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Synthesis and Characterization of Organometallic Ionic Liquids and a Heterometallic Carbene Complex Containing the Chromium Tricarbonyl Fragment

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Direct reaction between [Cr(CO)$_6$] and arenes with ionic substituents affords the corresponding arene−chromium tricarbonyl complexes, [Cr(CO)$_3$(arene)], in only modest yield. In contrast, these complexes can be prepared in pure form in excellent yield from the reaction of [Cr(CO)$_3$(η^6-C$_6$H$_5$CH$_2$Br)] with, for example, *N*-methylimidazole. The structures of [Cr(CO)$_3$(η^6-C$_6$H$_5$CH$_2$MIM)]Br (MIM = 3-methylimidazolium), [Cr(CO)$_3$(η^6-C$_6$H$_5$CH$_2$MMIM)]Br (MMIM = 2,3-dimethylimidazolium), and [Cr(CO)$_3$(η^6-C$_6$H$_5$CH$_2$NMe$_2$(CH$_3$)$_2$OH)]Br have been established by X-ray diffraction analysis. Subsequent exchange of the bromide anion for Tf$_2$N$^-$ affords new organometallic salts with melting points below 70°C. Reaction of the bromide salts include tosylation of [Cr(CO)$_3$(η^6-C$_6$H$_5$CH$_2$NMe$_2$(CH$_3$)$_2$OH)]Br to afford [Cr(CO)$_3$(η^6-C$_6$H$_5$CH$_2$NMe$_2$(CH$_2$)$_2$OTs)]Br and the formation of the heterometallic carbene complex [Ru(η^6-*p*-cymene)Cl$_2${C$_4$H$_5$N$_2$CH$_2$Ph-η^6-Cr(CO)$_3$}]. Both compounds were characterized in the solid state by X-ray diffraction.

Introduction

Ionic liquids are attracting a great deal of attention as alternative reaction media for synthesis and catalysis,[1] but they are also finding applications in many different areas including separation processes,[2] electrochemistry,[3] electrolytes in solar cells,[4] lubricants,[5] matrixes in MALDI mass spectrometry,[6] and even as propellants in small satellites.[7] As the range of applications for ionic liquids increases, the need for ionic liquids with specific chemical and physical properties also increases. With this in mind, the term “task-specific ionic liquids” has been introduced to described “designer” liquids prepared for specific applications.[2] The incorporation of functional groups into the ionic liquid represents one of the simplest and most effective strategies for the modification of the liquid’s properties, and a large number of salts with functional groups attached to the cation have now been reported. These include, for example, amines,[8] amides,[9] nitriles,[10] ethers and alcohols,[11] acids,[12] urea and thiourea,[13] and fluorous chains.[14] In addition, functional anions have also received some attention; those giving rise to low melting salts include amino acids,[15] alkene substituted anions,[16] triazole anions,[17] selenium based anion,[18] functionalized borate anion,[19] carboranes[20] and transition metal−carbonyl anions (see below).

In a relatively recent development, organometallic ionic liquids based on transition metals have started to

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generate interest.[21] Prior to this development, among the earliest ionic liquids were those composed of alkylaluminum chloride anions. In fact, the first transition metal catalyzed reactions were conducted in such ionic liquids, these being nickel catalyzed dimerization of alkenes[22] and titanium catalyzed polymerization of ethylene.[23] Transition metal−carbonyl anions including $[Co(CO)_4]^-$, $[Mn(CO)_5]^-$ and $[HFe(CO)_4]^-$,[24] and $[Rh(CO)_2I_2]^-$ [25] have since been combined with imidazolium cations to give low melting salts. Ionic liquids with organometallic cations have also been reported. For example, imidazolium rings with ferrocenyl appendages have been shown to exhibit, in some instances, low melting points.[26] Alkyne functionalized imidazolium salts have been derivatized with the dicobalt hexacarbonyl unit, and some of these have relatively low melting points.[27] This strategy works well as the reaction between the alkyne and the cobalt carbonyl precursor is high yielding.

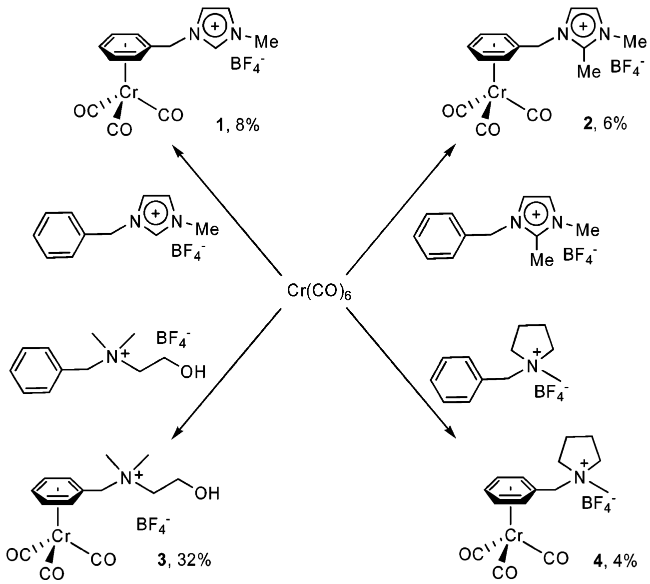
In this paper, we report the derivatization of imidazolium (and other salts) with an arene−chromium−tricarbonyl moiety to afford new organometallic ionic liquids. Preliminary reactivity studies of these salts was carried out, in particular, a heterometallic carbene complex was prepared from one of the imidazolium based salts.

Results and Discussion

The simplest method used to prepare arene−chromium tricarbonyl compounds involves the direct reaction between chromium hexacarbonyl and the appropriate arene in high boiling ethers, such as dioxane, using Strohmeier type reflux condensers to avoid loss of the $[Cr(CO)_6]$ via sublimation.[28] Unfortunately, using this method our attempts to prepare chromium−tricarbonyl complexes of cationic functioned benzene ligands resulted in only modest yields (see Scheme 1).

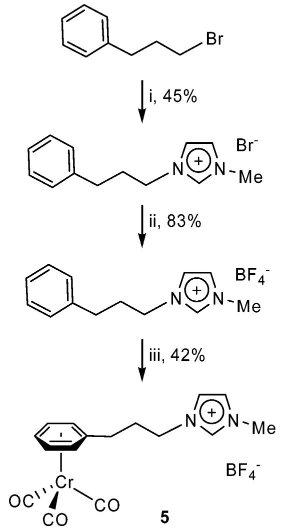
The deactivating influence of the electron withdrawing substituents are likely to be responsible for the low observed yields as has been previously noted by Christofi and co-workers, who reported the similar failure of the direct reaction between a polycationic arene and chromium hexacarbonyl or its activated tris-acetonitrile derivative.[29] Although we found yields could be increased in some cases with prolonged reaction times, e.g., **3**, others resulted in decomposition, e.g., **2**. For the 1-methylimidazolium based ligand, use of a larger alkyl-chain spacer to insulate the charge also resulted in an increased yield, 42% for **5** versus 8% for **1**, (Scheme 2). However, despite these improvements, a suitable procedure for the separation of the ensuing mixture of arene−chromium complex and precursor was not found, and accordingly an alternative synthetic route was sought.

Scheme 1. Synthesis of Ionic Arene−Chromium Tricarbonyl Complexes 1−4 by Direct Reaction in Refluxing Dioxane[a]



[a] **1**, 20 h; **2**, 17 h; **3**, 96 h; **4**, 20 h. Yields are approximate (based on integration of NMR spectra).

Scheme 2. Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5(CH_2)_3MIM)]BF_4$, 5[a]



[a] Yield for step iii is approximate (based on integration of the NMR spectrum). Reagents and conditions, (i) *N*-methylimidazole, CH_2Cl_2, rt; (ii) $NaBF_4$, CH_2Cl_2, rt; (iii) $[Cr(CO)_6]$, dioxane, reflux, 96 h

The alternative route, depicted in Scheme 3, involves the construction of the desired arene−chromium tricarbonyl salt on a preformed, functionalized, arene−

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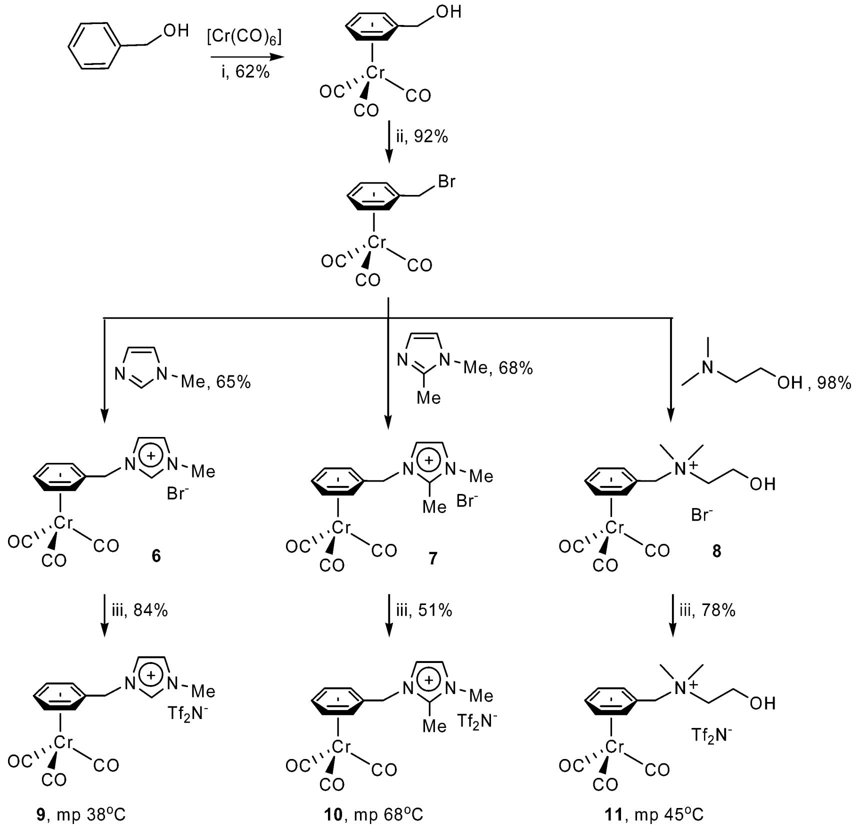
Scheme 3. Synthesis of Chromium Tricarbonyl Derivatized Ionic Liquids[a]



[a] Reagents and conditions, (i) dioxane, reflux, 90 h; (ii) BBr_3, CH_2Cl_2, −78°C, 90 min; (iii) $LiTf_2N$, H_2O, rt or 40°C, 3 h.

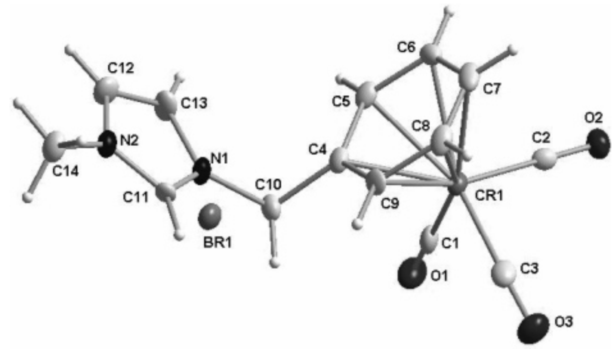


Figure 1. Representation of **6**; thermal ellipsoids are drawn at the 50% probability level. Key bond lengths (Å) and angles (deg): $Cr-\mathit{C}O_{avg}$, 1.856(5); $C-O_{avg}$, 1.165(6); $O\mathit{C}-Cr-\mathit{C}O_{avg}$, 89(2); $Cr-C-O_{avg}$, 178.4(6); $Cr-\mathit{C}_6H_{5,avg}$, 2.226(7); Cr−Centroid, 1.718; $C-C_{ring,avg}$, 1.41(1); C4−C10, 1.523(6), C10−N1, 1.475(5); C4−C10−N1, 111.2(3).

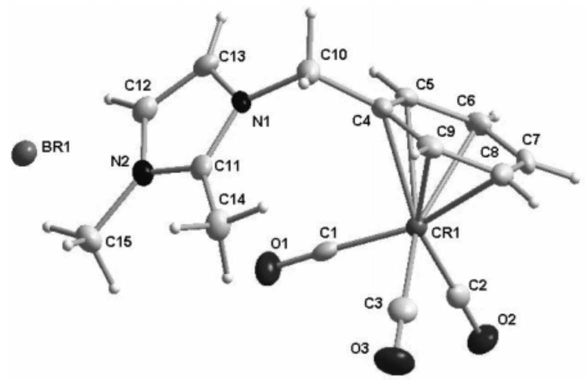


Figure 2. Representation of **7**; thermal ellipsoids are drawn at the 50% probability level. Key bond lengths (Å) and angles (deg): $Cr-\mathit{C}O_{avg}$, 1.84(1); $C-O_{avg}$, 1.159(7); $O\mathit{C}-Cr-\mathit{C}O_{avg}$, 88(2); $Cr-C-O_{avg}$, 178.2(8); $Cr-\mathit{C}_6H_{5,avg}$, 2.22(1); Cr−Centroid, 1.720; $C-C_{ring,avg}$, 1.40(2); C4−C10, 1.529(6), C10−N1, 1.470(6); C4−C10−N1, 113.6(4).

chromium tricarbonyl unit, $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$, prepared in two steps with an overall yield of ca. 60% using a procedure devised by Gibson and Schmid.[30] Using this procedure benzylic halide chromium tricarbonyl complexes are prepared in high yield by the treatment of the readily available chromium complexes of benzylic alcohols or ethers with appropriate boron halides, in this case reaction of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2OH)]$ with BBr_3. Subsequent reaction of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$ with *N*-methylimidazole or related amines affords the desired products, **6**−**8** (Figures 1−3), in good to excellent yield (ca. 44%, three steps), far superior to those achieved via direct reaction. Furthermore, purification of the product is facile and the bromide anion can be exchanged for other anions, we chose Tf_2N^-, affording low melting organometallic salts, **9**−**11**, that can be classed as ionic liquids.[31] The bromide counterion in $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2MIM)]Br$ (**6**) was also exchanged for BF_4^- (**12**), but the resulting salt had a high melting (decomposition) temperature in the region of 150°C.

The seven new, air-sensitive, salts were characterized by electrospray ionization mass spectrometry (ESI-MS) and IR and NMR spectroscopy. For each compound the positive ion ESI-MS shows a strong parent ion peak

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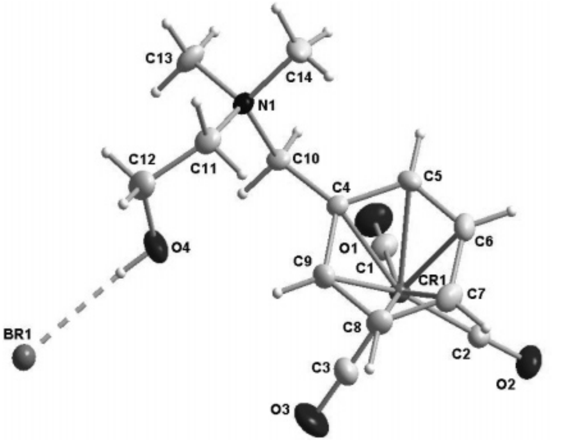
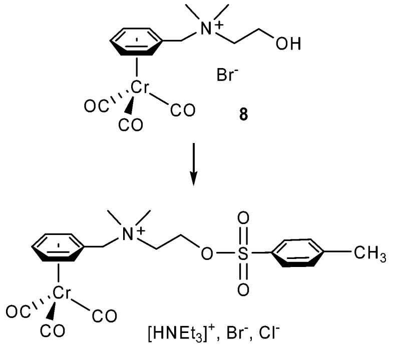


Figure 3. Representation of **8**; thermal ellipsoids are drawn at the 30% probability level. Key bond lengths (Å) and angles (deg): *Cr*–*C*O$_{avg}$, 1.844(5); C–O$_{avg}$, 1.154(6); O*C*–*Cr*–*C*O$_{avg}$, 88(1); Cr–C–O$_{avg}$, 178.2(7); *Cr*–*C*$_6$H$_{5,avg}$, 2.22(1); Cr–Centroid, 1.718; C–C$_{ring,avg}$, 1.41(2); C4–C10, 1.512(5), C10–N1, 1.539(4); C4–C10–N1, 114.3(3); C12–O4, 1.422(5); *O4*–H15···*Br1*, 3.241(3); O4–*H15*···*Br1*, 2.43.

corresponding to the intact cation. To gain structural information and confirm the identity of these peaks, selective fragmentation of the parent peak was carried out using the ion trap facility of the spectrometer (MS/MS).[32] Characteristic of the MS/MS fragmentation is the presence of a peak at *m/z* +227, corresponding to loss of an appropriate ionic moiety, assigned to $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2)]^+$ consistent with a correct assignment of the parent peak. All of the salts have carbonyl absorptions in the IR spectrum typical of arene coordinated chromium tricarbonyl complexes.[33] The A$_1$ band absorptions range from 1972 to 1976 cm^{-1}, and those of the E band range from 1895 to 1903 cm^{-1}. The ^{1}H NMR spectra show the expected upfield shifts, ca. 1.8 ppm, of the arene proton resonances, on coordination. For complexes **6** and **9**, the resonance of the imidazolium proton in the 2 position also undergoes a slight upfield shift, ca. 0.4 ppm, on arene coordination to the "Cr(CO)$_3$" fragment.

Scheme 4. Tosylation of 8[a]



13.HNEt$_3$Cl

[a] Reagents and conditions, TsCl, Et$_3$N, [Me$_3$NH]Cl, MeCN, 0°C, 2 h (74% yield).

The solid-state structures of **6**–**8** have been established using single-crystal X-ray diffraction analysis. All three complexes adopt the expected piano-stool geometries, the chromium atom ca. 1.72 Å from the arene ring centroid. The staggered conformation of the carbonyl ligands in each of these complexes is atypical of monosubstituted chromium tricarbonyl complexes, which generally adopt eclipsed geometries with respect to the arene ring,[34] although similar to their precursor, $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$, which also adopts a staggered conformation in the solid state.[29] Within the coordination sphere of the chromium atom, **6**–**8** show essentially equivalent bonding parameters and, in addition, the bonding within the ionic functionality shows no discernible differences with related imidazolium and ammonium salts.[35] The conformation of the substituent in complex **7** is, however, noteworthy. The benzyl carbon C10 deviates 0.160(7) Å above the arene plane and the imidazolium ring bends toward the chromium center, whereas in complexes **6** and **8** the ionic substituents are orientated away from the metal center with the benzyl carbons lying 0.066(7) and 0.127(5) Å below the arene plane, respectively. Differences in substituent conformation have previously been rationalized by Hunter and co-workers in terms of their π-donating or π-accepting ability,[33b] although in this case such effects are expected to be minimal, due to the similarity of the chromium coordination spheres for **6**–**8**. Instead, this conformational difference may be attributed to crystal packing forces. Consistent with this explanation, inspection of the packing motifs of **6** and **7** reveals slightly a higher degree of hydrogen bonding in the solid-state structure of **7**, with three hydrogen bonds per bromide, compared to that of **6**, with only two (see Figures S-1 and S-2, Supporting Information).

Pertinent reactivity studies have been carried out on salts **6** and **8**. Complex **8** was reacted with tosyl chloride, according to a procedure developed by Yoshida and co-workers.[36] The resultant tosylated product, **13** in Scheme 4, was obtained in good yield, and we envision that it will be a useful synthetic precursor for the preparation of other functionalized ionic liquids. The ^{1}H NMR spectrum and elemental analysis of the product both indicate the presence of 1 equiv of triethylammonium hydrochloride, and this proved difficult to remove. However, a crystalline sample of **13** suitable for X-ray diffraction analysis was obtained by slow diffusion of diethyl ether into an ethanol solution of the mixture. The melting point of the toslyated salt, **13**, was determined using this sample and was found to be lower than that of the parent salt **8**, ca. 148 versus 175 °C.

The salient features of **13** (Figure 4) in the solid state remain much the same as those of **6**–**8**, although in complex **13** the carbonyl ligands adopt the more common eclipsed conformation with the *anti*-configuration with respect to the substituent and the chromium–carbonyl bonds in **13** are marginally shorter than those found in

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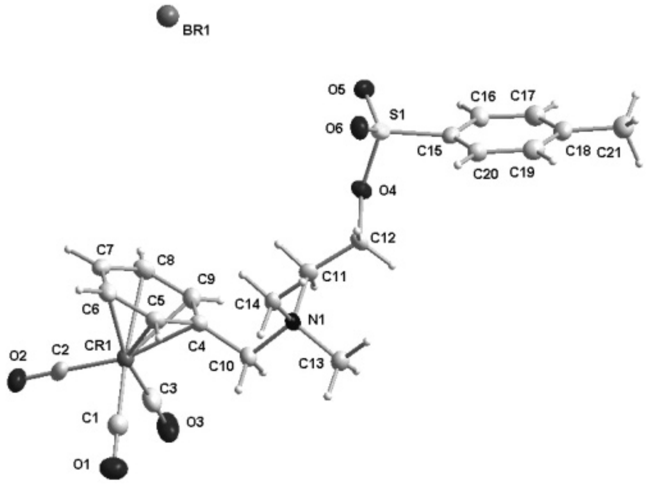
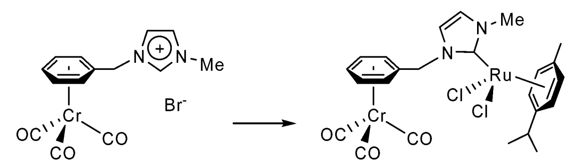


Figure 4. Representation of **13**; thermal ellipsoids are drawn at the 30% probability level. Key bond lengths (Å) and angles (deg): *Cr*−*C*O_{avg}, 1.82(1); C−O_{avg}, 1.17(1); O*C*−*Cr*−*C*O_{avg}, 88(1); Cr−C−O_{avg}, 178.9(4); *Cr*−*C*$_6H_{5,avg}$, 2.20(2); Cr−Centroid, 1.692; C−$C_{ring,avg}$, 1.40 (1); C4−C10, 1.48(1), C10−N1, 1.533(9); C4−C10−N1, 114.0(6); C12−O4, 1.456(8); S1−O4, 1.591(5); S1−O5, 1.425(8); S1−O6, 1.430(6); S1−C15, 1.743(8).

8 [ca. 1.82(1) versus 1.844(5) Å]. The tosylate group is directed away from the chromium center, and there is little change in the ammonium moiety conformation. Spectroscopic characterization is also comparable to the parent salt **8**, in particular the carbonyl IR absorptions remain virtually unchanged following tosylation [cf. 1975 and 1901 cm^{-1} for **8** versus 1976 and 1902 cm^{-1} for **13**].

N-heterocyclic carbenes are showing considerable potential as ligands for asymmetric catalysis, and indeed in homogeneous catalysis more generally,[37] with ferrocene functionalized derivatives representing some of the most successful ligands developed to date.[38] Of particular interest to us was the possibility of forming heteronuclear complexes via carbene formation through the imidazolium functionality, such as in complexes **6** and **9**, due to the potential of appropriately functionalized arene−chromium tricarbonyl complexes to act as chiral auxiliaries, like ferrocene.[39] Following the well-known carbene transfer methodology, complex **14** was prepared by the metathesis of the silver carbene complex, formed by the reaction of **6** with Ag_2O, with [$Ru_2(\eta^6$-*p*-cymene)$_2Cl_4$] (Scheme 5).[40] The intermediate silver dicarbene complex, [Ag{$C_4H_5N_2CH_2Ph$-η^6-$Cr(CO)_3$}$_2$]$^+$, was not isolated but identified by ESI-MS, giving a peak at *m*/*z* +723 with a characteristic isotope pattern; subsequent MS/MS of this species resulted in loss of one carbene ligand. Metathesis was best effected at room temperature (yield: 86%), with reactions carried out under reflux resulting in (unidentified) decomposition products.

Scheme 5. Formation of the Heteronuclear Carbene Complex, [Ru(η^6-*p*-cymene)Cl_2{$C_4H_5N_2CH_2Ph$-η^6-$Cr(CO)_3$}], 14[a]



[a] Reagents and conditions, Ag_2O, CH_2Cl_2, rt, 18 h, followed by, [$Ru_2(\eta^6$-*p*-cymene)$_2Cl_4$], CH_2Cl_2, rt, 7 h (86% yield).

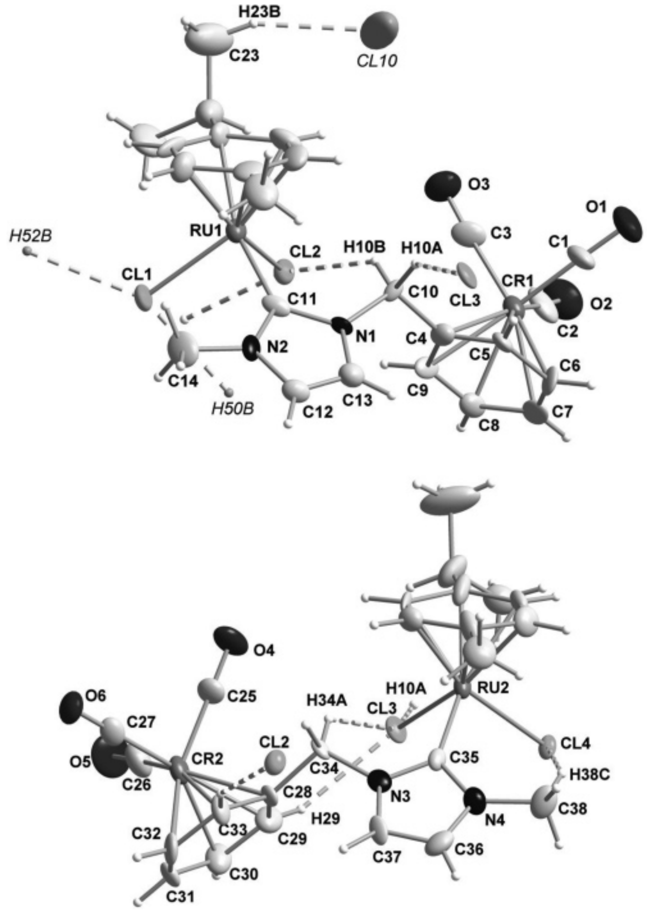


Figure 5. Different conformations of **14** found in the asymmetric cell; thermal ellipsoids are drawn at 50% probably level. Solvent molecules are excluded except for the atoms involved in hydrogen bonding (with italic labels). Key bond lengths and angles are given in Table 1 and in the caption of Figure S-3 (Supporting Information).

ESI-MS of the neutral complex **14** resulted in a number of ion fragments including those attributed to [Cl]$^-$ loss, *m*/*z* +578 (see Figure S-4, Supporting Information); [$Cr(CO)_3Cl$]$^-$ loss, *m*/*z* +443; and [$Cr(CO)_3Cl_2$]$^-$ loss, *m*/*z* +407, having characteristic isotope patterns deriving from the unique isotope distribution of ruthenium, in compliance with the formulated structure. Explicit confirmation of the molecular structure of **14** (Figure 5) was achieved by single-crystal X-ray diffraction analysis. The asymmetric cell contains two unique (enantiomeric) conformations held in place by a number of strong hydrogen bonding interactions between the coordinated chlorine atoms and the bridging methylene group [*C10*−H10B⋯*Cl2*, 3.35(1); C10−*H10B*⋯*Cl2*, 2.58; *C34*−H34A⋯*Cl3*,

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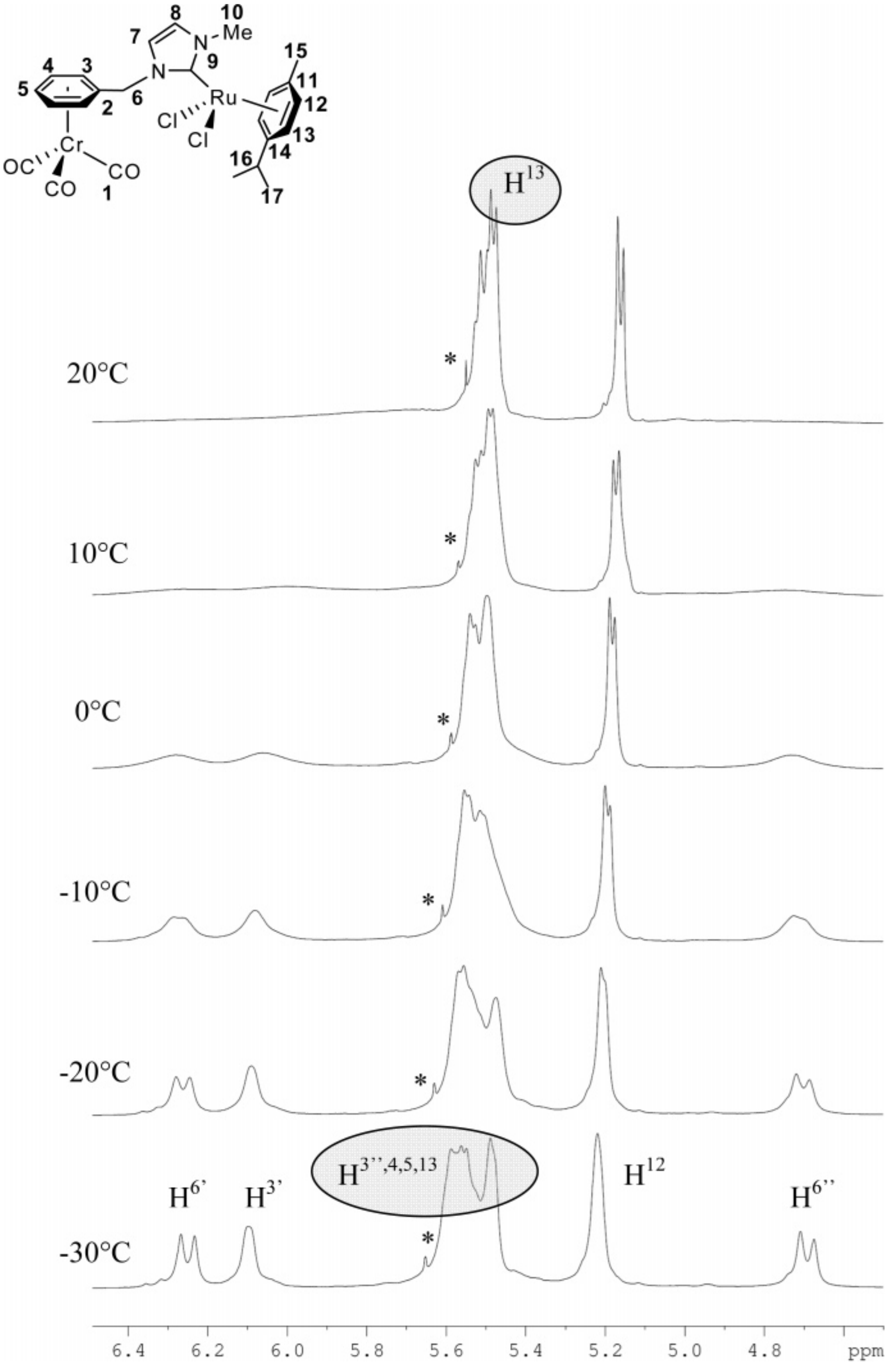

Figure 6. Variable temperature ^{1}H NMR spectra (aromatic region) of **14** in THF-d_8.

3.40(1); C34–*H34A*···*Cl3*, 2.67 Å], a chromium arene proton [*C9*–H9···*Cl2*, 3.62(1); C9–*H9*···*Cl2*, 2.85; *C29*–H29···*Cl3*, 3.53(2); C29–*H29*···*Cl3*, 2.70 Å], and the *N*-methyl group [*C14*–H14C···*Cl1*, 3.22(2); C14–*H14C*···*Cl1*, 2.86; *C38*–H38C···*Cl4*, 3.26(1); C38–*H38C*···*Cl4*, 2.46 Å]. Variable temperature ^{1}H NMR (Figure 6) indicates that while exchange between these two conformations occurs at room temperature (on the NMR time scale), below ca. 10°C the Ru–C bond rotation necessary for this exchange is sufficiently hindered and the two conformations persist in solution. In accordance, the Ru–C bonds [Ru1–C11, 2.03(2) and Ru2–C35, 2.02(2) Å] are not indicative of significant back-bonding,[37] although slightly shorter than those found in previously reported Ru(arene)X_2-*N*-heterocyclic carbene complexes (X = Halogen), ca. 2.08 Å.[8,41] The rotation hindrance could, instead, be attributed to the ability of the bridging methylene protons (H^6 in Figure 6) and the chromium *ortho*-arene protons (H^3 in Figure 6), both diastereotopic at low temperature, to form hydrogen bonds with coordinated Cl atoms as found in the solid state (the H^{10} protons are not diasterotopic over the measured temperature range), although steric interactions between the cymene ring and carbene ligands may also play a role.[42] The imidazolium H^7 resonance moves downfield as the temperature is lowered (δ 7.36

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Table 1. Key Intramolecular Bond Lengths and Angles of 14 in the Solid State

conformation 1 (Ru1, Cr1)	conformation 2 (Ru2, Cr2)
Ru1–Cl1, 2.438(4)	Ru2–Cl4, 2.462(3)
Ru1–Cl2, 2.455(3)	Ru2–Cl3, 2.455(3)
Ru1–C11, 2.03(2)	Ru2–C35, 2.02(2)
Cl1–Ru1–C11, 90.0(4)	Cl4–Ru2–C35, 92.4(4)
Cl2–Ru1–C11, 88.5(4)	Cl3–Ru2–C35, 88.9(3)
$Ru1-C_6H_{4,avg}$, 2.20(3)	$Ru2-C_6H_{4,avg}$, 2.20(3)
Ru1–Centroid, 1.682	Ru2–Centroid, 1.683
$C-C_{Ru1ring,avg}$, 1.42(6)	$C-C_{Ru2ring,avg}$, 1.42(4)
C11–N1, 1.43(2)	C35–N3, 1.36(2)
C11–N2, 1.37(2)	C35–N4, 1.39(2)
C10–N1, 1.46(2)	C34–N3, 1.47(2)
C4–C10, 1.53(2)	C28–C34, 1.54(2)
N1–C10–C4, 113(1)	N3–C34–C28, 112(1)
$Cr1-CO_{avg}$, 1.83(2)	$Cr2-CO_{avg}$, 1.85(2)
$C-O_{Cr1avg}$, 1.19(3)	$C-O_{Cr2avg}$, 1.16(2)
$OC{-}{-}Cr1-CO_{avg}$, 86.5(8)	$OC-Cr2-CO_{avg}$, 88(2)
$Cr1-C-O_{avg}$, 177(2)	$Cr2-C-O_{avg}$, 179(2)
$Cr1-C_6H_{5,avg}$, 2.22(2)	$Cr2-C_6H_{5,avg}$, 2.22(2)
Cr1–Centroid, 1.725	Cr2–Centroid, 1.712
$C-C_{Cr1ring,avg}$, 1.39(2)	$C-C_{Cr2ring,avg}$, 1.41(4)

at 20°C to δ 7.49 at −30°C), probably owing to a more pronounced interaction with the ring current from the chromium arene ring (cf. Figure 5) as the conformation of the molecule becomes increasingly more rigid, while the remaining resonances remain essentially unchanged.

The similarity of the chromium environs to that of the starting complex, **6**, is indicated by near equivalent bonding parameters, notably the carbonyl ligands adopt the same staggered conformation. However, in solution there is a slight shift of the carbonyl IR absorptions to lower wavenumber in accordance with the reduction in the electron withdrawing capacity of the arene substitutent [cf. 1972 and 1895 cm^{-1} for **6** versus 1968 and 1891 cm^{-1} for **14**]. In the two conformations, small deviations are found between the corresponding bonding parameters, likely to be the result of crystal packing owing to the considerable number of hydrogen bonding interactions observed, not only between the two different conformations but also between the CH_2Cl_2 solvate molecules (particularly for the conformation containing Ru1); see Figure 5 and Figure S-3 (Supporting Information).

Concluding Comments. The number of examples of organometallic ionic liquids (see introduction) has been extended with the introduction of the chromium tricarbonyl fragment onto the cation. Not only are organometallic ionic liquids of interest, but organometallic reactions in ionic liquids have also attracted some attention. Prior to the work described in this paper Lewis acidic chloroaluminate ionic liquids were exploited as reaction media for ring exchange reactions [43] and acylation reactions [44] of ferrocene, as well as in the synthesis of other transition metal–arene complexes.[45] The synthesis and isolation of carbene compounds has also been achieved in imidazolium chloroaluminate ionic liquids,[46] as well as having been implicated in C–C coupling reactions conducted in ionic liquids.[47] However, in this paper we not only describe the synthesis of new organometallic ionic liquids but also describe their reactivity, including tosylation, which should lead to other new ionic liquids, and the synthesis of a mixed-metal arene-chromium/carbene-ruthenium complex.

Experimental Section

All organometallic manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Dioxane, diethyl ether, CH_2Cl_2, and acetonitrile were dried and distilled under nitrogen from $LiAlH_4$, Na, CaH_2, and CaH_2, respectively, prior to use; other solvents were p.a. quality and purged with nitrogen prior to use. 1-Methyl-3-benzylimidazolium bromide,[48] 1,2-dimethyl-3-benzylimidazolium,[49] (2-hydroxyethyl)benzyldimethylammonium bromide,[50] *N*-methyl-*N*-benzylpyrrolidinium bromide,[50] $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$,[30] and $[Ru(\eta^6\text{-}p\text{-cymene})Cl_2]_2$ [51] were prepared as previously described. The tetrafluoroborate salts, used for the direct reactions with chromium hexacarbonyl, were prepared by methathesis of the corresponding bromide salts using procedures similar to those of Vidiš and co-workers.[52] All other chemicals are commercial products and were used as received. NMR spectra were recorded on a Bruker Avance 400 spectrometer at room temperature, unless stated otherwise. Chemical shifts are given in ppm, and coupling constants (*J*), in Hz. IR spectra were recorded on a Perkin-Elmer 2000 FT-IR. Elemental analyses were performed at the EPFL. Electrospray mass spectra were measured on a Thermo Finnigan LCQ Deca XPplus spectrometer according to a literature protocol.[32] Melting points were determined on a Stuart Scientific, SMPS, melting point apparatus.

Synthesis of 1-Methyl-3-benzylimidazolium Tetrafluoroborate. A solution of 1-methyl-3-benzylimidazolium bromide in CH_2Cl_2 (4.9 mL, ~0.56 M, 2.8 mmol) was added to a suspension of sodium tetrafluoroborate (0.36 g, 3.2 mmol) in CH_2Cl_2 (15 mL) and stirred at room temperature for 90 h. The resulting white suspension was filtered and washed with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 fractions were combined and the solvent was removed in vacuo, to afford the product as a pale yellow oil. Yield: 0.70 g (96%). ^1H NMR ($CDCl_3$): δ 9.62 (s, 1H, NC*H*N), 7.3–7.5 (m, 7H, NC*H*C*H*N and CH_2Ph), 5.44 (s, 2H, CH_2), 3.96 (s, 3H, CH_3N). ESI-MS positive ion: *m/z* 173 ($[C_{11}H_{13}N_2]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Synthesis of 1,2-Dimethyl-3-benzylimidazolium Tetrafluoroborate. A mixture of 1,2-dimethyl-3-benzylimidazolium bromide (0.7 g, 2.6 mmol) and sodium tetrafluoroborate (0.33 g, 3.0 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 90 h. The resulting white suspension was filtered and washed with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 fractions were combined and the solvent was removed in vacuo, to afford the product as a pale yellow solid. Yield: 0.64 g (90%). ^1H NMR ($CDCl_3$): δ 7.23–7.48 (m, 7H, NC*H*C*H*N and CH_2Ph), 5.40 (s, 2H, CH_2), 3.91 (s, 3H, CH_3N), 2.74 (s, 3H, $C(CH_3)$). ESI-MS positive ion: *m/z* 187 ($[C_{12}H_{15}N_2]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

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(42) The $^1J_{CH}$ values in $CDCl_3$ at −50 °C of the upfield diastereotopic H3″ (173 Hz) and H6″ (140 Hz) resonances are significantly smaller than those of the corresponding downfield resonances H3′ (176 Hz) and H6′ (144 Hz), consistent with the presence of hydrogen bonding in solution.

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Synthesis of (2-Hydroxyethyl)benzyldimethylammonium Tetrafluoroborate. A mixture of (2-hydroxyethyl)benzyldimethylammonium bromide (0.7 g, 2.7 mmol) and sodium tetrafluoroborate (0.36 g, 3.2 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 90 h. The resulting white suspension was filtered and first washed with CH_2Cl_2 (2 × 10 mL) and then stirred in acetonitrile (15 mL) for 20 min and filtered. The CH_2Cl_2 and acetonitrile fractions were combined and the solvent was removed in vacuo, to afford the product as a white solid. Yield: 0.56 g (78%). ^1H NMR (acetone-d_6): δ 7.7−7.8 (m, 2H, *o*-C_6H_5), 7.53−7.60 (m, 3H, *p,m*-C_6H_5), 5.03 (s, 2H, CH_2Ph), 4.19−4.27 (m, 2H, NCH_2), 3.67−3.74 (m, 2H, CH_2OH), 3.32 (s, 6H, NCH_3). ESI-MS positive ion: *m/z* 180 ($[C_{11}H_{18}NO]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Synthesis of *N*-Methyl-*N*-benzylpyrrolidinium Tetrafluoroborate. A mixture of *N*-methyl-*N*-benzylpyrrolidinium bromide (0.7 g, 2.7 mmol) and sodium tetrafluoroborate (0.36 g, 3.2 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 90 h. The resulting white suspension was filtered and washed with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 fractions were combined and the solvent was removed in vacuo, to afford the product as a pale yellow oil. Yield: 0.70 g (98%). ^1H NMR ($CDCl_3$): δ 7.55−7.65 (m, 2H, CH_2Ph), 7.42−7.47 (m, 3H, CH_2Ph), 4.66 (s, 2H, NCH_2Ph), 3.84−3.91 (m, 2H, NCH_2CH_2), 3.55−3.60 (m, 2H, NCH_2CH_2), 3.10 (s, 3H, $N(CH_3)_2$), 2.15−2.3 (m, 2H, $CH_2CH_2CH_2CH_2$), 2.3−2.4 (m, 2H, $CH_2CH_2CH_2CH_2$). ESI-MS positive ion: *m/z* 176 ($[C_{12}H_{18}N_2]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Synthesis of 1-Methyl-3-(3-phenylpropyl)imidazolium Bromide. 3-Bromo-1-phenylpropane (1.52 mL, 1.99 g, 10 mmol) was slowly added to *N*-methylimidazole (0.87 mL, 0.90 g, 11 mmol) in two equal portions, together with CH_2Cl_2 (5 mL) after the first portion of 3-bromo-1-phenylpropane. The solution was stirred for 2 h and the volatiles were removed under high vacuum (90 h), to afford the product as a pale yellow oil. Yield 1.27 g (45%). ^1H NMR ($CDCl_3$): δ 10.09 (s, 1H, NCHN), 7.49 (s, 1H, NCHCHN), 7.41 (s, 1H, NCHCHN), 6.9−7.2 (m, 5H, CH_2Ph), 4.22 (t, 2H, NCH_2, $^3J_{HH}$ = 7.2 Hz), 3.90 (s, 3H, CH_3N), 2.56 (t, 2H, CH_2Ph, $^3J_{HH}$ = 7.5 Hz), 2.12 (t, 2H, $CH_2CH_2CH_2$, $^3J_{HH}$ = 7.3 Hz). ESI-MS positive ion: *m/z* 201 ($[C_{13}H_{17}N_2]^+$).

Synthesis of 1-Methyl-3-(3-phenylpropyl)imidazolium Tetrafluoroborate. A mixture of sodium tetrafluoroborate (0.24 g, 2.2 mmol) and 1-methyl-3-(3-phenylpropyl)imidazolium bromide (0.58 g, 2.0 mmol) in CH_2Cl_2 (10 mL) was stirred at room temperature for 90 h. The resulting white suspension was filtered and washed with CH_2Cl_2 (2 × 10 mL). The CH_2Cl_2 fractions were combined and the solvent was removed in vacuo, to afford the product as a pale yellow oil. Yield: 0.46 g (83%). ^1H NMR ($CDCl_3$): δ 9.36 (s, 1H, NCHN), 7.1−7.4 (m, 7H, CHCH and CH_2Ph), 4.22−4.44 (m, 2H, NCH_2), 3.92−3.96 (m, 3H, NCH_3), 2.65−2.75 (m, CH_2Ph), 2.15−2.30 (m, $CH_2CH_2CH_2$). ESI-MS positive ion: *m/z* 201 ($[C_{13}H_{17}N_2]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Direct Reactions with Chromium Hexacarbonyl. Equimolar amounts of arene and $[Cr(CO)_6]$ were refluxed in dioxane for ca. 20 h. Following solvent removal, the residue was extracted with acetone and concentrated under high vacuum. The resulting yellow oils were mixtures of starting material and the desired chromium arene salts as indicated by ^1H NMR and electrospray mass spectrometry.

Reaction of 1-Methyl-3-benzylimidazolium Tetrafluoroborate with $[Cr(CO)_6]$. Refluxed for 20 h. Isolated as a yellow paste containing approximately 9% of **1** (overall yield: 8%) as determined by ^1H NMR (acetone-d_6).

Reaction of 1,2-Dimethyl-3-benzylimidazolium Tetrafluoroborate with $[Cr(CO)_6]$. Refluxed for 17 h. Isolated as a slightly brownish yellow oil containing approximately 11% of **2** (overall yield: 6%) as determined by ^1H NMR (acetone-d_6).

Reaction of (2-Hydroxyethyl)benzyldimethylammonium Tetrafluoroborate with $[Cr(CO)_6]$. Refluxed for 96 h. Isolated as a bright yellow viscous oil containing 47% of **3** (overall yield: 32%) as determined by ^1H NMR (acetone-d_6).

Reaction of *N*-methyl-*N*-benzylpyrrolidinium Tetrafluoroborate with $[Cr(CO)_6]$. Refluxed for 20 h. Isolated as a yellow paste containing approximately 7% of **4** (overall yield: 4%) as determined by ^1H NMR (acetone-d_6). ESI-MS positive ion: *m/z* 176 (starting material, $[C_{12}H_{18}N]^+$), 312 (M^+). MS/MS (+312): 227 ($[M - C_5H_{11}N]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Reaction of 1-Methyl-3-(3-phenylpropyl)imidazolium Tetrafluoroborate with $[Cr(CO)_6]$. Refluxed for 26 h. Isolated as a viscous yellow oil, containing approximately 60% of **5** (overall yield: 42%) as determined by ^1H NMR (acetone-d_6). ESI-MS positive ion: *m/z* 201 (starting material, $[C_{13}H_{17}N_2]^+$), 337 (M^+). MS/MS (+337): 253 ($[C_{11}H_9CrN_2O_2]^+$), 294 ($[M - C_2H_3O]^+$), 309 ($[M - CO]^+$). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2MIM)]Br$ 6. To a solution of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$ (0.405 g, 1.32 mmol) in acetonitrile (30 mL) was added *N*-methylimidazole (0.12 mL, 1.45 mmol). This solution was then stirred at room temperature for 64 h. The product was obtained as a microcrystalline yellow powder by slow addition of diethyl ether (30 mL) to the solution, collected by filtration and washed with diethyl ether (2 × 5 mL). Yield: 0.34 g (65%). An analytically pure same was obtained by slow diffusion of diethyl ether into a methanol solution of **6** at 4 °C. ^1H NMR(CD_3OD): δ 9.17 (s, <1H, NCHN), 7.79 (d, 1H, NCH, $^3J_{HH}$ = 1.9 Hz), 7.66 (d, 1H, NCH, $^3J_{HH}$ = 1.9 Hz), 5.79 (d, 2H, *o*-C_6H_5, $^3J_{HH}$ = 6.1 Hz), 5.63 (t, 1H, *p*-C_6H_5, $^3J_{HH}$ = 6.2 Hz), 5.58 (d, 2H, *m*-C_6H_5, $^3J_{HH}$ = 6.2 Hz), 5.19 (s, 2H, CH_2Ph), 3.97 (s, 3H, NCH_3). $^{13}C\{^1H\}$ NMR(CD_3OD): δ 232.0 ($Cr(CO)_3$), 124.0 (NCH), 122.3 (NCH), 94.1 (C_6H_5), 93.8 (C_6H_5), 92.3 (C_6H_5), 51.3 (CH_2Ph), 35.3 (NCH_3). Mp: 173−175 °C (decomp). IR (acetone, cm^{-1}) ν(CO): 1972, 1895. ESI-MS positive ion: *m/z* 173 (weak, $[M - Cr(CO)_3]^+$), 309 (M^+). MS/MS (+309): 227 ($[M - C_3H_3N_2CH_3]^+$). Anal. Calcd for $C_{14}H_{13}BrCrN_2O_3$: C, 43.21; H, 3.37; N, 7.20. Found: C, 43.08; H, 3.37; N, 7.18. Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a acetonitrile solution of **6** at 4 °C.

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5(CH_2)_3MMIM)]Br$ 7. To a solution of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$ (0.55 g, 1.79 mmol) in acetonitrile (30 mL) was added 1,2-dimethylimidazole (0.19 g, 1.97 mmol). The product as a yellow solid precipitated upon stirring this solution at room temperature for 87 h and was collected by filtration and washed with diethyl ether (2 × 5 mL). Yield 0.49 g (68%). An analytically pure sample was obtained by slow diffusion of diethyl ether into a methanol solution of **7** at 4 °C. ^1H NMR(CD_3OD): δ 7.68 (d, 1H, NCH, $^3J_{HH}$ = 2.1 Hz), 7.59 (d, 1H, NCH, $^3J_{HH}$ = 2.1 Hz), 5.72 (d, 2H, *o*-C_6H_5, $^3J_{HH}$ = 6.2 Hz), 5.64 (t, 1H, *p*-C_6H_5, $^3J_{HH}$ = 6.3 Hz), 5.57 (d, 2H, *m*-C_6H_5, $^3J_{HH}$ = 6.3 Hz), 5.19 (s, 2H, CH_2Ph), 3.87 (s, 3H, NCH_3), 2.77 (s, 3H, $NC(CH_3)N$). $^{13}C\{^1H\}$ NMR(CD_3OD): δ 232.1 ($Cr(CO)_3$), 122.8 (NCH), 121.1 (NCH), 94.1 (C_6H_5), 93.6 (C_6H_5), 92.2 (C_6H_5), 49.7 ($CH_2C_6H_4$), 34.4 (NCH_3), 8.8 ($NC(CH_3)N$). Mp: 168−170 °C (decomp). IR (acetone, cm^{-1}) ν(CO): 1972, 1895. ESI-MS positive ion: *m/z* 323 (M^+). MS/MS (+323): 295 (weak, $[M - CO]^+$), 227 ($[M - C_5H_8N_2]^+$). Anal. Calcd for $C_{15}H_{15}BrCrN_2O_3$: C, 44.68; H, 3.75; N, 6.95. Found: C, 44.86; H, 3.70; N, 6.75. Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a acetonitrile solution of **7** at 4 °C.

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2NMe_2(CH_3)_2OH)]Br$ 8. To a solution of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2Br)]$ (0.55 g, 1.79 mmol) in acetonitrile (30 mL) was added *N,N*-dimethylimidazole (0.176 g, 1.97 mmol). This solution was then stirred at room temperature for 88 h, resulting in the precipitation of the product as a yellow microcrystalline powder which was isolated by filtration and washed with ether (2 × 5 mL). Yield: 0.694

g (98%). An analytically pure same was obtained by slow diffusion of diethyl ether into a methanol solution of **8** at 4 °C. ^{1}H NMR(CD_3OD): δ 5.90 (d, 2H, *o*-C_6H_5, $^3J_{HH} = 6.2$ Hz), 5.70 (t, 1H, *p*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.61 (d, 2H, *m*-C_6H_5, $^3J_{HH} = 6.1$ Hz), 4.41 (s, 2H, CH_2), 4.09 (br, 2H, CH_2), 3.51−3.54 (m, 2H, CH_2OH), 3.25 (s, $N(CH_3)_2$). $^{13}C\{^1H\}$ NMR(CD_3OD): δ 231.3 ($Cr(CO)_3$), 97.5 (C_6H_5), 94.4 (C_6H_5), 91.9 (C_6H_5), 67.8 (s), 65.3 (s), 55.5 (s), 50.0 (s). Mp: 173−177 °C (decomp). IR (acetone, cm^{-1}) ν(CO): 1975, 1901. ESI-MS positive ion: *m/z* 316 (M^+). MS/MS (+316): *m/z* 227 ($[M - C_4H_{11}NO]^+$). Anal. Calcd for $C_{14}H_{18}BrCrNO_4$: C, 42.44; H, 4.58; N, 3.54. Found: C, 42.33; H, 4.57; N, 3.45. Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a acetonitrile solution of **8** at 4 °C.

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2MIM)]Tf_2N$ 9. A mixture of **6** (0.033 g, 0.085 mmol) and $LiTf_2N$ (0.029 g, 0.1 mmol) was stirred in water (2 mL) at 40 °C for 2.5 h. The water phase was removed with a syringe, and the remaining viscous yellow oil was washed with aliquots of water until the water washing no longer gave precipitates with an aqueous solution of $AgNO_3$. The oil was then azeotropically dried with acetonitrile (1 mL) under high vacuum. Remaining solvent was removed by a series of trituration (−196°C)−thaw cycles, to leave the product as a yellow powder. Yield: 0.043 g (83%). ^{1}H NMR(CD_3OD): δ 9.06 (s, <1H, NC*H*N), 7.75 (s, 1H, NC*H*), 7.64 (s, 1H, NC*H*), 5.72 (d, 2H, *o*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.61 (t, 1H, *p*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.56 (d, 2H, *m*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.15 (s, 2H, CH_2Ph), 3.95 (s, 3H, NCH_3). Mp: 37−39°C. IR (acetone, cm^{-1}) ν(CO): 1973, 1898. ESI-MS positive ion: *m/z* 173 (weak, $[M - Cr(CO)_3]^+$), 309 (M^+). ESI-MS negative ion: *m/z* 280 ($[Tf_2N]^-$).

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5(CH_2)_3MMIM)]Tf_2N$ 10. A mixture of **7** (0.149 g, 0.37 mmol) and $LiTf_2N$ (0.106 g, 0.37 mmol) was stirred in water (2 mL) at room temperature for 2.5 h. The water phase was removed with a syringe, and the remaining viscous yellow oil was washed with aliquots of water (2 × 1 mL). The oil was then azeotropically dried with acetonitrile (1 mL) under high vacuum for 3 days, during which time it solidified. Yield: 0.114 g (51%). ^{1}H NMR(CD_3OD): δ 7.66 (d, 1H, NC*H*, $^3J_{HH} = 2.0$ Hz), 7.57 (d, 1H, NC*H*, $^3J_{HH} = 1.6$ Hz), 5.68 (d, 2H, *o*-C_6H_5, $^3J_{HH} = 5.6$ Hz), 5.63 (t, 1H, *p*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.55 (d, 2H, *m*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.16 (s, 2H, CH_2Ph), 3.85 (s, 3H, NCH_3), 2.75 (s, 3H, NC(CH_3)N). Mp: 65−70 °C. IR (acetone, cm^{-1}) ν(CO): 1972, 1897. ESI-MS positive ion: *m/z* 187 ($[M - Cr(CO)_3]^+$), 323 (M). ESI-MS negative ion: *m/z* 280 ($[Tf_2N]^-$).

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2NMe_2(CH_3)_2OH)]Tf_2N$ 11. A mixture of **8** (0.085 g, 0.21 mmol) and $LiTf_2N$ (0.079 g, 0.25 mmol) was stirred in water (1 mL) at 40 °C for 3 h. The water phase was removed with a syringe, and the remaining viscous yellow oil was washed with aliquots of water until the water washing no longer gave precipitates with an aqueous solution of $AgNO_3$. The oil was then azeotropically dried with acetonitrile (1 mL) under high vacuum. Remaining solvent was removed by a series of trituration (−196°C)−thaw cycles, to leave the product as bright yellow powder. Yield: 0.122 g (78%). ^{1}H NMR(CD_3OD): δ 5.84 (d, 2H, *o*-C_6H_5, $^3J_{HH} = 6.4$ Hz), 5.70 (t, 1H, *p*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.60 (d, 2H, *m*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 4.37 (s, 2H, CH_2), 4.08 (br, 2H, CH_2), 3.56 (t, 2H, CH_2, $^3J_{HH} = 4.4$ Hz), 3.25 (s, $N(CH_3)_2$). Mp: 44−46 °C. IR (acetone, cm^{-1}) ν(CO): 1976, 1903. ESI-MS positive ion: *m/z* 173 (weak, $[M - Cr(CO)_3]^+$), 227 (weak, ($[M - C_4H_{11}NO]^+$), 316 (M^+). ESI-MS negative ion: *m/z* 280 ($[Tf_2N]^-$).

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2MIM)]BF_4$ 12. A mixture of **6** (0.071 g, 0.18 mmol) and $NaBF_4$ (0.021 g, 0.20 mmol) was stirred in acetonitrile (5 mL) for 2 days. The resulting white suspension was filtered and washed once with acetonitrile. The acetonitrile fractions were combined and the solvent was removed in vacuo, to afford the product as a yellow solid. Yield: 0.069 g (97%). ^{1}H NMR(CD_3OD): δ 9.07 (s, 1H, NC*H*N), 7.76 (s, 1H, NC*H*), 7.64 (s, 1H, NC*H*), 5.68−5.78 (m, 2H), 5.58−5.64 (m, 1H, *p*-C_6H_5), 5.51−5.58 (m, 2H, *m*-C_6H_5), 5.16 (s, 2H, CH_2Ph), 3.95 (s, 3H, NCH_3). Mp: 150−160 °C (decomp). IR (acetone, cm^{-1}) ν(CO): 1973, 1895. ESI-MS positive ion: *m/z* 309 (M^+). ESI-MS negative ion: *m/z* 87 ($[BF_4]^-$).

Synthesis of $[Cr(CO)_3(\eta^6\text{-}C_6H_5CH_2NMe_2(CH_3)_2OTs)]Br\cdot HNEt_3Cl$ 13·HNEt$_3$Cl. To a cooled (0°C, ice slurry) and well stirred suspension of **8** (0.349 g, 0.88 mmol), *p*-toluenesulfonyl chloride (0.426 g, 1.32 mmol), and trimethylamine hydrochloride (10 mg, 0.1 mmol) in acetonitrile (10 mL) was added triethylamine (0.38 mL, 0.27 g, 2.6 mmol) dropwise. Stirring was continued for 2 h before the solvent was removed in vacuo. The residue was then washed with ether and recrystallized from ethanol−diethyl ether to afford the product as a crystalline yellow powder. Yield: 0.53 g (74%). Crystals of **13** suitable for X-ray crystallography were obtained by slow diffusion of ether into an ethanol solution of **13**·NEt_3HCl at 4 °C. ^{1}H NMR (CD_3OD): δ 7.89 (d, 2H, *o/m*-C_6H_4, $^3J_{HH} = 8.0$ Hz), 7.52 (d, 2H, *m/o*-C_6H_4, $^3J_{HH} = 8.4$ Hz), 5.77 (d, 2H, *o*-C_6H_5, $^3J_{HH} = 6.0$ Hz), 5.70 (t, 1H, *p*-C_6H_5, $^3J_{HH} = 6.4$ Hz), 5.59 (t, 2H, *m*-C_6H_5, $^3J_{HH} = 6.4$ Hz), 4.63 (br, 2H, **13**−NCH_2), 4.33 (s, 2H, **13**−CH_2-Ph), 3.86 (t, 2H, **13**−CH_2OH, $^3J_{HH} = 4.4$ Hz), 3.23 (q, 6H, $N(CH_2CH_3)_3H$, $^3J_{HH} = 7.6$ Hz), 3.20 (s, 6H, $N(CH_3)_2$), 2.50 (s, 3H, $CH_3-C_6H_4$), 1.34 (t, 9H, $N(CH_2CH_3)_3H$, $^3J_{HH} = 7.6$ Hz). Mp(**13**): 136−140 °C (gas evolution). IR (acetone, cm^{-1}) ν(CO): 1976, 1902. ESI-MS positive ion: 470 ($C_{21}H_{24}CrNO_6S$). MS/MS (+470): 227 ($[C_{21}H_{24}CrNO_6S - C_{11}H_{17}NO_3S]^+$). Anal. Calcd for $C_{21}H_{24}CrBrNO_6S\cdot HNEt_3Cl$: C, 47.13; H, 5.86; N, 4.07. Found: C, 47.26; H, 6.30; N, 4.04.

Synthesis of $[Ru(\eta^6\text{-}p\text{-}cymene)Cl_2\{C_4H_5N_2CH_2Ph\text{-}\eta^6\text{-}Cr(CO)_3\}]$ 14. A mixture of **6** (0.074 g, 0.19 mmol) and silver(I) oxide (0.044 g, 0.19 mmol) in CH_2Cl_2 (30 mL) was stirred for 18 h at room temperature in the dark. The solution was then filtered through Celite into a flask containing $[Ru_2(\eta^6\text{-}p\text{-}cymene)_2Cl_4]$ (0.058 g, 0.095 mmol), washing with CH_2Cl_2 (5 mL), and stirred for a further 7 h at room temperature in the dark. The resulting suspension was filtered through Celite, washing with CH_2Cl_2 (5 mL). The ensuing orange solution was concentrated to ca. 5 mL, and the product isolated following precipitation with hexane (40 mL) and filtration, washing with hexane (20 mL). Yield: 0.1 g (86%). ^{1}H NMR (C_4D_8O): δ 7.36 (s, 1H, CH_2NCH), 7.33 (s, 1H, $HCNCH_3$), 5.4−5.6 (m, 3H, CrC_6H_5), 4.3−6.8 (br, 4H, $CrC_6H_5CH_2$), 5.46 (d, 2H, *m*-$CH_3C_6H_4$, $^3J_{HH} = 5.6$ Hz), 5.13 (d, 2H, *o*-$CH_3C_6H_4$, $^3J_{HH} = 5.6$ Hz), 4.07 (s, 3H, NCH_3), 3.00 (sept, 1H, $CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz), 1.99 (s, 3H, $CH_3C_6H_4$), 1.30 (d, 6H, $CH(CH_3)_2$, $^3J_{HH} = 6.9$ Hz). $^{13}C\{^1H\}$ NMR (C_4D_8O): δ 233.3 ($Cr(CO)_3$), 176.7 (C═Ru), 124.3 ($HCNCH_3$), 121.5 (CH_2NCH), 108.2 ($CCH(CH_3)_2$), 97.5 (*i*-$CH_3C_6H_4$), 94.5 (CrC_6H_5), 93.2 (CrC_6H_5), 93.1 (CrC_6H_5), 86.9 (*m*-$CH_3C_6H_4$), 81.7 (*o*-$CH_3C_6H_4$), 52.5 (CH_2N), 38.9 (NCH_3), 30.7 ($CH(CH_3)_2$), 21.7 ($CH(CH_3)_2$), 17.7 ($CH_3C_6H_4$). Mp: 118−124°C decomp. IR(acetone, cm^{-1}) ν(CO): 1968, 1891. ESI-MS positive ion: *m/z* 407 ([**14** − $Cr(CO)_3Cl_2]^+$), 443 ([**14** − $Cr(CO)_3Cl]^+$), 578 ([**14** − $Cl]^+$). MS/MS (+578): 417 ([**14** − $C_{10}H_{14}Cl_2]^+$), 543 ([**14** − $HCl_2]^+$). Crystals suitable for X-ray diffraction were obtained by recrystallization from CH_2Cl_2−hexane at 4 °C. Attempts to obtain correct elemental analysis failed owing to the ability of **14** to retain solvent during recrystallization, as demonstrated by three separate crystal structure determinations indicating the presence of four molecules of CH_2Cl_2 per asymmetric cell.

Structural Characterization of 6−8, 13, and 14 in the Solid State. Relevant details about the structure refinements are given in Table 2, and selected geometrical parameters are included in the captions of Figures 1− 4, Table 1, and Figure S-3 (Supporting Information). Data collection for the X-ray structure determinations for compounds **6**, **8**, and **14** was performed on a four-circle Kappa goniometer equipped with an Oxford Diffraction KM4 Sapphire CCD at 140(2) K. Diffraction data for **7** were measured similarly but at room

Table 2. Crystallographic Data for Compounds 6–8, 13, and 14

	6	**7**	**8**	**13**	**14**
chem formula	$C_{14}H_{13}BrCrN_2O_3$	$C_{15}H_{15}BrCrN_2O_3$	$C_{14}H_{18}BrCrNO_4$	$C_{21}H_{24}BrCrNO_6S$	$C_{52}H_{60}Cl_{12}Cr_2NO_6Ru_2$
fw	389.17	403.20	396.20	550.38	1568.58
cryst syst	triclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a (Å)	8.3713(13)	5.9434(13)	11.8561(11)	17.232(5)	12.446(5)
b (Å)	9.0861(12)	17.6518(13)	8.5321(5)	11.169(4)	13.638(5)
c (Å)	10.3104(11)	14.7067(15)	16.5160(13)	12.166(2)	20.258(5)
α (deg)	105.556(10)				78.037(5)
β (deg)	94.241(10)	100.586(13)	106.766(7)	101.63(2)	89.494(5)
γ (deg)	91.013(11)				72.735(5)
V (Å^3)	752.86(17)	1516.6(4)	1599.7(2)	2293.2(11)	3207.2(19)
Z	2	4	4	4	2
D_{calcd} (g cm^{-3})	1.717	1.766	1.645	1.594	1.624
F(000)	388	808	800	1120	1576
μ (mm^{-1})	3.423	3.402	3.226	2.369	1.340
temp (K)	140(2)	140(2)	293(2)	140(2)	140(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
no. of measd rflns	4469	8864	8802	14 142	19 297
no. of unique rflns	2313	2544	2740	4050	9935
no. of unique rflns ($I > 2\sigma(I)$)	1832	1837	1891	2021	4010
no. of data/restraints/params	2313/0/192	2544/0/201	2740/0/193	4050/0/283	9935/105/749
R1[a] ($I > 2\sigma(I)$)	0.0391	0.0401	0.0391	0.0633	0.0831
wR2[a] (all data)	0.0977	0.1016	0.0738	0.1854	0.2026
GOF[b]	0.983	0.946	0.968	0.908	0.868

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. [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.

temperature, whereas for compound **13** data were collected on an mar345 IPDS instrument at 140(2) K. Data reduction was performed using CrysAlis RED.[53] Structure solution and refinement were performed using the SHELXTL software package[54] for all compounds, except for the structure solution of compound **14**, which was performed using Sir97.[55] An empirical absorption correction (DELABS)[56] was applied to all data sets. The structures were refined using fullmatrix least squares on F^2 with all non-H atoms anisotropically defined. H atoms were placed in calculated positions using the riding model. Graphical representations of the structures were made with Diamond.[57]

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Supporting Information Available: Crystallographic information for **6–8**, **13**, and **14** in CIF format, Figures S-1, S-2, S-3, and S-4. This material is available free of charge via the Internet at http://pubs.acs.org.

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