2724 *Organometallics* **2010,** *29,* 2724–2734
DOI: 10.1021/om1002107

ORGANOMETALLICS
Article

Metal Complexes of Chiral NHCs Containing a Fused Six- and Seven-Membered Central Ring

Paul D. Newman,*,† Kingsley J. Cavell,*,‡ and Benson M. Kariuki‡

†*Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff, U.K. CF10 3AT, and*
‡*School of Chemistry, Cardiff University, Cardiff, U.K. CF10 3AT*

Received March 18, 2010

Azolium precursors to expanded-ring NHCs incorporating a chiral bicyclic skeleton derived from (1*R*)-camphor with *N,N′*-dibenzyl or *N,N′*-dipyridyl substituents have been prepared and used for the synthesis of a number of metal complexes of the resultant NHCs. The bicyclic framework contains two fused rings, one of which is seven-membered while the other is six-membered. Deprotonation of (1*R*,5*S*)-2,4-dibenzyl-1,8,8-trimethyl-4-aza-2-azoniabicyclo[3.2.1]oct-2-ene hexafluorophosphate, **1a**·HPF_6, produces a solution of "free carbene", **1a**, that can be used for the preparation of [Ag(**1a**)$_2$]OTf (**2a**), [Rh(1,5-COD)(**1a**)Cl] (**3a**), [Rh(CO)$_2$(**1a**)Cl] (**4a**), and [Ir(1,5-COD)(**1a**)Cl] (**5a**) complexes. The fused expanded ring NHC ligands display properties and reactivity patterns more akin to those of five-membered NHCs rather than monocyclic six- or seven-membered NHCs. Consistent with this premise, the red Ni(II) pincer complex [Ni(η^3-C_8H_{13})(**1b**)]PF_6, **6b**, was obtained via oxidative addition of the azolium salt **1b**·HPF_6 to Ni(1,5-COD)$_2$ in THF. This is the first unambiguous example of a saturated and/or expanded ring NHC oxidatively adding to a low-valent metal center. A single-crystal X-ray structure determination of **6b** showed the NHC to be coordinated in a pincer fashion through the carbene and two pyridine nitrogens at a square-pyramidal nickel(II) center. One of the original 1,5-COD ligands has undergone a 1,5 to 1,3 isomerization before migratory insertion of one of the alkene groups into the Ni−H function, generated on oxidative addition of the azolium salt, to give the allylic η^3-C_8H_{13} ligand. When **6b** was dissolved in $CHCl_3$ or CH_2Cl_2 in air, the allyl ligand was lost and a chloride was abstracted from the solvent to give yellow square-planar [Ni(**1b**)Cl]PF_6, **7b**, the structure of which was confirmed by single-crystal X-ray techniques.

Introduction

Although known since the late 1960s,[1] N-heterocyclic carbenes (NHCs) were virtually ignored as ligands in coordination/organometallic chemistry until the isolation of the first stable derivative in 1991.[2] Since this initial report of Arduengo, the study of NHCs has escalated exponentially to the extent that special issues dedicated solely to such ligands have appeared in a number of prominent journals.[3] With regard to their coordination chemistry, early comparisons with the well-established phosphines (particularly trialkylphosphines) were probably overstated, as NHCs possess unique electronic and steric properties.[4] In broad terms, NHCs are strong σ-donors with a low capacity for π-acceptance[5] and their steric features are best described by a "buried volume" model[6] dictated by the sp^2 nature of the C_{NHC} carbene donor as opposed to the well-established cone angle applicable for σ^3,λ^3-phosphines. While the majority of NHCs employed as ligands are based on an imidazole core, analogues with expanded six- and seven-membered heterocyclic rings have attracted attention, as it has been established that they possess quite different properties from the five-membered derivatives, most notably an enhanced basicity/nucleophilicity and greater steric demand.[7] Apart from a few reports, largely from the groups of Cavell[7b,c] and Stahl,[7a,f] little is known of the larger seven-membered NHCs as ligands, particularly for systems that are potentially multidentate through the inclusion of other secondary donors.

Of the numerous NHC frameworks that now exist, an appreciable number contain one or more chiral elements, which may be a classic stereogenic tetrahedral carbon or another form of asymmetry such as a chiral axis.[8] The source

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*Corresponding authors. E-mail: newmanp1@cardiff.ac.uk.

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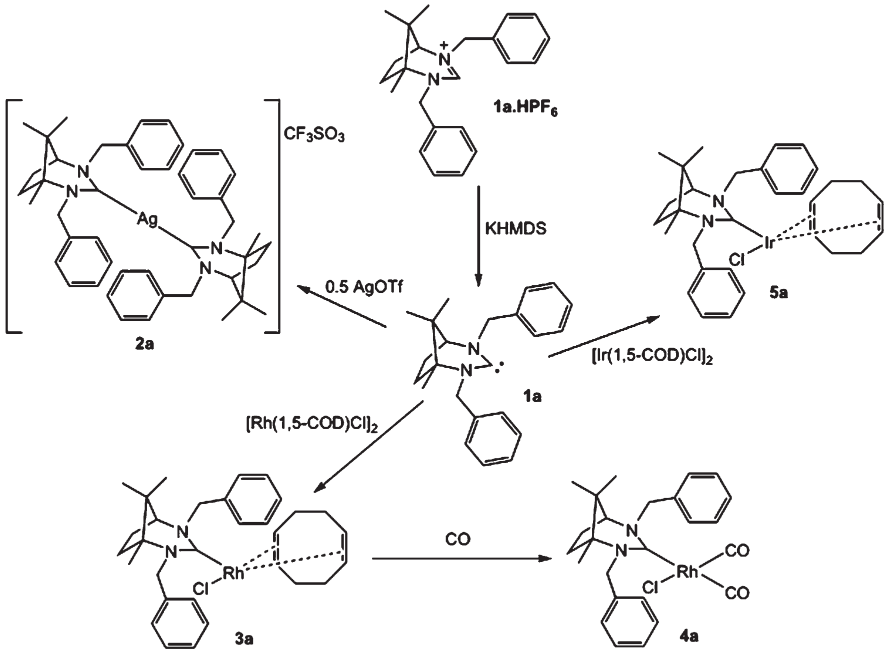
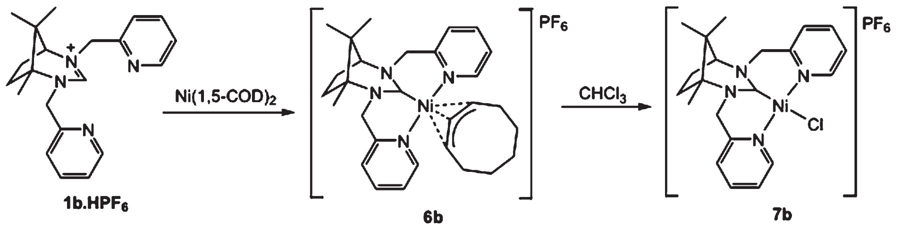
Scheme 1. Complexes of the Bicyclic NHC Ligands 1a and 1b





(1)

of the chirality can be within the central ring or form part of the flanking (exo) N-substituents. Our interests in the coordination chemistry of the asymmetric diamine *R*,*S*-tmcp and derivatives,[9] and in expanded-ring carbenes,[7b,c] led us to explore the synthesis and complexation chemistry of novel NHCs derived from *R*,*S*-tmcp. During our investigations of these novel ligand systems a report appeared describing the synthesis of **1a**·HBF_4 and aspects of the organic chemistry of the resultant carbene; however, no metal complexes were reported.[10] Here we report the synthesis of azolium salts **1a**·HPF_6 and **1b**·HPF_6 (Scheme 1) and the coordination chemistry of the resultant NHCs with a number of transition metals. Ligand **1b** is a pincer ligand with a NCN donor set. NHCs containing pyridine or other donor groups have been known for some time,[11] and the use of ligands of this type and other donor-functionalized systems in catalysis has been recently reviewed.[12] A major thrust of the present work was to explore the impact constraining the NHC carbon within a

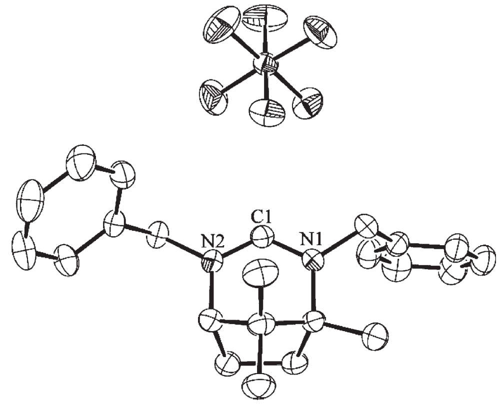


Figure 1. Ortep view of the molecular structure of **1a**·HPF_6. Thermal ellipsoids are drawn at 50% probability; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1a**·HPF_6: C1−N1 1.322(3), C1−N2 1.305(3), N1−C1−N2 123.5(2).

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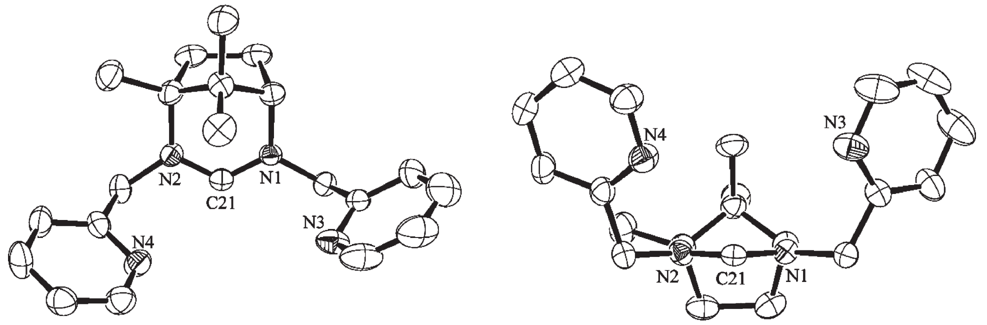

Figure 2. Two Ortep views of the molecular structure of the cation of **1b**·PF_6. Thermal ellipsoids are drawn at 50% probability; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **1b**·PF_6: C21−N1 1.303(6), C21−N2 1.310(5), N1−C21−N2 123.0(4).

fused, bicyclic framework has on its properties and chemical behavior.

Results and Discussion

Synthesis of the Azolium Precursors 1a·HPF_6 and 1b·HPF_6. As highlighted by Wilhelm,[10] Newman,[9] and others,[13] *R*,*S*-tmcp is a versatile chiral diamine with two distinct primary amines. The isopropyl-like 3-amino group can be selectively functionalized through virtue of it being less sterically encumbered than the 1-amino group, which is of a *tert*-butyl type. This distinction enables the stepwise introduction of different substituents at each nitrogen, facilitating the potential synthesis of a range of ligands with various donor sets. Considering the large number of functionalized aldehydes that are known, it is easy to envisage extending the current synthetic procedure to the preparation of a library of new ligand precursors with or without one or more additional donor functions.

The synthesis of **1a**·HBF_4 has been described by Wilhelm.[10] We have used a similar approach albeit employing NH_4PF_6 in the ring-closure step, as the resultant azolium salt precipitates from the reaction mixture upon forming. The synthesis of the carbene precursor salt **1b**·HPF_6 is achieved in an analogous fashion by employing the known (1*R*,3*S*)-*N*,*N*′-di(pyridin-2-ylmethyl)-1,3-diamino-1,2,2-trimethylcyclopentane. Here the azolium hexafluorophosphate salt did not precipitate directly from the reaction mixture but was acquired in high yield upon workup. Both **1a**·HPF_6 and **1b**·HPF_6 are nonhygroscopic salts that are easily handled in a normal atmosphere and can be readily recrystallized from diethyl ether or methanol. The NMR data for **1a**·HPF_6 are largely consistent with that of Wilhelm,[10] except that we observe a chemical shift of $\delta_H = 8.16$ ppm for the C2-H proton compared to a reported value of $\delta_H = 8.47$ ppm. As the relative chemical shift of this hydrogen has been used as a measure of the basicity of the resultant conjugate base, i.e., the carbene itself, it is somewhat surprising that a change of anion (PF_6^- or BF_4^-) can lead to such a shift in the resonance of this hydrogen. Thus with some caution we suggest that **1a** contains an azolium hydrogen with an acidity somewhere between that of a monocyclic seven-membered derivative and a five-membered imidazolium salt. Aside from the discrepancy in the chemical shift of the C2-H, there is no distinction between the NMR spectra for our sample and that of Wilhelm.

Single-crystal X-ray structures of **1a**·HPF_6 and **1b**·HPF_6 are shown in Figures 1 and 2, respectively. The structure of **1a**·HPF_6 includes the PF_6^- anion, as it is positioned close to the azolium hydrogen on C1; no such contact is evident in the crystal structure of **1b**·HPF_6, so in Figure 2 the counterion is excluded for clarity. The C1−N bond lengths at 1.305(3) and 1.322(3) Å in **1a** are typical and compare with average values of 1.317(2) and 1.311(14) Å,[14] 1.322(3) Å,[15] and 1.320(2) Å[16] for related seven-membered azolium salts and 1.311(3), 1.310(5), and 1.312(5) Å in reported six-membered azolium salts.[16,17] The N1−C1−N2 angle at 123.5(2)° is more akin to the values of 125.9(2)°, 125.8(3)°, and 123.7(4)° seen for the six-membered derivatives[16,17] as opposed to the more obtuse values ranging from 127.35(15)° to 135.9(10)° observed in the seven-membered examples.[14−16] The nitrogen atoms are trigonal planar, and the benzyl methylene carbons, both nitrogens, and the C1 atom are all coplanar. The phenyl groups reside either side of this five-atom plane and are thus *trans* orientated. There are close similarities in the geometric data for **1a**·HPF_6 and **1b**·HPF_6, with the latter having average $N-C_{NHC}$ bond lengths of 1.311(6) Å and an $N-C_{NHC}-N$ bond angle averaging 123.0(4)°. The most significant difference is in the arrangement of the phenyl groups, which are mutually *cis* in **1b**·HPF_6, unlike the *trans* configuration in **1a**·HPF_6.

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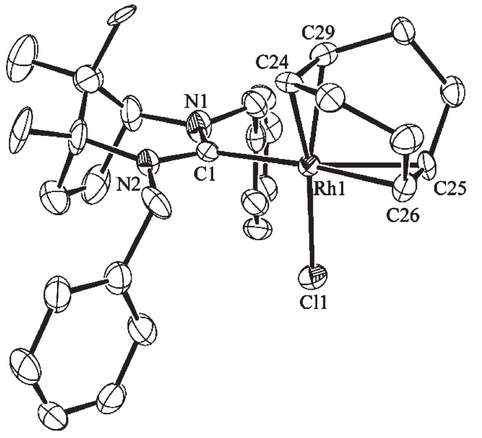

Figure 3. Ortep view of the molecular structure of one of the two units in the structure of **3a**. Thermal ellipsoids are drawn at 50% probability; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **3a**: Rh1−C1 2.063(8), Rh1−C24 2.125(7), Rh1−C25 2.204(7), Rh1−C26 2.206(8), Rh1−C29 2.113(7) Rh1−Cl1 2.384(2), C1−Rh1−Cl1 90.4(2), C1−Rh1−C26 162.2(3), Cl1−Rh1−C26 93.9(2), C1−Rh1−C24 88.2(3), N1−C1−N2 116.3(7).

Although several six- and seven-membered NHCs have been shown to be sufficiently stable to allow their full characterization in solution and in the solid state by single-crystal X-ray techniques, efforts to acquire pure products from the deprotonation of **1a**·HPF_6 and **1b**·HPF_6 were unsuccessful. The addition of base (KO^{t}Bu or KHMDS) to solutions of the salts in THF led to immediate color changes from colorless to yellow for **1a**·HPF_6 and from yellow to orange-red for **1b**·HPF_6, suggesting that the deprotonation had occurred, but ^{1}H NMR analysis of the products revealed a complex mixture of species. The use of alternative bases such as KH or solvents such as toluene or diethyl ether did not give improved results.

Synthesis of [Ag(1a)$_2$]OTf, 2a. Efforts to obtain Ag(I) complexes by the usual route from Ag_2O and the azolium salt in DCM,[18] 1,2-dichloroethane, or MeCN at RT or reflux with or without added NaBr and with various ratios of **1a**·HPF_6/**1b**·HPF_6 to Ag invariably failed. There was no evidence of complex formation, and on every occasion the starting azolium salt was recovered intact. However, silver complexes could be obtained by the addition of the "free carbene" mixtures (prepared by deprotonation of **1a**·HPF_6/**1b**·HPF_6 by KHMDS) to Ag(OTf) in THF in a 2:1 ratio for **1a**·HPF_6 and 1:1 for **1b**·HPF_6. When a solution of **1a** was added to a solution containing 0.5 molar equiv of Ag(OTf), an immediate darkening was observed with very little precipitation of Ag(0). After workup the silver(I) complex [Ag(**1a**)$_2$]OTf (**2a**) was obtained as a light yellow solid. There are few distinguishing features in the ^{1}H NMR spectrum of **2a**, which generally shows upfield shifts compared to the spectrum of **1a**·HPF_6. $^1J_{C-Ag}$ coupling to the NHC carbon is evident in the $^{13}C\{^1H\}$ NMR spectrum of **2a**, where two doublets are observed at 202.1 ppm with a $^1J_{C-Ag(109)}$ of 201 Hz and a $^1J_{C-Ag(107)}$ of 175 Hz. The chemical shift is upfield of those in related complexes containing seven-membered NHCs but close to the values reported for six-membered derivatives.[7b] The values of the one-bond C−Ag(107/109) coupling constants are consistent with those reported for related $[Ag(NHC)_2]^+$ complexes.[7b] Efforts to acquire pure compounds from the reaction of **1b**·HPF_6 with Ag(OTf) were frustrated by the presence of two or more species in solution. This is not surprising, as NHCs with pyridyl arms can lead to a wide variety of solution species including mono-, di-, and oligomeric compounds.[18,19] Indeed, this was a common feature with **1b**, and it would appear that the "free carbene" mixture resulting from the addition of base to **1b**·HPF_6 is not as amenable for the preparation of metal complexes as the mixture derived from **1a**.

Synthesis and Characterization of Rh(1,5-COD)(1a)Cl, 3a, Rh(CO)$_2$(1a)Cl, 4a, and Ir(1,5-COD)(1a)Cl, 5a. Although we were unable to isolate and characterize the free carbene **1a**, the mixtures generated upon addition of base to **1a**·HPF_6 could be employed for the synthesis of Rh(1,5-COD)(**1a**)Cl and the Ir analogue. These compounds were of interest to us because they enabled direct comparison with a series of monocyclic expanded-ring NHCs recently reported within our group. Despite the mixtures resulting from the deprotonation of **1a**·HPF_6 in THF, the rhodium complex Rh(1,5-COD)(**1a**)Cl, **3a**, was obtained in 67% yield through addition of a THF solution of **1a**·HPF_6 and KHMDS to the dimeric precursor [Rh(1,5-COD)Cl]$_2$; this might suggest that the complexity of the "free carbene" mixture is the result of Wanzlik equilibria allowing trapping of the desired carbene by the metal. However, using a similar synthetic approach, the iridium complex was obtained with a yield of only 35%. Rh(1,5-COD)(**1a**)Cl was crystallized from diethyl ether to give orange crystals of suitable quality for single-crystal X-ray analysis (Figure 3). The structure of the complex closely resembles that of related compounds bearing seven-membered NHCs[7c] with the N−C_{NHC}−N plane being orientated almost orthogonal to the square plane of the metal but virtually coplanar with one of the C=C double bonds of the diene, namely, the C25/C26/Rh link. The phenyl groups are mutually *cis* (unlike in the structure of **1a**·HPF_6), presumably to minimize unfavorable contacts with the 1,5-COD ligand, and lie on the side of the C_{benzyl}−N−C−N−C_{benzyl} plane that contains the dimethylene bridge of the bicyclic framework rather than the dimethylmethyl bridge. In such an orientation, the phenyl groups can impact on only one of the potential axial sites on the rhodium, although the phenyl rings are bent away from the metal in the crystal. The N−C_{NHC}−N angle averages 116.5(7)° (there are two independent molecules in the asymmetric unit), which is similar to reported values for other six- and seven-membered NHCs[7c,g,20,21] but still appreciably larger than for five-membered analogues. The C_{NHC}−N−C_{benzyl} angle shows an average value of 119.7°, again consistent with observations on other expanded-ring analogues.[7c,20] The Rh−C_{NHC} bond length is within the typical range at 2.060 Å (av), and there is nothing unusual about the structural features of the COD ligand; it is noteworthy that the average Rh−C_{COD} bond length to the alkene carbons coplanar with the

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N$-$C$_{NHC}$$-$N unit and *trans* to the NHC is appreciably longer at 2.205(8) Å than that for the other coordinated alkene (2.119(7) Å) of the cyclooctadiene, which is *trans* to chloride.

The ^{1}H NMR spectrum of Rh(1,5-COD)(**1a**)Cl is complicated by the presence of two isomers in an approximately 75:25 ratio; this is clearly evident from the doubling of peaks in the ^{1}H NMR spectrum, most notably the methyl resonances, the low-field *ortho*-phenyl signals, and the doublet for the bridgehead methine group at ~2.75 ppm. The resonances for the CH$_2$ hydrogens of the benzyl groups are broad at room temperature but sharpen appreciably at higher temperature (80 °C), enabling full characterization. The CH$_2$ groups are diastereotopic, as seen in symmetrical systems.[22] It is notable that no interconversion of isomers is observed upon heating the sample to 100 °C in d_8-toluene. There are a number of possible sources of isomerization in these systems, one of which may be restricted rotation about the N$-$C bond of the benzyl substituents in a similar vein to that observed for aryl-substituted NHCs.[7c] However it is likely that the isomerization observed here is caused by restricted rotation about the Rh$-$C$_{NHC}$ bond, as a result of which the carbene ligand can assume two extreme positions: one, which is observed in the solid state, where the C8 carbon and its methyl substituents lie *syn* to the *cis*-alkene function of the 1,5-COD ligand and a second where the C8 carbon and its methyls are *syn* with respect to the *cis* chloride. The presence of the two isomers is also evident in the ^{13}C{^{1}H} NMR spectrum, where all resonances are twinned in a roughly 75:25 ratio. The carbene carbon is observed at $\delta_C = 210.3$ ppm ($^1J_{C-Rh} = 46.2$ Hz) for the major isomer and 208.2 ppm ($^1J_{C-Rh} = 47.3$ Hz) for the minor isomer. These chemical shifts are similar to that for Rh(1,5-COD)(5-Me)I[23] but are at higher field by ~15 ppm compared to related expanded-ring NHC complexes,[7c,20] suggesting a closer electronic analogy with the five-membered species. The chemical shift of the carbene carbon in the ^{13}C{^{1}H} NMR spectra of NHC complexes has been correlated with the relative donor strength of the NHC, with the strongest donors showing the greatest downfield shifts.[24] Within the series of ligands examined by Huynh (which were all five-membered NHCs), based on ^{13}C{^{1}H} NMR shifts, those containing *N*-benzyl substituents were determined to be better donors than related ligands bearing *N*-mesityl groups, as, for any given like-pair, the position of the carbene resonance in the dibenzyl-NHC complex is downfield compared to that in the dimesityl-NHC complex.[24a] Thus, it would appear that the differences observed for the carbene chemical shift in **3a** compared to the literature examples are dominated by the effects of the central bicyclic skeleton rather than the exocyclic N-substituents.

In order to further assess the electronic properties of **1a**, we prepared the carbonyl complex Rh(CO)$_2$(**1a**)Cl, **4a**, in 84% yield from treatment of Rh(1,5-COD)(**1a**)Cl with CO. The infrared spectrum of Rh(CO)$_2$(**1a**)Cl in dichloromethane solution shows two strong peaks at 2078 and 1997 cm^{-1}, respectively. It has been well documented that these carbonyl stretches give an indication of relative electron density at the metal and hence the net donation from a given ligand. Most comparative studies using complexes of the type Rh(CO)$_2$(**L**)Cl tend to use the average value of the ν(CO) stretches rather than the absolute values. Thus, the average value of ν(CO) observed for **4a** is 2037.5 cm^{-1}, which compares directly with Rh(5-Mes)(CO)$_2$Cl (2037.5 cm^{-1}) but is appreciably higher than that observed for Rh(6-Mes)(CO)$_2$Cl and Rh(7-Mes)(CO)$_2$Cl, where average stretches of 2029 and 2028 cm^{-1} are seen.[7c] It would appear therefore that, even though the geometric features seen in the solid-state structure in Figure 3 are commensurate with other expanded-ring NHC complexes, the solution data support the NMR findings and suggest an electronic behavior more akin to five-membered NHCs. However, there is a caveat as the carbonyl stretches are known to be sensitive to the nature of the R substituents at the nitrogens,[22] and it may be that the differences noted here are the result of influences of the R groups rather than the bicyclic NHC skeleton.

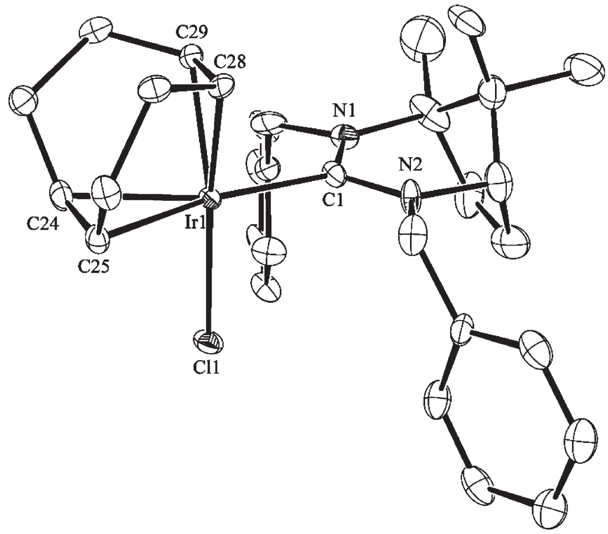

Figure 4. Ortep view of the molecular structure of one of the two units in the structure of **5a**. Thermal ellipsoids are drawn at 50% probability; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **5a**: Ir1$-$C1 2.075(9), Ir1$-$C24 2.184(10), Ir1$-$C25 2.173(8), Ir1$-$C28 2.098(9), Ir1$-$C29 2.113(9) Ir1$-$Cl1 2.367(2), C1$-$Ir1$-$Cl1 91.7(3), C1$-$Ir1$-$C28 92.3(4), Cl1$-$Ir1$-$C29 88.1(4), C1$-$Ir1$-$C25 161.2(4), N1$-$C1$-$N2 116.0(9).

The ^{1}H NMR spectrum of **4a** consists of a mixture of isomers in a similar ratio (75:25) to that observed for **3a**, suggesting the same likely source of isomerism. Unlike the COD complex, the benzyl CH$_2$ hydrogens are all clearly visible at RT for **4a** and share the same diastereotopic nature as noted in the Rh(1,5-COD)(**1a**)Cl species. Heating a solution of the complex to 100 °C in d_8-toluene did not interconvert the isomers. The ^{13}C{^{1}H} NMR spectrum has two sets of resonances for each isomer with the carbene carbon being observed at 199.2 ($^1J_{C-Rh} = 39.2$ Hz) ppm for the major isomer and 196.8 ($^1J_{C-Rh} = 40.4$ Hz) ppm for the minor. These chemical shifts are similar to that of 195.2 ppm reported for Rh(CO)$_2$(5-Me)I[25] but are at higher field than the literature values for Rh(5/6/7-Mes)(CO)$_2$Cl.[7c] The values of $^1J_{C-Rh}$ lie toward the low end of the known range for

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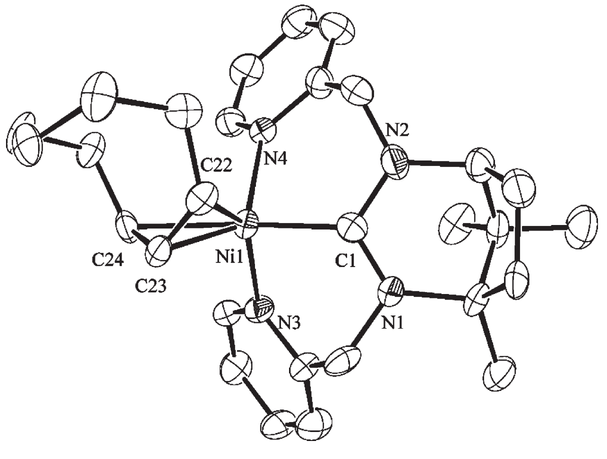

Figure 5. Ortep view of the molecular structure of one of the two units in the structure of the cation of **6b**. Thermal ellipsoids are drawn at 30% probability; hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (deg) for **6b**: Ni1−C1 1.922(13), Ni1−C22 2.083(10), Ni1−C23 1.939(10), Ni1−C24 2.102(11), Ni1−N3 2.045(9), Ni1−N4 2.127(10), C1−Ni1−N3 91.4(4), C1−Ni1−N4 91.9(5), N3−Ni1−N4 102.8(4), N1−C1−N2 115.7(11).

complexes of this type. The two distinct carbonyl resonances are observed at 186.1 ($^1J_{C-Rh}$ = 54.3 Hz) and 183.6 ($^1J_{C-Rh}$ = 77.3 Hz) ppm for the major isomer and at 185.5 ($^1J_{C-Rh}$ = 55.0 Hz) and 183.7 ($^1J_{C-Rh}$ = 77.1 Hz) ppm for the minor isomer. The chemical shifts and coupling constants conform to those values seen with other expanded-ring NHCs.[7c,14,20]

The Ir(1,5-COD)(**1a**)Cl complex was prepared in an analogous manner to that for the rhodium derivative but required chromatography in order to obtain a pure sample, hence the lower isolated yield. The spectroscopic analysis mimics that of Rh(1,5-COD)(**1a**)Cl except that the isomer ratio is 1:1 and there is no one-bond coupling to the spin-inactive iridium center in the $^{13}C\{^1H\}$ NMR spectrum. The C_{NHC} carbene occurs as a singlet at 202.4 ppm in the $^{13}C\{^1H\}$ NMR spectrum, and it would appear that this resonance is coincident for both isomers, which is not the case for the remainder of the $^{13}C\{^1H\}$ NMR spectrum, where the expected twinning of peaks is seen. Akin to the Rh(I) system, no interconversion of isomers is observed upon heating an NMR sample in d_8-toluene to 100 °C, although the clarity of the diastereotopic benzylic CH_2 resonances is improved at higher temperatures.

The molecular structure of **5a** is shown in Figure 4. The structure is largely similar to that of the rhodium complex **3a** and has geometric features closely analogous to those of related complexes with six-[26] and seven-membered NHC ligands.[27] The Ir−C1 bond length of 2.075(9)/ 2.071(8) Å and the N1−C1−N2/N3−C32−N4 bond angle of 116.0(9)°/ 117.4(8)° compare with values of 2.058(5), 2.079(4), and 2.072(3) Å and 115.1(6)°, 117.9(4)°, and 120.4(2)° in the literature.[26,27]

Complexes of 1b with Nickel. Reaction of the azolium salt **1b**·HPF_6 with $Ni(1,5\text{-}COD)_2$ in THF gave, after several days at room temperature, the complex [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6, **6b**, as a crystalline red solid in 92% yield (Scheme 1). The mechanism of formation of [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6 probably involves the oxidative addition of the azolium C−H bond to the Ni(0) center, possibly after initial coordination of one of the pyridyl donors, followed by hydride migration to one alkenic carbon of the coordinated COD to generate the allylic η^3-C_8H_{13} ligand. This would require a formal 1,5- to 1,3-isomerization of the 1,5-cyclooctadiene, as noted previously by Cloke.[28] The reaction represents a unique example of the oxidative addition of a saturated or large ring NHC to a metal center, confirming the unusual properties of these bicyclic structures. Oxidative addition is more typical of the unsaturated five-membered imidazolium salts.[29] The C2-H proton of azolium salts of saturated five-, six-, seven-membered NHCs is generally not acidic enough to allow facile oxidative addition. The complex **6b** was only sparingly soluble in THF, and while the majority was isolated by filtration of the reaction mixture, cooling of the mother liquor at 4 °C overnight gave red crystals suitable for structure determination by single-crystal X-ray diffraction (Figure 5). The structure shows the carbene ligand bound in a pincer fashion through the NHC carbon and the two pyridyl nitrogens at a formally five-coordinate Ni(II) center, which has a distorted square-pyramidal geometry with N3, C1, C22, and C24 defining the square plane and N4 occupying the axial position. The distortion is evident in the bond angles about the metal, where the C1−Ni−N3/4 angles are close to 90°, but the N3−Ni−N4 angle is expanded to 102.8(4)°. The N1−C1−N2 angle averages 117.8(12)° for the two independent molecules in the asymmetric unit, and the N1−C1−N2 plane lies more or less orthogonal to the C22−Ni−C24 plane. The Ni−C_{NHC} bond length averages 1.936(13) Å, which compares to values of 1.905(4),[28] 1.867(6),[11c] 1.908(3),[11b] and a range from 1.851(7) to 1.912(4) Å[30] for related Ni(II) systems with five-membered NHCs.[30,31] A further pertinent example of a Ni(II) complex containing a NHC donor (five-membered) and an η^3-allyl donor has a Ni−C bond length of 1.9025(16) Å.[32] The examples from Wang,[11c] Danopoulos,[11b] and Chen[30] contain pyridine or pyridyl arms on the NHC, which act as secondary donors with Ni−N bond lengths averaging 1.940(5) and 1.928(2) Å and a range from 1.900 to 1.944 Å (for equatorial N-donors in the five-coordinate systems, the axial Ni−N_{pyr} bonds were considerably longer, e.g., 2.336(4) Å), respectively. The average value of Ni−N in [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6 is 2.110(10) Å for the axial donors and 2.055(9) Å for the nitrogens in the basal plane, both of which are longer than in the literature examples, although direct comparison is perhaps inappropriate as the different complexes have distinct geometries. It has been noted by Chen that five-coordinate complexes of Ni(II) are

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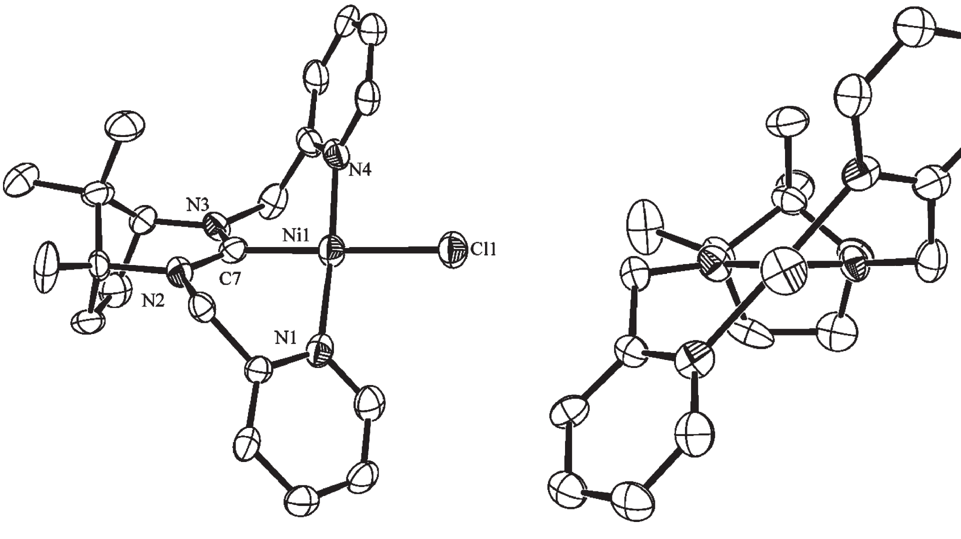

Figure 6. Two Ortep views of the molecular structure of the cation of **7b**. Thermal ellipsoids are drawn at 50% probability; hydrogens are omitted for clarity. The lower view is down the Cl−Ni−C_{NHC} axis to show the conformation of the ligand (see text). Selected bond lengths (Å) and angles (deg) for **7b**: Ni1−C7 1.874(7), Ni1−N1 1.911(7), Ni1−N4 1.899(6), Ni1−Cl1 2.219(2), C7−Ni1−N1 88.6(3), C7−Ni1−N4 87.7(3), C7−Ni1−Cl1 176.9(3), Cl1−Ni1−N1 93.2(2), Cl1−Ni1−N4 90.59(19), N2−C7−N3 118.9(7).

uncommon, and examples that include NHC donors are particularly scarce.[30]

The ^{1}H NMR spectrum of **6b** is complicated by the presence of two isomers in an approximately 2:1 ratio. Two sources of isomerization may be envisaged for the complex, the first being dictated by the choice of pyridyl group in the axial position of the square-pyramidal Ni(II); this happens to be the 4-(pyridin-2-ylmethyl) donor in the crystal structure, but there would appear to be no reason that the 2-(pyridine-2-ylmethyl) group could not occupy the axial site. The other source of isomerization is the η^3-C_8H_{13} ligand, which may orientate its $(CH_2)_5$ bridge *syn* or *anti* with respect to the axial pyridine. The central allylic hydrogen of the major isomer is identified in the ^{1}H NMR spectrum as a triplet at 5.35 ppm with a coupling constant of 8.6 Hz. The corresponding triplet for the minor isomer is seen at 5.50 ppm with a $^3J_{H-H}$ of 8.4 Hz. The two terminal hydrogens of the allyl function are coincident in the ^{1}H NMR spectrum and are observed as quartets at 3.91 (major) and 4.00 (minor) ppm; these data accord with those of Cloke.[28] Resonances assignable to the carbene ligand are also duplicated in the ^{1}H NMR spectrum including six singlets for the methyl groups in the aliphatic region and two sets of doublets for the *ortho*-hydrogens on the pyridine rings at low field; the shift of these *ortho*-protons to low field is indicative of coordination of the pyridyl donors.[11b,c,g,30] The carbene carbon is observed at $\delta_C = 210.0$ ppm in the $^{13}C\{^1H\}$ NMR spectrum, which is downfield from that reported in five-membered heterocyclic systems. Other obvious mirroring is seen in the duplication of peaks in the rest of the $^{13}C\{^1H\}$ NMR spectrum. During the NMR studies it was noticed that the CD_2Cl_2 solution of [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6 appeared to degrade over time until after several days a dark precipitate was evident and the color of the solution had lightened to an orange-yellow as opposed to the original orange. Analysis of the ^{1}H NMR spectrum at this time showed more or less complete loss of the characteristic signals for [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6 and the presence of a new set of resonances. The loss of the resonances for the η^3-C_8H_{13} group suggests that this had been replaced by a chloride presumably from the CD_2Cl_2 solvent (*vide infra*).

Exposure of the [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6 reaction mixture in THF to air gave, within minutes, a yellow suspension. Filtration of this mixture in air gave a new complex in near quantitative yield. The identity of this new complex was not easy to ascertain, but it was clear from preliminary ^{1}H NMR data that the η^3-C_8H_{13} had been lost from the metal complex. This observation implies a reactivity similar to that seen by Sigman for related Ni(5-NHC)(η^3-C_3H_5)Cl complexes, which were rapidly decomposed by O_2 to give hydroxo-bridged dimers of the type [Ni(NHC)(μ-OH)Cl]$_2$ and α,β-unsaturated carbonyl compounds.[32] In order to establish the sensitivity or otherwise of **6b** toward O_2 and/or H_2O, two separate experiments were performed. In the first, degassed H_2O was added to a suspension of [Ni(κ^3-N,C,N-**1b**)(η^3-C_8H_{13})]PF_6 in THF under a nitrogen atmosphere. Addition of H_2O alone did not lead to formation of the yellow suspension. Rather the red suspension slowly darkened through slow decomposition, taking several days for most of the red color to discharge. Even after several days, some **6b** appeared to remain. Subsequent exposure of this dark mixture to atmospheric air gave (after 24 h) a green gelatinous mixture presumably indicating the formation of hydrated Ni(II) hydroxides and complete decomposition of the complex. In a second experiment, a suspension of **6b** in THF was exposed to a stream of dry O_2, whereupon immediate loss of the red color was observed corresponding with the formation of the familiar yellow suspension; thus it is O_2 that leads to the conversion of **6b** to the yellow complex, as noted by Sigman in his related [Ni(5-NHC)(η^3-C_3H_5)Cl] complex.[32] It is interesting to note that the major species detected in the mass spectrum of **6b** is an adduct with O_2 at 533.2 amu.

Attempts to fully characterize the initial yellow complex from the reaction of **6b** with O_2 were frustrated by poorly resolved NMR spectra and equivocal infrared data. The ^{1}H NMR spectrum in dried, degassed CD_3CN was broadened, but it was evident that **1b** was still bound as the NCN pincer, as highlighted by the broad resonance at 9.23 ppm integrating to two hydrogens for the *ortho*-protons on the pyridine rings. Five separate singlets were observed for the methyl groups, suggesting the probable presence of two isomers, but the region between 4 and 6 ppm, where the methylene protons of the pyridyl arms resonate, was complicated. A minor signal at $\delta_H = -1.40$ ppm might suggest the presence of a Ni-OH group,[32,33] but the integration for this peak was much less than one hydrogen when compared to the other resonances, indicating that it is only a small component of the mixture. In addition, the infrared spectrum recorded as a KBr disk showed only a very weak peak at 3590 cm^{-1}; this absorption and a further one at 3651 cm^{-1} did grow relative to all the other peaks when the sample was rerun after leaving in air for several days. The mass spectrum of the compound did show a small peak at 409.2 amu, which corresponds to $[Ni(\kappa^3\text{-N,C,N-}\mathbf{1b})(OH)]^+$, but the major species observed in the spectrum was that for $[Ni(\kappa^3\text{-N,C,N-}\mathbf{1b})(CN)]^+$, where a CN^- ligand has been coordinated in the gas phase presumably from traces of HCN in the acetonitrile solvent. In an effort to establish the fate of the η^3-C_8H_{13} ligand, the solution that remained after isolation of the yellow nickel complex was concentrated and the oily residue examined by MS and NMR. The only organic compound detected in the ^1H NMR spectrum of the residue was 2-cycloocten-1-one,[34] confirming transfer of one oxygen of O_2 to the η^3-C_8H_{13} ligand akin to that observed by Sigman.[32] The yield of the 2-cycloocten-2-one was close to quantitative, emphasizing the specificity of the conversion.

Attempts to dissolve the putative complex $[Ni(\kappa^3\text{-N,C,N-}\mathbf{1b})(OH)]PF_6$ in $CHCl_3$ gave a mixture of a yellow crystalline complex and some sticky green residue. The yellow crystals could be redissolved by the addition of a small quantity of CH_2Cl_2 and filtered from the unwanted green material. (Unfortunately it was apparent that the workup procedures led to formation of the previously identified chloro complex **7b**.) Recrystallization from $CHCl_3$ gave X-ray quality crystals enabling the determination of the molecular structure in the solid state. Two views of the cation are shown in Figure 6. The metal has a square-planar geometry with the chloride *trans* to the C_{NHC} and two mutually *trans* pyridine nitrogens. Angular distortions about the metal are minimal, with N−Ni−C angles averaging 88.3(3)° and the N−Ni−Cl angles being 91.9(2)° (av). The Ni−C_{NHC} bond length of 1.874(7) Å and the average Ni−N bond length of 1.905(7) Å are toward the lower end of the reported range for related complexes.[11,30] The N−C−N angle of 118.9(7)° is similar to that seen in the rhodium and pentacoordinate nickel complexes above. The NCN plane of the carbene donor makes an angle of ~48° to the coordination plane of the metal, forcing the ligand backbone to adopt a conformation where the benzyl methylene carbons are mutually *trans* with respect to the N−Ni−N plane. The second view in Figure 6 emphasizes the dissymmetry in the backbone of the terdentate ligand, which assumes the λ conformation (this is similar to the conformational descriptors for bidentate donors, the classic example being 1,2-diaminoethane (en), except here the vector is defined from one terminal N-donor to the other of a terdentate ligand and the fulcrum is not at the midpoint of a bond, as is the case in the **en** systems, but at an atom, namely, the NHC carbon donor). Such a conformation has been observed in a related tetradentate macrocyclic nickel complex containing two NHC and two pyridine donors.[35]

The ^1H NMR spectrum of the complex shows the presence of two isomers in an approximately 1:1 ratio, as illustrated by the six singlets for the methyl groups, six doublets (two of which integrate to two protons, indicating coincidence for these hydrogens) for the benzyl methylene protons, and two doublets for the bridgehead methine proton. The source of the isomerization in this case is most likely the chelate backbone, which can assume two conformations, namely, λ (seen in the solid state) and δ. However, there is no interconversion of the two forms at temperatures up to 100 °C. Attempts to react $\mathbf{1a}\cdot HPF_6$ with $Ni(1,5\text{-COD})_2$ in a similar manner to that for $\mathbf{1b}\cdot HPF_6$ led to the deposition of metallic nickel and no isolable complex, probably due to the instability of resulting Ni−H formed after initial oxidative addition.

Conclusions

In conclusion, two bicyclic NHCs derived from camphor and containing fused six- and seven-membered diaza-heterocyclic rings have been prepared and coordinated to a number of transition metals. The *N,N′*-dibenzyl derivative, **1a**, has been coordinated to Ag(I), Rh(I), and Ir(I), and the resultant complexes show features that define the NHC ligand as a hybrid displaying coordination properties somewhere between those expected of an expanded-ring carbene and those of a more familiar five-membered NHC. The *N,N′*-dipyridyl-substituted azolium salt $\mathbf{1b}\cdot HPF_6$ does not give solutions of "free carbene' that are suitable for complexation because of inherent reactivity of the resultant NHC species **1b**. $\mathbf{1b}\cdot HPF_6$ does however react with the nickel(0) precursor $Ni(1,5\text{-COD})_2$ to give the complex $[Ni(\mathbf{1b})(\eta^3\text{-}C_8H_{13})]PF_6$, which contains an allylic ligand derived from 1,5-COD. This is an unusual example of the oxidative addition of an expanded ring 2-H-azolium salt. The complex is unstable to oxygen and when dissolved in $CHCl_3$ in air leads to the isolation of $[Ni(\mathbf{1b})Cl]PF_6$. Similar chemistry does not occur with $\mathbf{1a}\cdot HPF_6$, emphasizing the need for the secondary pyridine donors.

Experimental Section

Methods and Materials. All synthetic procedures and manipulations were performed under dry argon or nitrogen using standard Schlenk line techniques. All solvents were freshly distilled from sodium (toluene), sodium/benzophenone (THF), or calcium hydride (acetonitrile, methanol, and dichloromethane) under nitrogen before use. All other chemicals were obtained commercially and used as received. ^1H and ^{13}C NMR spectra were obtained using a Bruker 500 MHz spectrometer, operating at 500.0 and 125.8 MHz, respectively, and referenced to tetramethylsilane ($\delta = 0$ ppm). Unless stated otherwise, infrared spectra were recorded as Nujol mulls on a Jasco FTIR spectrometer. Mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Elemental analyses were performed by Medac Ltd., UK.[36]

Syntheses. (1*R*,3*S*)-*N,N′*-Dibenzyl-1,3-diamino-1,2,2-trimethylcyclopentane. A solution of *R,S*-tmcp (2 g, 0.014 mol) and benzaldehyde (3 g, 2 molar equiv) in EtOH (50 mL) was heated close to boiling for 4 h. After cooling, the solvent was removed on the rotavap and the residue triturated with diethyl ether (100 mL).

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(36) *Medac LTD*; Brunel Science Cntr: Englefield Green, Egham, Surrey, TW20 0JZ.

An unwanted white solid was removed by filtration and the diethyl ether removed at the pump to give the diimine as a clear oil. The oil was dissolved in EtOH (80 mL) and solid $NaBH_4$ (1.06 g, 0.028 mol) added portionwise over 2 h. The resulting mixture was stirred overnight; then concentrated HCl (3 mL) was added carefully with stirring to precipitate the white hydrochloride salt of the diamine. After storing at 4 °C overnight the nonhygroscopic hydrochloride salt was isolated by filtration, washed with cold EtOH, then diethyl ether, and air-dried. Yield = 4.15 g (75%). The free amine could be obtained from the hydrochloride salt as a clear oil by extraction from basic aqueous solution with dichloromethane. All spectroscopic and analytical data were as detailed previously.[10]

(1*R*,5*S*)-2,4-Dibenzyl-1,8,8-trimethyl-4-aza-2-azoniabicyclo[3.2.1]oct-2-ene Hexafluorophosphate, 1a·HPF_6. A mixture of (1*R*,3*S*)-*N*,*N*′-dibenzyl-1,3-diamino-1,2,2-trimethylcyclopentane (1.3 g, 4.0 mmol) and NH_4PF_6 (0.72 g, 4.4 mmol) in triethyl orthoformate (15 mL) was heated at 120 °C for 4 h. After cooling, the white solid was filtered off and washed sparingly with triethyl orthoformate, then diethyl ether, and air-dried. Yield = 1.3 g (68%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.16 (1H, s), 7.35 (10H, m), 4.65 (4H, m), 3.16 (1H, d, *J* 4.9 Hz), 2.42 (1H, m), 2.21 (1H, m), 1.99 (1H, m), 1.78 (1H, m), 1.25 (3H, s), 0.99 (3H, s), 0.85 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 62.9 MHz): δ 153.7 (CH), 134.9 (C), 132.7 (C), 129.5 (CH), 129.2 (CH), 128.7 (CH), 128.0 (CH), 71.5 (C), 65.7 (CH), 57.6 (CH_2), 54.3 (CH_2), 40.7 (C), 39.8 (CH_2), 31.3 (CH_2), 21.4 (CH_3), 16.9 (CH_3), 14.8 (CH_3) ppm.

(1*R*,3*S*)-*N*,*N*′-Di(pyridin-2-ylmethyl)-1,3-diamino-1,2,2-trimethylcyclopentane. This was prepared in a similar manner to the dibenzyl derivative above. It was isolated as the nonhygroscopic hydrochloride salt as above in 90% yield. The following NMR data are for the free base, which is obtained as a slightly yellow oil after treatment of the HCl salt with base. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.46 (2H, m), 7.55 (2H, m), 7.30 (2H, m), 7.06 (2H, m), 3.84 (4H, m), 2.79 (1H, t, *J* 7.5 Hz), 1.97 (1H, m), 1.90 (2H, br), 1.80 (1H, m), 1.57 (1H, m), 1.40 (1H, m), 1.04 (3H, s), 0.97 (3H, s), 0.93 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 161.4 (C), 160.7 (C), 149.1 (CH), 148.5 (CH), 136.6 (CH), 136.4 (CH), 122.2 (CH), 122.1 (CH), 121.7 (CH), 121.5 (CH), 66.7 (CH), 64.7 (C), 54.2 (CH_2), 48.9 (CH_2), 47.3 (C), 29.7 (CH_2), 26.8 (CH_2), 23.5 (CH_3), 21.1 (CH_3), 17.0 (CH_3) ppm.

(1*R*,5*S*)-2,4-Di(pyridin-2-ylmethyl)-1,8,8-trimethyl-4-aza-2-azoniabicyclo[3.2.1]oct-2-ene Hexafluorophosphate, 1b·HPF_6. This was prepared in a similar manner to that discussed for **1a**·HPF_6 above except that the azolium salt did not precipitate as readily from the reaction mixture, which was taken to dryness and the residue triturated with diethyl ether to give a pale yellow solid. Traces of inorganic salts could be removed by dissolution in a small volume of DCM and filtration through a plug of Celite. Yield = 81%. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.52 (1H, d, *J* 4.7 Hz), 8.50 (1H, d, *J* 4.7 Hz), 8.14 (1H, s), 7.72 (1H, t, *J* 7.7 Hz), 7.67 (1H, t, *J* 7.7 Hz), 7.51 (1H, d, *J* 7.7 Hz), 7.34 (1H, d, *J* 7.7 Hz), 7.25 (2H, m), 4.72 (1H, d, *J* 16.5 Hz), 4.69 (1H, d, *J* 15.5 Hz), 4.63 (1H, d, *J* 16.5 Hz), 4.62 (1H, d, *J* 15.5 Hz), 3.41 (1H, d, *J* 4.9 Hz), 2.20 (1H, m), 2.03 (1H, m), 1.94 (1H, m), 1.60 (1H, m), 1.15 (3H, s), 0.95 (3H, s), 0.71 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz): δ 155.2 (CH), 154.3 (C), 152.9 (C), 149.7 (CH), 149.6 (CH), 137.8 (CH), 137.6 (CH), 124.3 (CH), 124.0 (CH), 123.6 (CH), 122.6 (CH), 71.3 (C), 67.0 (CH), 58.6 (CH_2), 54.7 (CH_2), 40.9 (C), 39.7 (CH_2), 31.5 (CH_2), 21.5 (CH_3), 16.7 (CH_3), 14.6 (CH_3) ppm.

$[Ag(1a)_2]OTf \cdot 2H_2O$, 2a. A solution of "**1a**" was prepared *in situ* in THF by the addition of KHMDS (0.256 g, 1.29 mmol) to **1a**·HPF_6 (0.560 g, 1.17 mmol) in THF (15 mL). After stirring at RT for 1 h, the filtered solution was added to a stirred solution of Ag(OTf) (0.15 g, 5.8×10^{-4} mol) in THF (5 mL), and the solution was stirred overnight. After filtering through Celite, the volatiles were removed *in vacuo* to give a light tan solid, which was triturated thoroughly with dry Et_2O and dried at the pump. Yield = 480 mg (90%). ^1H NMR (CD_2Cl_2, 500 MHz): δ 7.16 (10H, m), 4.65 (1H, d, *J* 16.5 Hz), 4.58 (1H, d, *J* 16.5 Hz), 4.48 (1H, d, *J* 15.0 Hz), 4.33 (1H, d, *J* 15.0 Hz), 2.85 (1H, d, *J* 3.5 Hz), 2.05 (1H, m), 1.77 (2H, m), 1.60 (1H, m), 0.97 (3H, s), 0.76 (3H, s), 0.71 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR (CD_2Cl_2, 125.8 MHz): δ 202.1 (C, d, *J* 201 Hz), 202.1 (C, d, *J* 175 Hz), 137.7 (C, s), 134.7 (C, s), 127.9 (CH), 127.8 (CH), 127.6(CH), 127.5 (CH), 127.0 (CH), 125.5 (CH), 69.0 (C), 65.5 (CH), 62.0 (CH_2), 57.4 (CH_2), 39.6 (C), 38.5 (CH_2), 30.4 (CH_2), 20.6 (CH_3), 17.5 (CH_3), 14.3 (CH_3) ppm. MS: 773.4 ([M^+], 100%). Anal. Calcd for $C_{47}H_{60}N_4O_5F_3SAg$: C, 58.92; H, 6.33; N, 5.85. Found: C, 59.3; H, 6.4; N, 5.6.

Rh(1,5-COD)(1a)Cl, 3a. A solution of **1a** was prepared as detailed in the synthesis of **2a** using 200 mg (4.17×10^{-4} mol) of **1a**·HPF_6 and 102 mg (2.07×10^{-4} mol) of $[Rh(1,5\text{-}COD)Cl]_2$. The reaction mixture was filtered and pumped to dryness, and the residue was extracted into Et_2O (30 mL). Orange crystals of the desired compound formed from the ethereal extracts upon standing at RT. Yield = 97 mg (40%). ^1H NMR ($CDCl_3$, 500 MHz, major isomer): δ 7.53 (2H, d, *J* 7.5 Hz), 7.46 (2H, d, *J* 7.5 Hz), 7.35−7.15 (6H, m), 6.39 (1H, d br, *J* 14.0 Hz), 6.30 (1H, br), 5.80 (1H, br), 5.29 (1H, d br, *J* 13.5 Hz), 4.74 (2H, s br), 3.59 (1H, m br), 3.42 (1H, m br), 2.74 (1H, d, *J* 5.0 Hz), 2.31 (1H, m), 2.2−1.4 (11H, m), 1.01 (3H, s), 0.99 (3H, s), 0.75 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz, major isomer): δ 210.3 (C, d, *J* 46.2 Hz), 140.6 (C, s), 137.2 (C, s), 130.0 (CH, s), 129.0−126.0 (CH's), 96.0 (CH, d, *J* 6.3 Hz), 95.8 (CH, d, *J* 6.3 Hz), 70.0 (C, s), 68.6 (CH, d, *J* 15.0 Hz), 68.5 (CH, d, *J* 15.0 Hz), 65.0 (CH, s), 60.6 (CH_2, s), 58.6 (CH_2, s), 41.7 (C, s), 38.4 (CH_2, s), 32.9 (CH_2, s), 31.9 (CH_2, s), 30.1 (CH_2, s), 28.9 (CH_2, s), 28.3 (CH_2, s), 22.4 (CH_3, s), 18.8 (CH_3, s), 16.9 (CH_3, s) ppm. ^1H NMR ($CDCl_3$, 500 MHz, minor isomer): δ 7.65 (2H, d, *J* 7.5 Hz), 7.55 (2H, d, *J* 7.5 Hz), 7.35−7.15 (6H, m), 6.93 (1H, d br, *J* 16.1 Hz), 5.48 (1H, br), 4.74 (2H, br), 3.28 (1H, m br), 3.22 (1H, m br), 2.76 (1H, d, *J* 5.0 Hz), 2.33 (1H, m), 2.2−1.4 (11H, m), 0.86 (3H, s), 0.83 (3H, s), 0.00 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz, minor isomer): δ 208.2 (C, d, *J* 47.3 Hz), 140.6 (C, s), 136.8 (C, s), 129.0−126.0 (CH's), 96.8 (CH, d, *J* 6.3 Hz), 96.6 (CH, d, *J* 6.3 Hz), 70.4 (CH, d, *J* 13.8 Hz), 69.2 (CH, d, *J* 15.0 Hz), 64.3 (CH, s), 60.5 (CH_2, s), 59.9 (CH_2, s), 40.3 (C, s), 40.2 (CH_2, s), 31.3 (CH_2, s), 29.1 (CH_2, s), 28.4 (CH_2, s), 22.3 (CH_3, s), 18.7 (CH_3, s), 18.0 (CH_3, s) ppm. MS: 570.2 ([M^+] − Cl^- + CN^-, 100%; 543.2 [M^+] − Cl^-, 15%). Anal. Calcd for $C_{31}H_{40}N_2ClRh$: C, 64.29; H, 6.98; N, 4.84. Found: C, 64.1; H, 6.9; N, 4.6.

$Rh(CO)_2(1a)Cl$, 4a. Carbon monoxide was bubbled through a solution of **3a** in CH_2Cl_2 for 1 h. The resultant mixture was filtered and the volatiles were removed *in vacuo* to give **5a** as a yellow solid. Yield = 84%. ^1H NMR ($CDCl_3$, 500 MHz, major isomer): δ 7.5−7.1 (10H, m), 5.96 (2H, d, *J* 14.9 Hz), 4.89 (1H, d, *J* 16.8 Hz), 4.55 (1H, d, *J* 14.9 Hz), 2.92 (1H, d, *J* 4.5 Hz), 2.50 (1H, m), 2.22 (1H, m), 1.87 (1H, m), 1.71 (1H, m), 1.06 (3H, s), 0.99 (3H, s), 0.82 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz, major isomer): δ 199.2 (C, d, *J* 39.2 Hz), 186.1 (CO, d, 54.3 Hz), 183.6 (CO, d, *J* 77.3 Hz), 139.2 (C), 135.9 (C), 129.0−126.4 (CH's), 71.1 (C), 65.7 (CH), 60.7 (CH_2), 57.6 (CH_2), 41.3 (C), 38.9 (CH_2), 30.7 (CH_2), 22.2 (CH_3), 18.9 (CH_3), 16.6 (CH_3) ppm. ^1H NMR ($CDCl_3$, 500 MHz, minor isomer): δ 7.5−7.1 (10H, m), 6.14 (1H, d, *J* 16.3 Hz), 5.48 (1H, d, *J* 14.4 Hz), 5.17 (1H, d, *J* 14.4 Hz), 4.84 (1H, d, *J* 16.3 Hz), 2.97 (1H, d, *J* 4.5 Hz), 2.6−1.5 (4H, m obs), 1.18 (3H, s), 1.12 (3H, s), 0.80 (3H, s) ppm. $^{13}C\{^1H\}$ DEPT NMR ($CDCl_3$, 125.8 MHz, minor isomer): δ 196.8 (C, d, *J* 40.4 Hz), 185.5 (CO, d, *J* 55.0 Hz), 183.7 (CO, d, *J* 77.1 Hz), 138.7 (C), 135.7 (C), 129.0 − 126.4 (CH's), 70.7 (C), 65.8 (CH), 61.6 (CH_2), 59.4 (CH_2), 40.8 (C), 39.6 (CH_2), 31.3 (CH_2), 22.1 (CH_3), 17.5 (CH_3), 16.3 (CH_3) ppm. IR ν(CO) (CH_2Cl_2): 2078s, 1997s cm^{-1}.

$[Ir(1,5\text{-}COD)(1a)Cl]4H_2O$, 5a. This was prepared as for **3a**. The compound was purified by chromatography on silica using

Table 1. Details of X-ray Crystallographic Data Collection for the Compounds 1a·HPF$_6$, 1b·HPF$_6$, 3a, 5a, 6b, and 7b

	1a·HPF$_6$	**1b**·HPF$_6$	**3a**	**5a**	**6b**	**7b**
empirical formula	$C_{23}H_{29}F_6N_2P$	$C_{21}H_{27}F_6N_4P$	$C_{31}H_{40}ClN_2Rh$	$C_{31}H_{40}ClN_2Ir$	$C_{37}H_{54}F_6N_4NiO_2P$	$C_{21}H_{26}ClF_6N_4NiP$
cryst size/mm^3	0.30 × 0.30 × 0.20	0.30 × 0.25 × 0.25	0.30 × 0.30 × 0.20	0.30 × 0.20 × 0.08	0.30 × 0.30 × 0.04	0.20 × 0.08 × 0.05
fw	478.45	480.44	579.01	668.30	790.52	573.59
cryst syst	orthorhomibic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P2_12_12_1$	$P2_1$	$P2_12_12_1$	$P2_12_12_1$	$P2_1$	$P2_12_12_1$
a/Å	11.0984(2)	10.57300(10)	14.2752(3)	17.6218(3)	18.6743(10)	8.0670(4)
b/Å	14.5283(2)	11.8530(2)	17.6422(3)	14.3216(3)	11.3718(7)	14.0748(7)
c/Å	14.7057(3)	18.6130(3)	21.5550(4)	21.4272(4)	19.8153(8)	20.5513(10)
β/deg		100.7240(10)			114.746(3)	
U/Å^3	2371.16(7)	2291.87(6)	5428.54(18)	5407.63(18)	3821.6(3)	2333.4(2)
Z	4	4	8	8	4	4
D_c/Mg m^{-3}	1.340	1.392	1.417	1.642	1.374	1.633
F(000)	1000	1000	2416	2672	1668	1176
indep reflns	5429	9445	12 403	14 343	12 313	3328
restraints/params	0/293	125/621	0/636	0/635	66/819	0/310
goodness of fit on F^2	1.044	1.049	1.025	1.030	1.023	1.105
final R_1, wR_2 [$I > 2\sigma(I)$]	0.0481, 0.0993	0.0704, 0.1679	0.0610, 0.1341	0.0507, 0.1096	0.1083, 0.2315	0.0650, 0.1106
(all data)	0.0688, 0.1101	0.0894, 0.1818	0.0865, 0.1501	0.0770, 0.1240	0.1831, 0.2781	0.1007, 0.1231
largest diff peak, hole/e Å^{-3}	0.208, −0.203	0.589, −0.501	1.550, −0.636	1.283, −1.815	0.535, −0.646	0.327, −0.352
Flack param	0.01(11)	−0.15(15)	0.05(6)	0.030(15)	0.03(3)	−0.03(3)

$CHCl_3$ as eluent. Yield = 28%. The compound was recrystallized from diethyl ether to give orange crystals suitable for single-crystal X-ray analysis. ^{1}H NMR ($C_6D_5CD_3$, 300 MHz, 80 °C, two isomers): δ 7.73 (1H, d, J 7.5 Hz), 7.65 (1H, d, J 7.7 Hz), 7.62 (1H, d, J 7.7 Hz),7.54 (1H, d, J 7.5 Hz), 7.2−6.9 (6H, m), 6.63 (0.5H, d, J 15.8 Hz), 6.17 (0.5H, d, J 15.8 Hz), 5.73 (0.5H, d, J 14.7 Hz), 5.65 (0.5H, d, J 14.7 Hz), 5.54 (0.5H, d, J 16.1 Hz), 5.11 (0.5H, d, J 15.6 Hz), 4.68 (2H, m), 4.44 (0.5H, d, J 13.8 Hz), 3.31 (0.5H, t, J 6.8 Hz), 3.13 (0.5H, m), 2.94 (1H, m), 2.76 (0.5H, d, J 4.4 Hz), 2.69 (0.5H, d, J 5.1 Hz), 2.25 − 0.8 (14H, m), 1.05 (1.5H, s), 0.96 (1.5H, s), 0.82 (3H, s), 0.73 (1.5H, s), 0.60 (1.5H, s) ppm. ^{13}C{^{1}H} DEPT NMR ($CDCl_3$, 75.6 MHz, two isomers): δ 202.4 (C), 140.4 (C), 140.0 (C), 136.9 (CH), 136.7 (CH), 129.9 (CH), 129.1 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 128.2 (CH), 127.9 (CH), 127.8 (CH), 127.7 (CH), 127.5 (CH), 126.9 (CH), 126.7 (CH), 82.0 (CH), 81.6 (CH), 81.4 (CH), 81.2 (CH), 70.7 (C), 70.5 (C), 65.6 (CH), 64.9 (CH), 60.7 (CH_2), 59.7 (CH_2), 58.8 (CH_2), 58.4 (CH_2), 54.0 (CH_2), 52.7 (CH_2), 52.6 (CH_2), 41.4 (C), 40.1 (CH_2), 38.5 (CH_2), 33.6 (CH_2), 33.0 (CH_2), 32.6 (CH_2), 31.4 (CH_2), 31.0 (CH_2), 30.5 (CH_2), 29.7 (CH_2), 29.4 (CH_2), 28.9 (CH_2), 22.5 (CH_3), 18.6 (CH_3), 18.1 (CH_3), 18.0 (CH_3), 16.5 (CH_3) ppm. MS: 660.3 ([M$^+$] − Cl$^-$ + CN$^-$, 100%; 633.3 [M$^+$] − Cl$^-$, 5%). Anal. Calcd for $C_{31}H_{40}N_2ClIr$: C, 55.71; H, 6.03; N, 4.19. Found: C, 55.8; H, 6.0; N, 4.0.

[Ni(η^3-C_8H_{13})(1b)]PF$_6$, 6b. To a stirred solution of [Ni(1,5-COD)$_2$] (100 mg, 3.64 × 10^{-4} mol) in THF (10 mL) was added a solution of **1b**·HPF$_6$ (184 mg, 3.82 × 10^{-4} mol) in THF (8 mL) and the solution stirred for 4 days. The resultant orange-red suspension was filtered to give a microcrystalline orange-red solid and a pale orange solution. The precipitate was dried at the pump and the filtrate left at 4 °C for 48 h to yield red crystals suitable for analysis by single-crystal X-ray methods. Total yield = 210 mg (90%). ^{1}H NMR (CD_2Cl_2, 300 MHz, major isomer): δ 8.64 (1H, d, J 5.9 Hz), 8.54 (1H, d, J 5.9 Hz), 7.85 (1H, m), 7.77 (1H, m), 7.38 (4H, m), 5.35 (1H, t, J 8.6 Hz), 5.18 (1H, d, J 15.4 Hz), 5.00 (1H, d, J 15.2 Hz), 4.87 (1H, d, J 15.4 Hz), 4.60 (1H, d, J 15.2 Hz), 3.91 (2H, q, J 8.6 Hz), 3.12 (1H, d, J 4.6 Hz), 2.4 − 1.1 (14H, m), 1.39 (3H, s), 1.15 (3H, s), 0.98 (3H, s) ppm. ^{13}C{^{1}H} DEPT NMR (CD_2Cl_2, 75.6 MHz, major isomer): δ 210.0 (C), 157.1 (C), 156.0 (C), 152.7 (CH), 151.2 (CH), 138.6 (CH), 137.7 (CH), 124.1 (CH), 123.9 (CH), 123.7 (CH), 123.1 (CH), 108.5 (CH), 74.4 (C), 70.2 (CH), 69.6 (CH), 61.6 (CH_2), 55.7 (CH_2), 42.1 (C), 40.8 (CH_2), 39.5 (CH_2), 31.4 (CH_2), 31.3 (CH_2), 27.1 (CH_2), 26.9 (CH_2), 22.9 (CH_2), 21.9 (CH_3), 18.0 (CH_3), 16.1 (CH_3) ppm. ^{1}H NMR (CD_2Cl_2, 300 MHz, minor isomer): δ 8.84 (1H, d, J 5.3 Hz), 8.76 (1H, d, J 5.3 Hz), 7.9−7.2 (6H, m), 5.50 (1H, t, J 8.4 Hz), 5.10 (1H, d, J 15.4 Hz), 4.91 (1H, obs), 4.41 (1H, d, J 14.5 Hz), 4.00 (2H, q, J 8.4 Hz), 3.10 (1H, d, J 4.6 Hz), 2.4−1.1 (14H, m), 1.25 (3H, s), 0.80 (3H, s), −0.42 (3H, s) ppm. MS: 533.2 ([M$^+$] + O$_2$, 100%). Anal. Calcd for $C_{29}H_{39}N_4PF_6Ni$: C, 53.81; H, 6.07; N, 8.65. Found: C, 53.2; H, 5.9; N, 8.2.

[Ni(1b)Cl]PF$_6$, 7b. A suspension of **6b** (100 mg, 1.54 × 10^{-4} mol) in THF (8 mL) was exposed to air for 1 h, whereupon the suspension became bright yellow. The solid was isolated by filtration, washed sparingly with THF then thoroughly with Et_2O, and air-dried. The dry solid was treated with $CHCl_3$ (3 mL), whereupon a golden yellow solution and sticky green solid resulted. CH_2Cl_2 (3 mL) was added to dissolve some yellow crystals that had started to form, and the mixture was filtered through a fiberglass filter paper to remove the sticky green residue. The volatiles were then removed to give **7b** as a golden yellow solid. Yield = 50 mg (76%). Crystals suitable for single-crystal X-ray analysis were grown from CH_2Cl_2. ^{1}H NMR (CD_2Cl_2, 500 MHz, two isomers): δ 8.99 (0.5H, d, J 6.5 Hz), 8.97 (0.5H, d, J 6.5 Hz), 8.91 (1H, d, J 5.0 Hz), 7.82 (2H, m), 7.40 (4H, m), 6.07 (0.5H, d, 15.5 Hz), 5.91 (0.5H, d, J 15.0 Hz), 5.85 (0.5H, d, J 15.0 Hz), 5.66 (0.5H, d, 15.5 Hz), 4.82 (1H, d, J 15.0 Hz), 4.53 (0.5H, J 15.0 Hz), 4.49 (0.5H, d, J 15.0 Hz), 3.36 (0.5H, d, J 4.5 Hz), 3.34 (0.5H, d, J 4.5 Hz), 2.2−1.3 (4H, m), 1.33 (1.5H, s), 1.23 (1.5H, s), 0.96 (1.5H, s), 0.94 (1.5H, s), 0.31 (1.5H, s), 0.27 (1.5H, s) ppm. ^{13}C{^{1}H} DEPT NMR (CD_2Cl_2, 75.6 MHz, major isomer): δ 209.0 (C), 155.7 (CH), 154.0 (C), 140.5 (CH), 140.4 (CH), 125−122 (6 × CH), 73.3 (CH), 73.2 (C), 73.0 (CH), 72.9 (C), 60.5 (CH_2), 60.3 (CH_2), 42.1 (C), 42.0 (CH_2), 40.5 (CH_2), 32.4 (CH_2), 21.2 (CH_3), 16.7 (CH_3), 14.9 (CH_3), 14.5 (CH_3) ppm. MS: 418.2 ([M$^+$] − Cl$^-$ + CN$^-$, 100%). Anal. Calcd for $C_{21}H_{26}N_4ClPF_6Ni$: C, 43.98; H, 4.57; N, 9.76. Found: C, 44.1; H, 4.7; N, 9.7.

Reaction of 6b with O$_2$. A suspension of **6b** [prepared as above from 100 mg of Ni(1,5-COD)$_2$] in THF was exposed to an atmosphere of dry oxygen for 2 min, whereupon the red color of the suspension changed to yellow. The yellow solid was filtered off, washed sparingly with THF, and dried at the pump. The filtrate was taken to dryness and the oily residue extracted with Et_2O. After filtering the Et_2O was removed at the pump to give a clear oil, which was shown by ^{1}H NMR spectroscopy and GC-MS to be 2-cycloocten-1-one.

Crystallography. Data collection was carried out on a Bruker-Nonius Kappa CCD diffractometer using graphite-monochromoated Mo Kα radiation (λ(Mo Kα) = 0.71073 Å). The instrument was equipped with an Oxford Cryosystems cooling apparatus, and all data were collected at 150 K. Data collection and cell refinement were carried out using COLLECT[37] and HKL SCALEPACK.[38] Data reduction was applied using HKL DENZO and SCALEPACK.[38] The structures were solved using direct methods (Sir92)[39] and refined with SHELX-97.[40] Absorption corrections were performed using SORTAV.[41] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms were inserted in idealized positions with U_{iso} set at 1.2 or 1.5 times the U_{eq} of the parent atom. In the final cycles of refinement, a weighting scheme that gave a relatively flat analysis of variance was introduced, and refinement continued until convergence was reached. The geometry was restrained during refinement for the solvent molecules **6b** and one PF_6^- ion in **1b**$\cdot HPF_6$. The details of the data collection and structure solution are summarized in Table 1.

Supporting Information Available: Crystallographic information files (CIF) for compounds **1a**$\cdot HPF_6$, **1a**$\cdot HPF_6$, **3a**, **5a**, **6b**, and **7b** are available free of charge via the Internet at http://pubs.acs.org.

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