MS (H_2O; *m/z*): positive ion, $[HC\equiv C(CH_2)_3N{=}C(H)N\{(CH_2)_3C\equiv CH\}CH{=}CH]^+$ 201; negative ion, 35, 37 $[Cl]^-$. ^1H NMR (CD_3CN): δ 9.02 (s, 1H, NC*H*N), 7.47 (s, 2H, NC*H*=C*H*N), 4.30 (t, 4H, ^3J(HH) = 7.45 Hz, 2 × $C\mathit{H}_2CH_2CH_2C\equiv CH$), 2.29 (m, 4H, 2 x $CH_2CH_2C\mathit{H}_2C\equiv CH$), 2.08 (m, 4H, 2 × $CH_2C\mathit{H}_2CH_2C\equiv CH$), 1.96 (dd, 2H, ^4J(HH) = 2.73 Hz, 2 × $CH_2CH_2CH_2C\equiv C\mathit{H}$). ^{13}C NMR (CD_3CN): δ 140.31 (s, N*C*HN), 125.60 (s, NCH=*C*HN), 84.38 (s, $CH_2CH_2CH_2\mathit{C}\equiv CH$), 73.57 (s, $CH_2CH_2CH_2C\equiv \mathit{C}H$), 51.51 (s, $\mathit{C}H_2CH_2CH_2C\equiv CH$), 31.91 (s, $CH_2CH_2\mathit{C}H_2C\equiv CH$), 18.31 (s, $CH_2\mathit{C}H_2CH_2C\equiv CH$). IR ($cm^{-1}$): 3377 (s, $H{-}C\equiv C(CH_2)_3N$), 3280, 3078 (m, H−C=C), 2112 (m, C≡C). Anal. Calcd for $C_{13}H_{17}ClN_2$: C, 65.95; H, 7.24; N, 11.83. Found: C, 66.01; H, 7.31; N, 11.95.

Synthesis of $[HC\equiv CCH_2N{=}C(H)N(CH_2C\equiv CH)CH{=}CH]BF_4$ (3). A mixture of **1** (1.806 g, 0.01 mol) and $NaBF_4$ (1.098 g, 0.01 mol) in acetone (30 mL) was stirred at room temperature for 24 h. The resulting solid was filtered off, and the solid was washed with diethyl ether (2 × 5.0 mL). The filtrates were collected, and the solvent was removed under vacuum. The product **3** was obtained as a white solid. Yield: 2.10 g, 91%. Mp: 67 °C. ESI-MS (H_2O; *m/z*): positive ion, 145 $[HC\equiv CCH_2N{=}C(H)N(CH_2C\equiv CH)CH{=}CH]^+$; negative ion, 87 $[BF_4]^-$. ^1H NMR (CD_3CN): δ 8.79 (s, 1H, NC*H*N), 7.57 (s, 2H, NC*H*=C*H*N), 5.05 (d, ^4J(HH) = 2.44 Hz, 4H, 2 × $C\mathit{H}_2C\equiv CH$), 3.07 (t, ^4J(HH) = 2.44 Hz, 2H, 2 × $CH_2C\equiv C\mathit{H}$). ^{13}C NMR (CD_3CN): δ 139.21 (s, N*C*HN), 125.86 (s, NCH=*C*HN), 80.98 (s, $CH_2\mathit{C}\equiv CH$), 75.00 (s, $CH_2C\equiv \mathit{C}H$), 42.15 (s, $N\mathit{C}H_2C\equiv CH$). IR (cm^{-1}): 3277 (s, $H{-}C\equiv CCH_2N$), 3265, 3176, 3159 (m, H−C=C), 2132 (m, C≡C). Anal. Calcd for $C_9H_9BF_4N_2$: C, 46.60; H, 3.91; N, 12.08. Found: C, 46.71; H, 3.96; N, 12.15.

Synthesis of $[HC\equiv CCH_2N{=}C(H)N(CH_2C\equiv CH)CH{=}CH]BPh_4$ (4). A mixture of **1** (1.806 g, 0.01 mol) and $NaBPh_4$ (3.422 g, 0.01 mol) in acetone (30 mL) was stirred at room temperature for 48 h. The resulting solid was filtered off, and the solid was washed with diethyl ether (2 × 5.0 mL). The filtrates were collected, and solvent was removed under vacuum. The product **4** was obtained as a white solid. Yield: 4.41, 95%. Mp: 185 °C. ESI-MS (H_2O; *m/z*): positive ion, 145 $[HC\equiv CCH_2N{=}C(H)N(CH_2C\equiv CH)CH{=}CH]^+$; negative ion, 319 $[BPh_4]^-$. ^1H NMR (CD_3CN): δ 8.61 (s, 1H), 7.57 (s, 2H, NC*H*=C*H*N), 7.30 (m, 8H, C_6H_5 *ortho*), 7.02 (m, 8H, C_6H_5 *meta*), 6.86 (m, 4H, C_6H_5 *para*), 4.73 (s, 4H, 2 × $C\mathit{H}_2C\equiv CH$), 3.05 (t, ^4J(HH) = 2.44 Hz, 2H, 2 × $CH_2C\equiv C\mathit{H}$). ^{13}C NMR (CD_3CN): δ 166.80 (q, ^1J(BC) = 49.73 Hz, C_6H_5 *ipso*), 138.68 (s, N*C*HN), 128.69 (s, C_6H_5 *ortho*), 125.42 (s, NCH=*C*HN), 124.85 (s, C_6H_5 *meta*), 80.64 (s, $CH_2\mathit{C}\equiv CH$), 74.84 (s, $CH_2C\equiv \mathit{C}H$), 42.27 (s, $N\mathit{C}H_2C\equiv CH$). IR (cm^{-1}): 3256 (s, $H{-}C\equiv CCH_2N$), 3160, 3131, 3050 (m, H−C=C), 2129 (m, C≡C). Anal. Calcd for $C_{33}H_{29}BN_2$: C, 85.35; H, 6.29; N, 6.03. Found: C, 85.51; H, 6.31; N, 6.10.

Synthesis of $[HC\equiv C(CH_2)_3N{=}C(H)N\{(CH_2)_3C\equiv CH\}CH{=}CH]BF_4$ (5). Compound **5** was obtained as a colorless liquid in a similar manner as for **3** from **2** (2.367 g, 0.01 mol) and $NaBF_4$ (1.098 g, 0.01 mol). Yield: 2.70 g, 94%. Oil. Viscosity: 512 mPa s^{-1}. ESI-MS (H_2O; *m/z*): positive ion, 201 $[HC\equiv C(CH_2)_3N{=}C(H)N\{(CH_2)_3C\equiv CH\}CH{=}CH]^+$; negative ion, 87 $[BF_4]^-$. ^1H NMR (CD_3CN): δ 8.52 (s, 1H, NC*H*N), 7.43 (s, 2H, NC*H*=C*H*N), 4.26 (t, 4H, ^3J(HH) = 7.00 Hz, 2 × $C\mathit{H}_2CH_2CH_2C\equiv CH$), 2.29 (m, 4H, 2 × $CH_2CH_2C\mathit{H}_2C\equiv CH$), 2.03 (m, 4H, 2 × $CH_2C\mathit{H}_2CH_2C\equiv CH$), 1.95 (m, 2H, 2 × $CH_2CH_2CH_2C\equiv C\mathit{H}$). ^{13}C NMR (CD_3CN): δ 138.76 (s, N*C*HN), 125.62 (s, N*C*H=*C*HN), 84.99 (s, $CH_2CH_2CH_2\mathit{C}\equiv CH$), 73.27 (s, $CH_2CH_2CH_2C\equiv \mathit{C}H$), 51.43 (s, $\mathit{C}H_2CH_2CH_2C\equiv CH$), 31.10 (s, $CH_2CH_2\mathit{C}H_2C\equiv CH$), 17.74 (s, $H_2\mathit{C}H_2CH_2C\equiv CH$). IR ($cm^{-1}$): 3282 (s, $H{-}C\equiv CCH_2N$), 3151, 3138 (m, H−C=C), 2125 (m, C≡C). Anal. Calcd for $C_{13}H_{17}BF_4N_2$: C, 54.20; H, 5.95; N, 9.72. Found: C, 54.29; H, 6.01; N, 9.75.

Synthesis of $[HC\equiv C(CH_2)_3N{=}C(H)N\{(CH_2)_3C\equiv CH\}CH{=}CH]BPh_4$ (6). Compound **6** was obtained as a colorless solid in a similar manner from **2** (2.367 g, 0.010 mol) and $NaBPh_4$ (3.422 g, 0.010 mol). Yield: 5.15 g, 99%. Mp: 135 °C. ESI-MS (H_2O; *m/z*): positive ion, 201 $[HC\equiv C(CH_2)_3N{=}C(H)N\{(CH_2)_3C\equiv CH\}CH{=}CH]^+$; negative ion, 319 $[BPh_4]^-$. ^1H NMR (CD_3CN): δ 8.47 (s, 1H, NC*H*N), 7.41 (s, 2H, NC*H*=C*H*N), 7.29 (m, 8H, C_6H_5 *ortho*), 7.02 (m, 8H, C_6H_5 *meta*), 6.86 (m, 4H, C_6H_5 *para*), 4.24 (t, 4H, ^3J(HH) = 7.17 Hz, 2 × $C\mathit{H}_2CH_2CH_2C\equiv CH$), 2.29 (m, 2H, 2 × $CH_2CH_2CH_2C\equiv C\mathit{H}$), 2.24 (m, 4H, 2 × $CH_2CH_2C\mathit{H}_2C\equiv CH$), 1.97 (m, 4H, 2 × $CH_2C\mathit{H}_2CH_2C\equiv CH$). ^{13}C NMR (CD_3CN): δ 166.80 (q, ^1J(BC) = 49.43 Hz, C_6H_5 *ipso*), 138.71, 138.35, 128.70, 125.48, 124.84, 84.87 (s, $CH_2\mathit{C}\equiv CH$), 73.34 (s, $CH_2C\equiv \mathit{C}H$), 51.36 (s, $\mathit{C}H_2CH_2CH_2C\equiv CH$), 31.05 (s, $CH_2CH_2\mathit{C}H_2C\equiv CH$), 17.78 (s, $CH_2\mathit{C}H_2CH_2C\equiv CH$). IR ($cm^{-1}$): 3268 (s, $H{-}C\equiv CCH_2N$), 3077, 3051, 3035 (m, H−C=C), 2120 (m, C≡C), Anal. Calcd for $C_{37}H_{37}BN_2$: C, 85.38; H, 7.16; N, 5.38. Found: C, 84.01; H, 7.21; N, 5.41.

Synthesis of $[\{\mu_2\text{-}HCCCH_2N{=}C(H)N(\mu_2\text{-}CCHCH_2)CH{=}CH\}\{Co_2(CO)_6\}_2]BF_4$ (7). $Co_2(CO)_8$ (0.700 g, 2.05 mmol) was added to a solution of **3** (0.232 g, 1.0 mmol) in dichloromethane (10 mL). The reaction mixture was stirred at room temperature for 2 h, during which time the CO gas bubbled out from the reaction solution completely. The solvent was removed under vacuum. The remaining solid was washed with diethyl ether (3 × 10 mL) to give the product **7** as a dark red solid. Yield: 0.65 g, 81%. Mp: 110 °C. ESI-MS (CH_2Cl_2; *m/z*): positive ion, 717 $[\{\mu_2\text{-}HCCCH_2N{=}C(H)N(\mu_2\text{-}CCHCH_2)CH{=}CH\}\{Co_2(CO)_6\}_2]^+$; negative ion, 87 $[BF_4]^-$. ^1H NMR (CD_3CN): δ 8.90 (s, 1H, NC*H*N), 7.68 (s, 2H, NC*H*=C*H*N), 6.49 (broad signal, 2H, 2 × $CH_2C\equiv C\mathit{H}$), 5.56 (broad signal, 4H, 2 × $C\mathit{H}_2C\equiv CH$). ^{13}C NMR (CD_3CN): δ 201.96, 138.85, 126.22, 90.80, 74.81, 54.86. IR (cm^{-1}): 3153 (w, $H{-}CCCo_2(CO)_6$), 3121, (w, H−C=C), 2001, 2014, 2100 (s, C≡O), 1559 (m, $CCCo_2(CO)_6$). Anal. Calcd for $C_{21}H_9BCo_4F_4N_2O_{12}$: C, 31.38; H, 1.13; N, 3.48. Found: C, 31.21; H, 1.11; N, 3.45.

Synthesis of $[\{\mu_2\text{-}HCCCH_2N{=}C(H)N(\mu_2\text{-}CCHCH_2)CH{=}CH\}\{Co_2(CO)_6\}_2]BPh_4$ (8). Compound **8** was obtained as a dark red solid in a manner similar to that for **7** from **4** (0.464 g, 1 mmol) and $Co_2(CO)_8$ (0.7000 g, 2.05 mmol) in dichloromethane (30 mL). Yield: 0.78 g, 75%. Mp: 115 °C. ESI-MS (CH_2Cl_2; *m/z*): positive ion, 717 $[\{\mu_2\text{-}HCCCH_2N{=}C(H)N(\mu_2\text{-}CCH\ CH_2)CH{=}CH\}\{Co_2(CO)_6\}_2]^+$; negative ion, 319 $[BPh_4]^-$.

^{1}H NMR (CD$_3$CN): δ 8.89 (s, 1H, NC*H*N), 7.68 (s, 2H, NC*H*=C*H*N), 7.28 (m, 8H, C$_6$H$_5$ *ortho*), 7.00 (m, 8H, C$_6$H$_5$ *meta*), 6.86 (m, 4H, C$_6$H$_5$ *para*), 6.50 (broad signal, 2H, 2 × CH$_2$C≡C*H*), 5.53 (broad signal, 4H, 2 × C*H*$_2$C≡CH). ^{13}C NMR (CD$_3$CN): δ 201.82 (broad signal, *C*≡O), 167.18 (q, ^1J(BC) = 48.50 Hz, C$_6$H$_5$ *ipso*), 138.75, 128.71, 126.11, 124.94. 94.42, 74.95, 54.86. IR (cm^{-1}): 3155 (w, H−CCCo(CO)$_6$), 3058 (w, H−C=C), 2099, 2057, 1999 (s, C≡O), 1548 (m, CCCo$_2$(CO)$_6$). Anal. Calcd for C$_{45}$H$_{29}$BCo$_4$N$_2$O$_{12}$: C, 52.16; H, 2.82; N, 2.70. Found: C, 52.21; H, 2.81; N, 2.75.

Synthesis of [{μ_2-HCC(CH$_2$)$_3$N=C(H)N(μ_2-CCH(CH$_2$)$_3$-CH=CH}{Co$_2$(CO)$_6$}$_2$]BF$_4$ (9). Compound **9** was obtained as a dark red solid in a manner similar to that for **7** from **5** (0.288 g, 1 mmol) and Co$_2$(CO)$_8$ (0.7000 g, 2.05 mmol) in dichloromethane (30 mL). Yield: 0.76 g, 88%. Mp: 100 °C. ESI-MS (CH$_2$Cl$_2$; *m*/*z*): positive ion, 772 [{μ_2-HCCCH$_2$N=C(H)N(μ_2-CCHCH$_2$)CH=CH}{Co$_2$(CO)$_6$}$_2$]$^+$; negative ion, 87 [BF$_4$]$^-$. ^{1}H NMR (CD$_3$CN): δ 8.57 (s, 1H, NC*H*N), 7.47 (s, 2H, NC*H*=C*H*N), 6.31 (broad signal, 2H, 2 × CH$_2$CH$_2$CH$_2$C≡C*H*), 4.28 (broad signal, 4H, 2 × C*H*$_2$CH$_2$CH$_2$C≡CH), 2.92 (m, 4H, 2 × CH$_2$CH$_2$C*H*$_2$C≡CH), 1.98 (m, 4H, 2 × CH$_2$C*H*$_2$CH$_2$C≡CH). ^{13}C NMR (CD$_3$CN): δ 203.09, 138.47, 125.55, 98.22, 76.66, 51.89, 34.61, 32.98. IR (cm^{-1}): 3156 (w, H−CCCo$_2$(CO)$_6$), 3098 (w, H−C=C), 2043, 2012, 1988 (s, C≡O), 1565 (m, CCCo$_2$(CO)$_6$). Anal. Calcd for C$_{25}$H$_{17}$BCo$_4$F$_4$N$_2$O$_{12}$: C, 34.92; H, 1.99; N, 3.26. Found: C, 34.99; H, 2.01; N, 3.31.

Synthesis of [{μ_2-HCC(CH$_2$)$_3$N=C(H)N(μ_2-CCH(CH$_2$)$_3$-CH=CH}{Co$_2$(CO)$_6$}$_2$]BPh$_4$ (10). Compound **9** was obtained as a dark red solid in a manner similar to that for **7** from **6** (0.521 g, 1 mmol) and Co$_2$(CO)$_8$ (0.7000 g, 2.05 mmol) in dichloromethane (30 mL). Yield: 0.88 g, 81%. Mp: 132 °C. ESI-MS (CH$_2$Cl$_2$; *m*/*z*): positive ion, 772 [{μ_2-HCC(CH$_2$)$_3$N=C(H)N-(μ_2-CCH(CH$_2$)$_3$CH=CH}{Co$_2$(CO)$_6$}$_2$]$^+$; negative ion, 319 [BPh$_4$]$^-$. ^{1}H NMR (CD$_3$CN): δ 8.40 (s, 1H, NC*H*N), 7.43 (s, 2H, NC*H*=C*H*N), 7.27 (m, 8H, C$_6$H$_5$ *ortho*), 7.00 (m, 8H, C$_6$H$_5$ *meta*), 6.84 (m, 4H, C$_6$H$_5$ *para*), 6.31 (broad signal, 2H, 2 × CH$_2$CH$_2$CH$_2$C≡C*H*), 4.23 (broad signal, 4H, 2 × C*H*$_2$CH$_2$CH$_2$C≡CH), 2.86 (m, 4H, 2 × CH$_2$CH$_2$C*H*$_2$C≡CH), 1.95 (m, 4H, 2 × CH$_2$C*H*$_2$CH$_2$C≡CH). ^{13}C NMR (CD$_3$CN): δ 203.29 (broad signal, *C*=O), 166.59 (q, ^1J(BC) = 48.00 Hz, C$_6$H$_5$ *ipso*), 138.70, 138.11, 128.69, 125.45, 124.82, 98.18, 76.76, 51.83, 34.66, 33.07. IR (cm^{-1}): 3108 (w, H−CCCo$_2$(CO)$_6$), 3056 (w, H−C=C), 2090, 2045, 1989 (s, C≡O), 1557 (w, H−CCCo$_2$(CO)$_6$). Anal. Calcd for C$_{49}$H$_{37}$BCo$_4$N$_2$O$_{12}$: C, 53.88; H, 3.41; N, 2.56. Found: C, 53.91; H, 3.45; N, 2.60.

X-ray Determination of 4, 6, and 10. Details about the crystals and their structure refinement are given in Table 2, whereas relevant geometrical parameters, including bond lengths and angles, are included in the captions to Figures 1−3. Data collections were performed at 140 K on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD for compound **6**. Diffraction data for **4** and **10** were measured at room temperature on a Marresearch mar345 IPDS instrument. Data reduction was carried out with CrysAlis RED, release 1.7.0.[36] An empirical absorption correction[37] was applied to all data sets. Structure solution and refinement as well as molecular graphics and geometrical calculations were performed for all structures with the SHELXTL software package, release 5.1.[38] The structures were refined using full-matrix least squares on F^2 with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the riding model.

Table 2. Crystal Data and Details of the Structure Determination for 4, 6, and 10

	4	6	10
chem formula	C$_{33}$H$_{29}$BN$_2$	C$_{37}$H$_{37}$BN$_2$	C$_{50}$H$_{41}$BCl$_2$-Co$_4$N$_2$O$_{13}$
formula wt	464.39	520.50	1195.28
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$C2/c$
a (Å)	14.606(6)	10.7263(16)	35.331(18)
b (Å)	8.780(4)	17.092(2)	19.2780(17)
c (Å)	20.378(2)	16.239(2)	16.489(9)
α (deg)	90	90	90
β (deg)	95.701(19)	92.631(12)	110.76(5)
γ (deg)	90	90	90
V (Å^3)	2600.4(16)	2974.1(7)	10502(8)
Z	4	4	8
D_{calcd} (g cm^{-3})	1.186	1.162	1.512
F(000)	984	1112	4848
μ (mm^{-1})	0.068	0.066	1.407
temp (K)	140	140	140
wavelength (Å)	0.710 70	0.710 73	0.710 70
no. of measd rflns	15 846	17 251	32 633
no. of unique rflns	4344	4938	8973
no. of unique rflns ($I > 2\sigma(I)$)	2958	1976	3166
no. of data/params	4344/326	4938/362	8973/659
R1^a ($I > 2\sigma(I)$)	0.0492	0.0504	0.0887
wR2^a (all data)	0.1526	0.1692	0.2860
GOF^b	1.072	0.868	0.972

[a] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [b] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of data and p is the number of parameters refined.

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Supporting Information Available: Crystallographic data, as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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