Synthesis and Structural Variation of Iron, Rhodium, Palladium, and Silver Complexes of a Chiral N-Heterocyclic Carbene−Phenoxyimine Hybrid Ligand

Gavin Dyson, Jean-Cédric Frison, Stevan Simonovic, Adrian C. Whitwood, and Richard E. Douthwaite*

Department of Chemistry, University of York, Heslington, York, U.K., YO10 5DD

Received September 24, 2007

A new class of chiral N-heterocyclic carbene (NHC) precursors has been prepared incorporating a phenoxyimine moiety. Reaction between 3-((1*R*,2*R*)-2-{[1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)meth-(*E*)-ylidene]amino}cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide [C(H)NO(H))][Br] (**2a**) and $Pd(OAc)_2$ gives the complex [Pd(κ^3-*CNO*)Br] (**3**), which exhibits tridentate ligand coordination via double deprotonation of **2a**. The NHC ligand transfer agents [Ag(κ^1-*C*NO(H))X] (X = Br (**5a**), Cl (**5b**)) are prepared from **2a**, chloride analogue **2b**, and Ag_2O. Reaction between **5b** and $[Rh(COD)Cl]_2$ gives the NHC complex [Rh(κ^1-*C*NO(H))Cl] (**6**) and, on chloride abstraction, the bidentate NHC-imine-coordinated complex [Rh(κ^2-*CN*O(H))][B{3,5-$(CF_3)_2C_6H_3$}$_4$] (**7**). For complexes **5** and **6** coordination of the phenoxyimine and deprotonation of the phenoxy moiety appear to be modified by intramolecular hydrogen bonding between hydroxyl and imine nitrogen groups. Reaction between **5a** and Fe{N$(SiMe_3)_2$}$_2$ gives an unusual bimetallic complex, [Fe(κ^2-C(AgBr)*NO*)$_2$] (**8**), that exhibits a 1-D polymeric chain motif in the solid state. Preliminary catalytic properties of an acetonitrile adduct of **3**, [Pd(κ^3-*CNO*)MeCN][BF_4] (**4**), and **7** are reported for hydroamination and phenylation of enones, respectively, that show good activity but poor enantioselectivity.

Introduction

The coordination chemistry of N-heterocyclic carbenes (NHC) has been extensively developed since the first reported examples nearly four decades ago.[1] Isolation of the first free NHC by Arduengo and co-workers[2] led directly to the current resurgence in the synthesis and application of NHC complexes from across the periodic table. The majority of reported complexes contain the later metals, particularly from groups 8–10, principally because of their thermodynamic and kinetic stability and application as ancillary ligands in metal-mediated catalysis.[3] NHCs form strong covalent bonds with later metals, but for the more electropositive transition metals NHC ligands are more labile, presumably due to the lack of a sufficient ionic bonding contribution. The lability of an NHC moiety can be reduced by incorporation of hard donor moieties into chelating NHC hybrid ligands, allowing the isolation of new classes of NHC transition metal complex.[4] Of particular relevance to the work reported here are NHC hybrids containing aryloxy substituents that have been prepared for polymerization, coupling, metathesis, and allylic substitution reactions[4a,g,k,5] and particularly an example of a nickel complex derived from an achiral NHC−phenoxyimine that exhibits activity for styrene polymerization.[6]

In a previous study we described the synthesis of new chiral imidazolium−imine salts that served as precursors to NHC−imine hybrid ligands for application to palladium-catalyzed enantio-

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* Corresponding author. E-mail: red4@york.ac.uk.

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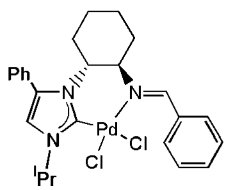

Figure 1. A palladium complex incorporating a chiral NHC−imine ligand.

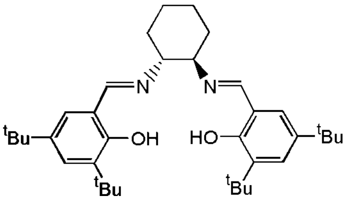

Figure 2. Salen ligand example.

selective allylic substitution.[7] Palladium complexes (Figure 1) were prepared from analogous silver(I) precursors using established methodology[8] that circumvents the need to prepare a free NHC ligand. In subsequent work we have attempted to synthesize other metal complexes of these ligands using silver(I) NHC transfer agents and via typical deprotonation routes that generate NHC molecules in situ. However, success has largely been limited by the apparent instability of free NHC derivatives.

In our earlier work,[7,9] examples were restricted to imines containing hydrocarbyl substitutents, and we envisaged that incorporation of an additional donor atom would potentially provide access to new classes of catalyst. One type of imine moiety that has been extensively applied to metal coordination chemistry and catalytic applications is Schiff bases derived from phenolimines, most notably the Salen class of ligands (Figure 2) for enantioselective chemistry.[10] Here we report the synthesis of a new chiral imidazolium−phenolimine salt and related coordination chemistry giving complexes of iron, palladium, rhodium, and silver. Preliminary catalytic data are also reported.

Results and Discussion

Access to NHC−imine ligand precursors is achieved from condensation reactions between the imidazolium−amine salt 3-((1*R*,2*R*)-2-aminocyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium bromide (**1a**) (Scheme 1) and aldehydes or ketones.[7] Using similar methodology, reaction between **1a** or the chloride analogue (**1b**) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde gives the imidazolium−phenolimine compounds 3-((1*R*,2*R*)-2-{[1-(3,5-di-*tert*-butyl-2-hydroxyphenyl)meth-(*E*)-ylidene]amino}cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium halide, [C(H)NO(H)][X] (X = Br (**2a**), Cl (**2b**)) in high yield (Scheme 1). The chloride **2a** was prepared to circumvent potential halide exchange and subsequent separation problems in reactions involving metal chlorides. Compounds **2a** and **2b** are hygroscopic powders that are soluble in water and most organic solvents including alcohols, ethers, and aromatic and chlorinated compounds, and the NMR spectroscopic data of **2a** and **2b** are indistinguishable. ^{1}H NMR spectroscopy clearly shows characteristic signals at δ 8.38, 11.22, and 12.86 corresponding to CH_{imine}, imidazolium NC(*H*)N, and O*H* protons, respectively, and corresponding signals are observed at δ 135.4, 157.2, and 166.9 for N*C*(H)N, *C*OH, and $^{\text{imine}}C$H in the ^{13}C NMR spectrum. It should be noted that, in comparison to other phenols, the significant downfield shift of the phenolic O*H* proton is due to hydrogen-bonding interaction between the OH and imine nitrogen moieties (Scheme 1).[11]

There are a number of potential routes to NHC metal complexes derived from an imidazolium salt including deprotonation to give a free NHC for coordination, direct reaction with a metal precursor containing a coligand capable of deprotonation, and the use of a metal NHC complex as a transfer agent. With respect to compound **2**, deprotonation of imidazolium and phenol moieties is potentially required, and attempts to prepare an NHC−phenoxyimine from reaction between **2** and 2 equiv of a base were not successful. However, use of suitable metal precursors did allow isolation of several new NHC metal complexes exhibiting a variety of coordination modes.

Direct metalation of **2a** occurs from reaction between **2** and Pd(OAc)$_2$ to give the complex [Pd(κ^3-*CNO*)Br] (**3**) (Scheme 1) as an air-stable orange solid. NMR spectroscopy shows several significant changes in comparison to compound **2a** that are indicative of κ^3-ligand coordination. In the ^{1}H NMR spectrum the chemical shift of the cyclohexyl proton adjacent to the imine nitrogen atom ($^{\text{c-hex}}$CH_{imine}) is observed significantly upfield at δ 2.53, whereas the chemical shift of $^{\text{c-hex}}$CH_{NHC} is relatively unchanged at δ 4.65. Other significant features are shifts of signals attributable to the isopropyl substituent, where the C*H*(CH$_3$)$_2$ signal is observed at δ 6.15 (4.87 for **2a**) and two doublets of CH(CH_3)$_2$ are separated by a greater chemical shift difference (δ 1.52 and 1.54 for **2a** and δ 0.82 and 1.28 for **3**). The absence of imidazolium NC(*H*)N and O*H* signals also suggests κ^3-coordination. Comparison of ^{13}C NMR spectra of **2a** and **3** indicates that as expected the *C*O signal is sensitive to O coordination, being observed at δ 166.0 for **3**, exhibiting a characteristic downfield shift (vide infra). However, there is no corresponding obvious trend in the chemical shift of the $^{\text{imine}}C$H carbon indicative of imine coordination. A signal for the Pd*C* carbene carbon atom is observed at δ 156.3.

The coordination motif was confirmed by a single-crystal X-ray diffraction study, and the molecular structure is shown in Figure 3. Crystallographic and select distance and angle data are given in Tables 1 and 2 respectively. Two molecules are present in the asymmetric unit, which differ essentially only in the orientation of the ^{t}Bu substituents. The geometry about the palladium atom is square-planar comprising trans C$_{\text{NHC}}$−OH and N$_{\text{imine}}$−Br moieties (C(1)−Pd(1)−O(1) = 173.4(2)° and N(3)−Pd(1)−Br(1) = 173.43(17)°), respectively. Bond lengths and angles are not considered exceptional with, for example, Pd(1)−C(1) = 1.952(6) Å and Pd(1)−N(3) = 1.993(6) Å, similar to related PdCl$_2$(NHC−imine) derivatives and with the Pd(1)−O(1) = 2.034(5) Å distance similar to known palla-

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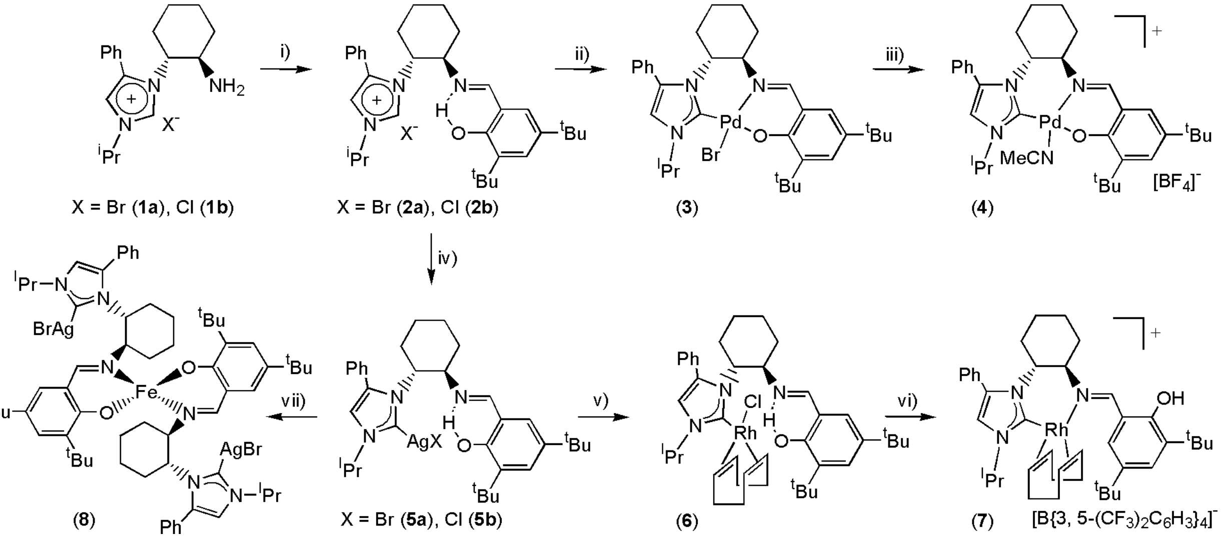
Scheme 1. Synthetic Routes to Compounds and Complexes 2–8[a]



[a] Reaction conditions: (i) 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 12 h, EtOH, 80 °C; (ii) **2a**, $Pd(OAc)_2$, THF, 12 h, 75 °C; (iii) $AgBF_4$, MeCN, 1 h, 20 °C; (iv) Ag_2O, CH_2Cl_2, 12–24 h, 20 °C; (v) **6b**, 0.5 $[Rh(COD)Cl]_2$, CH_2Cl_2, 1 h, 20 °C; (vi) $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, CH_2Cl_2, 15 min, 20 °C; (vii) **5a**, 0.5 $Fe\{N(SiMe_3)_2\}_2$, THF, 12 h, −78 to 20 °C.

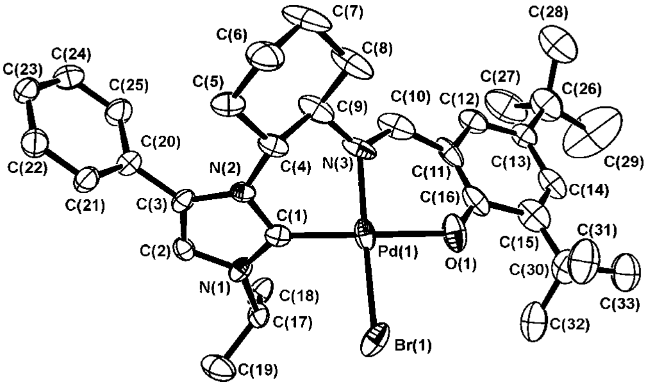


Figure 3. Molecular structure of complex **3**. Probability displacement ellipsoids are set at 50%. Hydrogen atoms have been omitted for clarity.

dium(II) Schiff base complexes.[12] The two six-atom palladacycles exhibit boat-like confirmations that are staggered with respect to each other.

Addition of $AgBF_4$ to an acetonitrile solution of complex **3** gives the cationic acetonitrile derivative $[Pd(\kappa^3\text{-}CNO)MeCN][BF_4]$ (**4**), which we envisaged would aid substrate binding via displacement of the acetonitrile ligand. NMR spectroscopy shows similar features to **3**, with the more significant shifts observed for $^{c\text{-}hex}CH_{imine}$ and $CH(CH_3)_2$ at δ 3.75 and 5.14, respectively, and Pd*C* at δ 149.5. Additional signals attributable to coordinated acetonitrile are observed at δ 1.91 in the ^1H NMR spectrum and ^{13}C NMR signals at δ 2.1 and 123.9, respectively. Unfortunately a single crystal could not be grown, but elemental analysis was consistent with the proposed formulation.

Attempts to affect double deprotonation of **2** using other $M(OAc)_2$ (M = Mn, Co) precursors did not give analogous $[M(\kappa^3\text{-}CNO)Br]$ products. Paramagnetism prevented any detailed NMR analysis, but ESI mass spectrometry showed two significant signals in a ca. 60:40 ratio corresponding to the cation of **2** and a *m*/*z* ratio suggestive of $[M(\kappa^2\text{-}C(H)NO)_2][Br]_2$, respectively, where it is presumed that coordination to the metal atom is via the phenoxyimine moiety. In related reactions between $M\{N(SiMe_3)_2\}_2$ (M = Mn, Fe, Co) and 1 equiv of **2** similar results were obtained.

An alternative strategy was therefore investigated via transmetalation of a silver(I) NHC complex. The advantage of silver(I) NHC complexes include simple preparation directly from an imidazolium salt,[8,13] ease of handling due to air stability, and additionally interesting properties are exhibited in their own right including antibacterial activity.[14] Reaction between 2 equiv of **2a** or **2b** and Ag_2O in dichloromethane gave the air-stable complexes $[Ag(\kappa^1\text{-}CNO(H))X]$ (X = Br (**5a**), Cl (**5b**)) (Scheme 1) in high yield. Only minor differences in the data of **5a** and **5b** are observed, and therefore discussion will be limited to **5a**. NMR spectroscopy is consistent with the proposed formulation and shows signals attributable to a CH_{imine} and phenol O*H* protons at δ 8.14 and 13.01, respectively, which are comparable to compound **2a** and are indicative of no significant interaction between the phenol–imine moiety and the silver atom. Further spectroscopic corroboration is provided by signals at δ 157.1 and 166.0 attributed to *C*OH and $^{imine}CH$, respectively, in the ^{13}C NMR spectrum, which are also similar to **2a** and in contrast to **3** and **4**. The carbene atom Ag*C* could not be observed, which is not unusual for this class of complexes. Structurally related silver(I) NHC–imine complexes do not exhibit a silver–imine interaction.[7] However, the formulation of **5** is in contrast to known complexes that incorporate an aryl (phenyl or naphthyl) alcohol moiety that exhibit a silver(I) NHC–aryloxy composition as a net result of spontaneous HBr elimination.[5a–c] No elimination of HX for **5a** or **5b** was observed at room temperature, and heating did not give silver(I) NHC phenoxyimine complexes, as judged by ^1H NMR spectroscopy. Presum-

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Table 1. Crystallographic Data for Complexes [Pd(κ^3-*CNO*)Br] (3), [Rh(κ^1-CNO(H))Cl] (6), and [Fe(κ^2-C(AgBr)*NO*)$_2$] (8)

	3	6	8
formula	$C_{84}H_{106}Br_2N_6O_3Pd_2$	$C_{41}H_{57}ClN_3ORh$	$C_{73}H_{96}Ag_2Br_2FeN_6O_2$
formula wt	1620.37	746.26	1520.97
temp, K	100(2)	110(2)	110(2)
wavelength, Å	0.71073	0.71073	0.71073
cryst size, mm	0.15 × 0.15 × 0.10	0.23 × 0.05 × 0.02	0.15 × 0.05 × 0.05
cryst syst	orthorhombic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a, Å	14.5583(8)	12.786(3)	16.8959(14)
b, Å	20.1309(11)	16.419(3)	18.3946(16)
c, Å	26.9433(15)	18.434(4)	23.265(2)
V, Å^3	7896.3(8)	3870.1(13)	7230.7(11)
Z	4	4	4
d_{calcd}, g cm^{-1}	1.363	1.281	1.397
μ, mm^{-1}	1.518	0.544	1.886
F(000)	3352	1576	3128
θ range (deg)	1.59 to 25.09	1.66 to 25.09	1.49 to 20.21
no. reflns measd	84 948	40 982	46 262
no. indep reflns	13 987	6857	6874
no. reflns with $I \geq 2\sigma(I)$	13 014	6008	5827
no. params	890	452	792
abs corr	semiempirical	semiempirical	semiempirical
transmn coeff range	0.805–0.860	0.816–0.990	0.830–0.910
$R(F)$ ($I \geq 2\sigma(I)$)^a	0.0511	0.0342	0.0418
$R_w(F^2)$ (all data)^b	0.1323	0.0689	0.0940
GOF(F^2)	1.027	1.016	1.056
absol strct param	0.021(9)	0.00(2)	0.048(13)
$\Delta\rho$ (max./min.), e Å^{-3}	3.176/−1.620	0.589/−0.487	0.617/−0.432

^{a} $R(F) = \Sigma\triangle F_o| - |F_c\triangle/\Sigma\triangle F_o|$. ^{b} $R_w(F^2) = \{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Pd(κ^3-*CNO*)Br] (3)

Distances			
Pd(1)−Br(1)	2.4341(10)	C(1)−N(1)	1.347(8)
Pd(1)−C(1)	1.952(6)	C(1)−N(2)	1.361(8)
Pd(1)−N(3)	1.993(6)	C(10)−N3	1.286(9)
Pd(1)−O(1)	2.034(5)	C(16)−O(1)	1.294(9)
Angles			
C(1)−Pd(1)−N(3)	87.2(3)	C(1)−Pd(1)−O(1)	173.4(2)
O(1)−Pd(1)−Br(1)	87.37(18)	N(3)−Pd(1)−Br(1)	173.43(17)
C(1)−Pd(1)−Br(1)	94.53(17)	N(1)−C(1)−N(2)	105.4(5)
N(3)−Pd(1)−O(1)	91.6(3)	C(9)−N(3)−C(10)	119.8(6)

ably deprotonation is hindered due to intramolecular hydrogen bonding between phenol OH and imine N atoms.

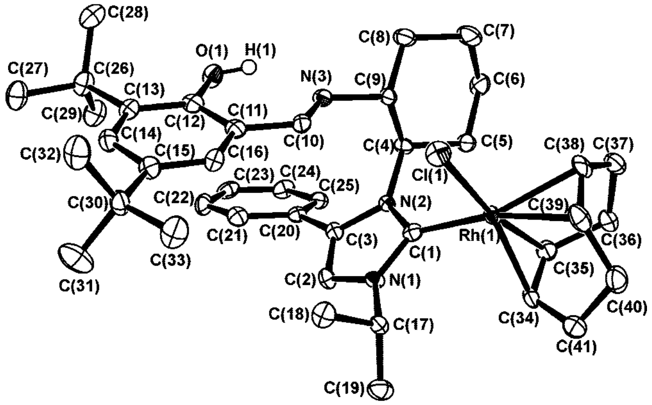

Figure 4. Molecular structure of complex **6**. Probability displacement ellipsoids are set at 50%. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) for [Rh(κ^1-*C*NO(H))Cl] (6)

Distances			
Rh(1)−C(1)	2.048(3)	C(1)−N(1)	1.356(5)
Cl(1)−Rh(1)	2.3797(9)	C(1)−N(2)	1.374(4)
Rh(1)−C(34)	2.095(4)	C(10)−N(3)	1.279(4)
Rh(1)−C(35)	2.124(4)	C(12)−O(1)	1.346(4)
Rh(1)−C(38)	2.202(3)	O(1)−H(1)	0.87(4)
Rh(1)−C(39)	2.219(4)	N(3)−H(1)	1.80(4)
Angles			
C(1)−Rh(1)−Cl(1)	92.21(9)	C(12)−O(1)−H(1)	106(3)
C(34)−Rh(1)−C(39)	81.01(16)	O(1)−H(1)−N(3)	153(4)
C(35)−Rh(1)−C(38)	81.97(15)	C(10)−N(3)−H(1)	96(4)
N(1)−C(1)−N(2)	111.5(3)		

Complex **5b** does indeed act as a ligand transfer agent to late metals including rhodium, as exemplified by reaction between 2 equiv of **5** and [Rh(COD)Cl]$_2$ (where COD = 1,4-cyclooctadiene) to give [Rh(κ^1-*C*NO(H))Cl] (**6**) (Scheme 1). NMR spectroscopy shows similar features to **5** indicative of ligand binding at the NHC carbon atom. A Rh−NHC bond is clearly shown by a doublet signal at δ 183.3 ($^1J_{\text{Rh-C}}$ = 52 Hz) in the ^{13}C NMR spectrum for the carbene carbon atom, and similarly to **5**, signals attributable to *C*OH and $^{\text{imine}}$*C*H are observed at δ 158.6 and 168.7 indicative of κ^1-ligand coordination. The ^{1}H NMR clearly shows signals at δ 9.25 and 13.95 for the C*H*$_{\text{imine}}$ and O*H* protons, respectively. Single crystals of **6** could be grown from benzene that were suitable for an X-ray diffraction study, and the molecular structure is shown in Figure 4. Crystallographic data and select distance and angle data are given in Tables 1 and 3, respectively. Coordination of the chiral ligand is confirmed as κ^1, and it is clear that there is no direct intra- or intermolecular interaction between the phenoxyimine moiety and a rhodium atom. The geometry at the rhodium atom is essentially square planar if COD is considered a bidentate ligand. A difference map revealed the phenolic OH hydrogen atom H(1) that is incorporated into a plane comprising N(3)−C(10–12)−O(1)−H(1) with distances O(1)−H(1) and N(3)−H(1) of 0.87(4) and 1.80(4) Å, respectively. Attempts to deprotonate the phenol with bases such as NaOH, NEt$_3$, and KO^{t}Bu or to thermally eliminate HCl unfortunately did not give a single major product, as judged by ^{1}H NMR spectroscopy.

Chloride abstraction could be achieved from reaction between **6** and Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] in dichloromethane to give [Rh(κ^2-*C*N*O*(H))][B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (**7**). Unfortunately, single

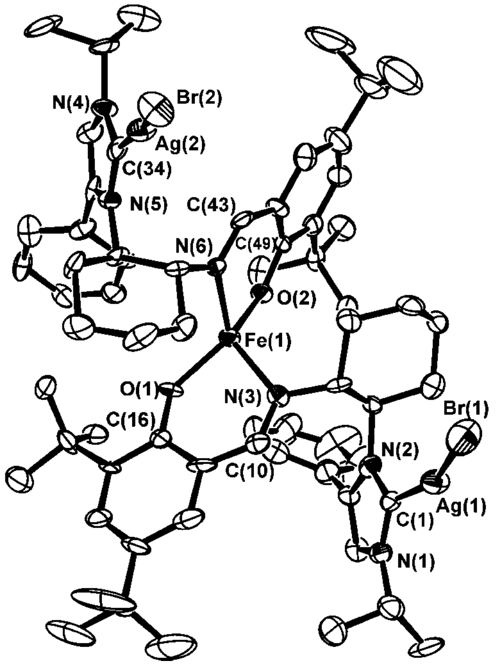

Figure 5. Molecular structure of complex **8**. Probability displacement ellipsoids are set at 50%. Hydrogen atoms have been omitted for clarity.

crystals of sufficient quality have not been obtained, but other characterization is consistent with the proposed formulation. Elemental analysis is consistent with the composition, and NMR spectroscopy indicates that, in contrast to **6**, complex **7** exhibits κ^2-*CN*O(H) coordination where NHC and imine moieties are coordinated to the metal atom. Perhaps the most compelling piece of evidence for imine coordination is provided by the ^{1}H NMR signal attributable to the phenol O*H* atom at δ 6.57 that is typical of phenols in nonprotic media where hydrogen bonding or strong noncovalent interactions are absent. Consistent with complexes **2**–**6**, the ^{13}C NMR signal for the *C*OH atom at δ 155.8 indicates no metal–oxygen bond and a doublet ($^1J_{\text{Rh-C}}$ = 51 Hz) at 174.9 ppm is observed for the carbene carbon.

Attempts were also made to use complexes **5a** and **5b** as an NHC ligand transfer agent to earlier metals by precoordination of the phenoxyimine moiety in the hope that silver halide precipitation would drive NHC−metal bond formation. For example reaction between $FeBr_2$ and **5a** did not give a tractable product. Furthermore, Fe{N(SiMe$_3$)$_2$}$_2$ and 1 equiv of **5a** did not give Fe(κ^3-*CNO*)N(SiMe$_3$)$_2$ but the deep red complex [Fe(κ^2-C(AgBr)*NO*)$_2$] (**8**) resulting from reaction between the metal precursor and two ligand equivalents, representing an example of a multimetallic complex based on an NHC ligand. Several modifications to the experimental procedure including order and rate of addition, dilution, temperature, and attempted conproportionation did not give the target complex. Paramagnetism precluded analysis by NMR spectroscopy, but single crystals of **8** suitable for an X-ray diffraction study were obtained and the molecular structure is shown in Figure 5. Crystallographic and select distance and angle data are given in Tables 1 and 4, respectively. The geometry at the iron atom is pseudotetrahedral, comprising two, essentially planar, C$_3$NFeO metallocycles subtending an angle of 85° at the common iron atom. In comparison to known related structures[15] containing only phenoxyimines in the primary coordination sphere the Fe−O and Fe−N bond lengths are slightly longer and O−Fe−N angles more acute presumably due to noncovalent interactions. A pseudolinear geometry at the silver atoms is observed and the C−Ag−Br vectors are approximately parallel. Figure 6 shows resulting intermolecular interactions between adjacent molecules, resulting in a 1-D polymeric structure connected via an Ag$_2$Br$_2$ parallelogram motif where two distinct bond distances allow identification of intra- and intermolecular Ag−Br bonds. Related dimeric structures have been reported for NHC complexes,[9,16] which exhibit similar Ag−Br bond distances; however the intermolecular distance Ag(1)−Br(2) = 3.241(2) Å for **8** is at the long extreme of the range.

Table 4. Selected Bond Distances (Å) and Angles (deg) for [Fe(κ^2-C(AgBr)*NO*)$_2$] (8)[a]

	Distances		
Ag(1)−C(1)	2.111(9)	Ag(2)−C(34)	2.099(9)
Ag(1)−Br(1)	2.4736(14)	Ag(2)−Br(2)	2.4399(13)
Br(1)−Ag(2)*	3.241(2)	Br(2)−Ag(1)*	3.090(2)
Fe(1)−O(1)	1.912(6)	C(10)−N(3)	1.295(11)
Fe(1)−O(2)	1.896(6)	C(43)−N(6)	1.301(10)
Fe(1)−N(3)	2.062(7)	C(16)−O(1)	1.317(10)
Fe(1)−N(6)	2.081(7)	C(49)−O(2)	1.319(10)
	Angles		
C(1)−Ag(1)−Br(1)	162.5(2)	C(34)−Ag(2)−Br(2)	171.3(3)
Ag(1)−Br(1)−Ag(2)*	81.4(3)	Ag(2)−Br(2)−Ag(1)*	85.2(3)
Br(1)−Ag(1)−Br(2)*	97.6(3)	Br(2)−Ag(2)−Br(1)*	94.5(3)
N(1)−C(1)−N(2)	103.7(8)	N(4)−C(34)−N(5)	105.5(7)
O(1)−Fe(1)N(3)	90.6(3)	O(1)−Fe(1)−O(2)	128.0(3)
O(2)−Fe(1)−N(6)	90.8(3)	N(3)−Fe(1)−N(6)	110.4(3)

[a] Asterisk denotes atoms at symmetry positions (1 − *x*, 0.5 + y, 0.5 − *z*).

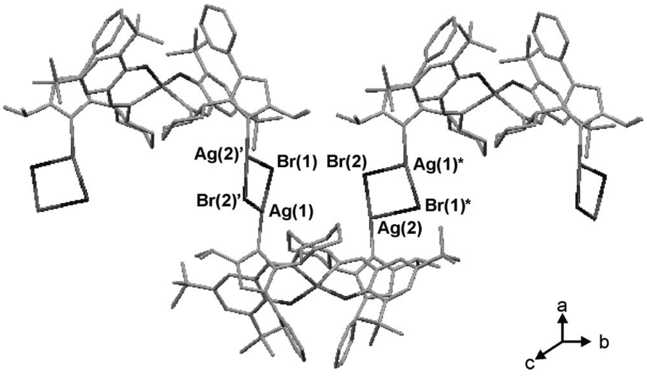

Figure 6. Chain structure of complex **8**. Atoms marked with a (′) and (*) are at symmetry positions (1 − *x*, −0.5 + *y*, 0.5 − *z*) and (1 − *x*, 0.5 + *y*, 0.5 − *z*), respectively.

In preliminary experiments complex **4** has been examined as a precatalyst for hydroamination and **7** for conjugate addition of phenylboronic acids to enones. Reaction between piperidine and methacrylonitrile at 40 °C using 2 mol % **4** gave 3-(piperidin-1-yl)butanenitrile in 90% yield after 24 h; however no enantioselectivity was observed. The activity is similar to that reported for tridentate P−NHC−P complexes, which do show moderate enantioselectivity for this reaction.[17]

Complex **7** is a precatalyst for the addition of phenyl moieties to enones as shown in Table 5. The use of related NHC imidazolidenes has previously been described including mono-

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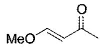
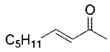
(15) (a) Torzilli, M. A.; Colquhoun, S.; Kim, J.; Beer, R. H. *Polyhedron* **2002**, *21*, 705. (b) Bao, X.; Wang, F. W.; Wei, Y. J. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *62*, M1298.

(16) (a) Tulloch, A. A. D.; Danopoulos, A. A.; Winston, S.; Kleinhenz, S.; Eastham, G. *J. Chem. Soc., Dalton Trans.* **2000**, 4499. (b) Lee, C. K.; Lee, K. M.; Lin, I. J. B. *Organometallics* **2002**, *21*, 10.

(17) (a) Gischig, S.; Togni, A. *Organometallics* **2004**, *23*, 2479. (b) Gischig, S.; Togni, A. *Eur. J. Inorg. Chem.* **2005**, 4745.

Table 5. Conjugate Addition of Phenylboronic Acids to Enones Using 7 as Precatalyst

Entry	R	n or enone	Yield (%)[b]
1	Ph	1	>99
2	Ph	2	>99
3	4-$MeOC_6H_4$	1	95
4	4-$McOC_6H_4$	2	95
5	3-ClC_6H_4	1	0[c]
6	3-ClC_6H_4	2	0[c]
7	Ph		0
8	Ph		95

[a] Conditions: dioxane/H_2O, 3 mol % **7**, 2 Et_3N, reflux, 3 h. [b] Determined by ^1H NMR. [c] Boronic acid coupling product formed.

NHC derived from cyclophanes and a chelating NHC−phosphine, both of which can lead to excellent enantioselectivities for cyclic and acyclic precursors.[18] Unfortunately complex **7** does not give good enantioselectivites; however complex **7** is an active catalyst and some chemoselectivity is observed with respect to the boronic acid and enone precursors. Addition to cyclopentenone and cyclohexenone using phenyl and 4-methoxyphenyl boronic acid (entries 1–4) gave very high yields, whereas the use of the 4-chlorophenyl derivative gave exclusively biaryl products presumably resulting from Suzuki-type coupling (entries 5 and 6). Selectivity was also observed between (*E*)-4-methoxybut-3-en-2-one and (*E*)-non-3-en-2-one (entries 7 and 8), where the presence of an electron-donating methoxy group prevents reaction.

Conclusions

Variable coordination is observed for an imidazolium−phenoxyimine ligand precursor exhibiting κ^3-CNO (Pd), κ^2-NO (Fe), κ^2-CN (Rh), and κ^1-C (Rh, Ag) motifs. For early metal examples coordination of a second phenoxyimine moiety is kinetically favored and probably more thermodynamically preferred than coordination of an NHC group. Cationic derivatives **4** and **7** are precatalysts for hydroamination and conjugate addition reactions, respectively, exhibiting good activity but poor enantioselectivity for the substrates investigated. The mixed metal complex **8** and the observed disparate coordination chemistry of the phenoxyimine and NHC moieties provide the opportunity for the synthesis of bimetallic precatalysts. Perhaps more fundamentally to the synthesis of monometallic κ^3-*CNO* complexes the hydrogen bonding present in the phenol−imine moiety appears to retard formal deprotonation and access to mononuclear phenoxyimine catalysts. It is known that in contrast to phenol−imines related naphthol−imines are better represented as the enolized keto−amine tautomer[11a] and therefore may allow more facile access to κ^3-*CNO* complexes.

Experimental Section

All manipulations were performed under argon using standard Schlenk techniques unless stated otherwise. All solvents were dried over the appropriate drying agent and distilled under dinitrogen according to literature methods.[19] Reagents were purchased from Aldrich, Acros, or Lancaster and used as supplied. $[PdCl_2(MeCN)_2]$[20] and $[Rh(COD)Cl]_2$[21] were prepared using literature procedures. NMR spectra were recorded at probe temperature on a JEOL 270 (^1H, 270 MHz; ^{13}C, 67.9 MHz), Brüker AV-300 (^1H, 300 MHz; ^{13}C, 75.5 MHz), Brüker AMX-500 (^1H, 500 MHz; ^{13}C, 125.7 MHz), or Brüker AV-700 (^1H, 700 MHz, ^{13}C, 175 MHz), respectively. Chemical shifts are described in parts per million downfield shifted from $SiMe_4$ and are reported consecutively as position (δ_H or δ_C), relative integral, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, br = broad), coupling constant (*J*/Hz), and assignment. Proton NMR spectra were referenced to the chemical shift of residual proton signals ($CHCl_3$ δ 7.27, C_6D_5H δ 7.16, and CD_2HCN δ 1.94). Carbon spectra were referenced to a ^{13}C resonance of the solvent ($CDCl_3$ δ 77.2, C_6D_6 δ 128.1, and CD_3CN δ 118.3). ^{13}C HSQC, PENDANT, and gradient HMBC experiments were performed using standard Brüker pulse sequences. Mass spectra were recorded on VG 70-250E or Kratos MS-50 spectrometers. Electrospray (ES) was recorded using methanol or acetonitrile as the mobile phase. Major fragments are given as percentages of the base peak intensity (100%). Elemental analyses were performed at the University of North London.

Synthesis of 3-((1*R*,2*R*)-2-Aminocyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium Chloride [C(H)NH$_2$][Cl] (1b). To a water solution (200 mL) of **1a** (3.50 g, 9.61 mmol) was added NaCl (1 g, 0.02 mol). The solution was stirred for 10 min, the volatiles were removed under reduced pressure, and the resulting solid was extracted with dichloromethane (3 × 50 mL). Removal of the volatiles gave **1b** as a light orange solid. Yield = 3.01 g, 98%. ^1H NMR data are indistinguishable from **1a**.[7]

Synthesis of 3-((1*R*,2*R*)-2-{[1-(3,5-Di-*tert*-butyl-2-hydroxyphenyl)meth-(*E*)-ylidene]amino}cyclohexyl)-1-isopropyl-4-phenyl-3*H*-imidazol-1-ium Bromide [C(H)NO(H))][Br] (2a). A mixture (**1a**) (250 mg, 0.69 mmol), 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (193 mg, 0.82 mmol) and 4 Å molecular sieves (500 mg) were refluxed for 12 h in dry ethanol (5 mL). On cooling the volatiles were removed under reduced pressure to give a yellow solid, which was dissolved in dichloromethane (2 mL) and added dropwise to petroleum ether (50 mL) with stirring, precipitating a yellow solid. The solid was collected by filtration, and residual volatiles were removed under reduced pressure to give **2a** as a yellow powder. Yield: 365 mg, 92%. ^1H NMR ($CDCl_3$, 270 MHz): δ 1.15 (9 H, s, $C(CH_3)_3$), 1.33–1.51 (4 H, m, $^{c\text{-hex}}CH_2$), 1.52 (3 H, d, $^3J_{H\text{-}H}$ = 6.7 Hz, $CH(CH_3)_2$), 1.54 (3 H, d, $^3J_{H\text{-}H}$ = 6.7 Hz, $CH(CH_3)_2$), 1.85 (2 H, m, $^{c\text{-hex}}CH_2$) 2.05 (1 H, m, $^{c\text{-hex}}CH_2$) 2.41 (1 H, m, $^{c\text{-hex}}CH_2$), 4.05 (1 H, m, CHN_{imine}), 4.42 (1 H, m, CHN_{imid}), 4.87 (1 H, sep, $^3J_{H\text{-}H}$ $CH(CH_3)_2$), 6.92 (1 H, s, NCHC), 7.12–7.43 (7 H, m, ^{Ph}CH), 8.38 (1 H, s, $^{imine}CH$), 11.22 (NCHN), 12.86 (OH). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 67.9 MHz): δ 22.9, 23.0 ($CHCH_3$), 24.9, 27.3, 28.6, 32.5 ($^{c\text{-hex}}CH_2$) 29.0, 31.1 ($CH(CH_3)_3$), 33.8, 34.6 ($C(CH_3)_3$), 53.4 ($CH(CH_3)_2$), 62.6 ($^{c\text{-hex}}CHN_{imid}$), 71.0 ($^{c\text{-hex}}CHN_{imine}$), 116.0 (NCHC), 117.1 ($C_{ipso}$), 124.4 ($C_{ipso}$), 126.1, 127.2, 129.0, 129.8, 130.5 (^{Ph}CH) 135.4 (NCHN), 135.9, 135.7, 140.1 (C_{ipso}), 157.2 (COH), 166.9 ($^{imine}CH$). MS (ESI): *m*/*z* 500 ($[M - Br]^+$, 100%). MS (HRES): calc for $C_{33}H_{46}N_3O$:500.3641, found 500.3637. Anal. [Found (calc)] $C_{33}H_{46}BrN_3O$: C, 68.19 (68.26); H, 7.87 (7.99); N, 7.32 (7.24).

[C(H)NO(H))][Cl] (2b). The procedure used for the synthesis of **2a** was replicated for **2b** using **1b** (250 mg, 0.78 mmol) and 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (218 mg, 0.93 mmol) to

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(18) (a) Ma, Y. D.; Song, C.; Ma, C. Q.; Sun, Z. J.; Chai, Q.; Andrus, M. B. *Angew. Chem., Int. Ed.* **2003**, *42*, 5871. (b) Becht, J. M.; Bappert, E.; Helmchen, G. *Adv. Synth. Catal.* **2005**, *347*, 1495.

(19) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Butterworth-Heinemann: Oxford, 1997.

(20) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60.

(21) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1990**, *28*, 88.

give **2b** as a light yellow solid. Yield = 386 mg, 92%. ^{1}H NMR data are indistinguishable from **2a**.

Synthesis of [Pd(κ^3-*CNO*)Br] (3). To a THF (40 mL) solution of **2a** (300 mg, 0.51 mmol) was added Pd(OAc)$_2$ (120 mg, 0.51 mmol) dissolved in THF (15 mL), and the pale yellow solution was refluxed for 12 h to give a dark mixture. On cooling, the volatiles were removed under reduced pressure to give a black solid, which was dissolved in dichloromethane (10 mL) and dropped into hexane (50 mL) to give a black precipitate. Removal of the filtrate volatiles gave an orange solid, which was purified by flash chromatography (silica, eluted with toluene) to give **3** as an orange solid. Yield = 227 mg, 65%. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 0.56 (2 H, m, $^{c\text{-hex}}$C*H*$_2$), 0.82 (3 H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$), 0.99 (4 H, m, $^{c\text{-hex}}$C*H*$_2$), 1.14 (2 H, m, $^{c\text{-hex}}$C*H*$_2$), 1.28 (2 H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.43 (9 H, s, C(C*H*$_3$)$_3$), 1.89 (9 H, s, C(C*H*$_3$)$_3$), 2.53 (1 H, m, $^{c\text{-hex}}$C*H*$_{\text{imine}}$), 4.65 (1 H, m, $^{\text{c-hex}}$C*H*$_{\text{NHC}}$), 6.04 (1 H, s, NC*H*CPh), 6.15 (1 H, m, C*H*(CH$_3$)$_2$), 7.09 (1 H, s, $^{\text{imine}}$C*H*), 7.08–7.67 (7 H, m, $^{\text{Ph}}$C*H*). ^{13}C NMR (C$_6$D$_6$, 67.9 MHz): δ 23.3 (CH(*C*H$_3$)$_2$), 23.4 ($^{c\text{-hex}}$CH$_2$), 24.4 (CH(*C*H$_3$)$_2$), 24.6 ($^{c\text{-hex}}$CH$_2$), 30.3 (C(*C*H$_3$)$_3$), 30.5 ($^{c\text{-hex}}$C*H*$_2$), 31.7 (C(*C*H$_3$)$_3$), 34.0 (*C*(CH$_3$)$_3$), 36.4 (*C*(CH$_3$)$_3$), 36.6 ($^{c\text{-hex}}$C*H*$_2$), 52.9 (*C*H(CH$_3$)$_2$), 65.4 (*C*HN$_{\text{imine}}$), 67.9 (*C*HN$_{\text{NHC}}$), 117.6 (NCH*C*Ph), 122.6 (N*C*HCPh), 125.6 ($^{\text{Ph}}$*C*$_{ipso}$), 127.3, 129.4, 130.8, 131.0, 131.1 ($^{\text{Ph}}$*C*H), 132.9, 135.1, 143.3 ($^{\text{Ph}}$*C*$_{ipso}$), 156.3 (Pd*C*), 163.1 ($^{\text{imine}}$*C*H), 166.0 (*C*O). MS (ESI): *m/z* 735 ([M]$^+$,10%), 655 ([M − Br]$^+$, 100%). Anal. [Found (calc)] C$_{33}$H$_{44}$N$_3$BrOPd·1.5CH$_2$Cl$_2$: C 52.56 (52.78), H 6.71 (6.26), N 4.88 (4.92).

Synthesis of [Pd(κ^3-*CNO*)MeCN][BF$_4$] (4). To an acetonitrile solution of **3** (100 mg, 0.146 mmol) was added an acetonitrile solution of AgBF$_4$ (26 mg, 0.146 mmol), immediately giving an off-white precipitate. The mixture was stirred in the absence of light for 1 h at 20 °C and filtered, and the volatiles were removed from the filtrate to give **4** as an orange solid. Yield = 96 mg, 90%. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 0.58, 0.75, 0.86, 0.97, 1.05, 1.09 (1 H, m, $^{c\text{-hex}}$C*H*$_2$), 1.29 (9 H, s, C(C*H*$_3$)$_3$), 1.30, 1.33 (1 H, m, $^{c\text{-hex}}$C*H*$_2$), 1.50 (3 H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.62 (3 H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.74 (9 H, s, C(C*H*$_3$)$_3$), 1.91 (3 H, s, C*H*$_3$CN), 3.75 (1 H, m, $^{c\text{-hex}}$C*H*$_{\text{imine}}$), 4.37 (1 H, m, $^{\text{c-hex}}$C*H*$_{\text{NHC}}$), 5.14 (1 H, m, C*H*(CH$_3$)$_2$), 6.59 (1 H, s, NC*H*CPh), 7.08–7.23 (6 H, m, $^{\text{Ph}}$C*H*), 7.49 (1 H, s, $^{\text{imine}}$C*H*), 7.65 (1 H, s, $^{\text{Ph}}$C*H*). ^{13}C NMR (C$_6$D$_6$, 67.9 MHz): δ 2.1 (*C*H$_3$CN), 23.6 (CH(*C*H$_3$)$_3$), 23.8 (CH(*C*H$_3$)$_3$), 24.2 ($^{c\text{-hex}}$*C*H), 24.9 ($^{c\text{-hex}}$*C*H), 30.0 (C(*C*H$_3$)$_3$), 30.7 ($^{c\text{-hex}}$*C*H), 31.4 (C(*C*H$_3$)$_3$), 33.8 ($^{c\text{-hex}}$*C*H), 35.9 (*C*(CH$_3$)$_3$), 36.9 (*C*(CH$_3$)$_3$), 53.0 (*C*H(CH$_3$)$_3$), 64.9 (*C*HN$_{\text{imine}}$), 68.1 (*C*HN$_{\text{NHC}}$), 117.3 (N*C*HCPh), 123.6 (NCH*C*Ph), 123.9 (Me*C*N), 129.5 (2 over lapping signals), 131.1 (2 over lapping signals), 132.2 ($^{\text{Ph}}$*C*H), 134.3, 136.1, 141.1 ($^{\text{Ph}}$*C*$_{\text{ipso}}$), 149.5 (Pd*C*), 163.7 ($^{\text{imine}}$*C*H), 165.9 (*C*O). MS (ESI): *m/z* 633 ([M − MeCN]$^+$, 100%). Anal. [Found (calc)] C$_{35}$H$_{44}$N$_4$BF$_4$OPd: C 57.25 (57.35), H 6.40 (6.46), N 7.63 (7.64).

Synthesis of [Ag(κ^1-CNO(H))Br] (5a). A mixture of **2a** (250 mg, 0.43 mmol) and silver(I)oxide (54 mg, 0.24 mmol) in dichloromethane (10 mL) was stirred in the absence of light for 24 h at 20 °C. The mixture was filtered through a Celite plug, and the volatiles were removed under reduced pressure to give **5a** as a dark yellow solid. Yield = 270 mg, 91%. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 1.27 (9 H, s, C(C*H*$_3$)$_3$), 1.39 (3 H, d, $^3J_{\text{H-H}}$ = 6.8 Hz CH(C*H*$_3$)$_2$), 1.47 (12 H, m, C(C*H*$_3$)$_3$ + CH(C*H*$_3$)$_2$), 1.30–2. 22, (7 H, m, $^{c\text{-hex}}$C*H*$_2$), 2.62 (1 H, m, $^{c\text{-hex}}$C*H*$_2$), 4.05, (1 H, m, $^{c\text{-hex}}$C*H*N$_{\text{imine}}$) 4.20 (1 H, m, $^{c\text{-hex}}$C*H*N$_{\text{NHC}}$), 4.76 (1 H, sep, $^3J_{\text{H-H}}$ = 6.7 Hz, C*H*(CH$_3$)$_2$), 6.75 (1 H, s, NC*H*C), 6.93 (1 H, s, $^{\text{Ph}}$C*H*), 7.18–7.47 (6 H m, $^{\text{Ph}}$C*H*), 8.14 (1 H, s, $^{\text{imine}}$C*H*), 13.01 (1 H, s, O*H*). ^{13}C{^{1}H} NMR (CDCl$_3$, 67.5 MHz): δ 23.1, 23.4 (CH(*C*H$_3$)$_2$), 23.6, 25.0 ($^{c\text{-hex}}$C*H*$_2$), 28.9, 31.0 (C(*C*H$_3$)$_3$), 33.6 ($^{c\text{-hex}}$C*H*$_2$), 33.7, 33.9 (*C*(CH$_3$)$_3$), 34.5 ($^{c\text{-hex}}$C*H*$_2$), 55.1 (*C*H(CH$_3$)$_2$), 60.5 ($^{c\text{-hex}}$*C*HN$_{\text{NHC}}$) 73.7 ($^{c\text{-hex}}$*C*HN$_{\text{imine}}$), 113.7 ($^{\text{Ph}}$*C*$_{ipso}$), 117.0 (N*C*HC) 125.0 ($^{\text{Ph}}$C$_{ipso}$) 126.8, 127.0, 128.4, 129.1, 129.8, ($^{\text{Ph}}$*C*H), 135.9, 137.0, 139.9 ($^{\text{Ph}}$*C*$_{ipso}$), 156.7 (*C*OH), 157.0 (Ag*C*), 165.6 ($^{\text{imine}}$*C*H). MS (ESI): *m/z* 500 [M − AgBr]$^+$ (100%), 606 [M − HBr]$^+$ (55%). M/S (HRES): calc for C$_{66}$H$_{90}$AgN$_6$O$_2$, 1105.6171; found, 1105.6171.

Synthesis of [Ag(κ^1-*C*NO(H))Cl] (5b). A mixture of **2b** (1.100 g, 2.05 mmol), silver(I) oxide (285 mg, 1.23 mmol), and 4 Å (500 mg) molecular sieves in dichloromethane (50 mL) was stirred in the absence of light for 12 h at 20 °C. The mixture was filtered, and the volatiles were removed from the filtrate under reduced pressure to give **5b** as a light brown solid. Yield = 1.300 g, 98%. ^{1}H NMR (CDCl$_3$, 270 MHz): δ 1.26 (9 H, s, C(C*H*$_3$)$_3$), 1.38 (3 H, d, CH(C*H*$_3$)$_2$), 1.43 (9 H, s, C(C*H*$_3$)$_3$), 1.45 (3 H, d, CH(C*H*$_3$)$_2$), 1.73, 1.92, 2.14, 2.54 (8 H, m, $^{c\text{-hex}}$C*H*$_2$), 4.04 (1 H, m, $^{c\text{-hex}}$C*H*$_{\text{imine}}$), 4.22 (1 H, m, $^{c\text{-hex}}$C*H*$_{\text{NHC}}$), 4.75 (1 H, m, C*H*(CH$_3$)$_2$), 6.75 (1 H, s, NC*H*CPh), 6.92–7.46 (7 H, m, $^{\text{Ph}}$C*H*), 8.12 (1 H, s, $^{\text{imine}}$C*H*), 12.99 (1 H, s, O*H*). ^{13}C{^{1}H} NMR (CDCl$_{3,}$ 67.9 MHz): δ 23.5 (CH(*C*H$_3$)$_2$), 23.8 (*C*H$_2$), 24.1 (CH(*C*H$_3$)$_2$), 25.4 (*C*H$_2$), 29.3 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 34.0 (*C*H$_2$), 34.1 (*C*(CH$_3$)$_3$), 34.4 (*C*H$_2$), 34.9 (*C*(CH$_3$)$_3$), 55.4 (*C*H(CH$_3$)$_2$), 60.9 ($^{c\text{-hex}}$*C*H$_{\text{NHC}}$), 74.1 ($^{c\text{-hex}}$*C*H$_{\text{imine}}$), 114.1 (N*C*HCPh), 117.5 (NCH*C*Ph), 126.2, 127.1 ($^{\text{Ph}}$*C*H), 127.4 ($^{\text{Ph}}$*C*$_{\text{ipso}}$) 128.8, 129.6, 130.2 ($^{\text{Ph}}$*C*H), 136.3, 137.2 140.4 ($^{\text{Ph}}$*C*$_{\text{ipso}}$), 157.1 (*C*OH), 166.0 ($^{\text{imine}}$*C*H), Ag*C* not observed. MS (ESI): *m/z* 1107 ([2M − Ag − 2Cl]), 100%. Anal. [Found (calc)] C$_{33}$H$_{45}$N$_3$ClOAg: C 61.72 (61.64), H 7.13 (7.05), N 6.50 (6.53).

Synthesis of [Rh(κ^1-*C*NO(H))Cl] (6). To a dichloromethane (10 mL) solution of **5** (174 mg, 0.43 mmol) was added a dichloromethane (5 mL) solution of [Rh(COD)Cl]$_2$ (105 mg, 0.21 mmol), immediately giving a white precipitate. The mixture was stirred for 1 h at 20 °C and filtered, and the solvent was removed from the filtrate to give a yellow solid, which was purified by flash chromatography (silica, eluted with dichloromethane) to give **6** as a yellow solid. Yield = 192 mg, 60%. ^{1}H NMR (C$_6$D$_6$, 500 MHz): δ 1.10 (3 H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.28 (9 H, s, C(C*H*$_3$)$_3$), 1.47 (3 H, d, ^3J = 6.5 Hz, CH(C*H*$_3$)$_2$), 1.71 (9 H, s, C(C*H*$_3$)$_3$), 1.99–2.11 (7 H, m, $^{\text{c-hex}}$C*H*$_2$), 2.53 (4 H, m, $^{\text{COD}}$C*H*$_2$), 3.13 (1 H, m, $^{\text{c-hex}}$C*H*$_2$)), 3.35 (1 H, m, $^{\text{COD}}$C*H*), 4.22 (1 H, m, $^{\text{c-hex}}$C*H*$_{\text{NHC}}$), 4.77 (1 H, m, $^{\text{COD}}$C*H*), 5.05 (1 H, m, $^{\text{c-hex}}$C*H*$_{\text{imine}}$), 5.37 (1H, m, $^{\text{COD}}$C*H*), 5.57 (1 H, s, $^{\text{Ph}}$C*H*), 5.62 (1 H, m, $^{\text{COD}}$C*H*), 6.10 (1 H, s, NC*H*CPh), 6.35 (1 H, m, NC*H*(CH$_3$)$_2$), 7.11–7.58 (6 H, m, $^{\text{Ph}}$C*H*), 9.25 (1 H, s, $^{\text{imine}}$C*H*), 13.94 (1 H, s, O*H*). ^{13}C{^{1}H} NMR (C$_6$D$_6$, 126 MHz): δ 22.0 (CH(*C*H$_3$)$_2$), 24.4 (*C*H$_2$), 25.0 (CH(*C*H$_3$)$_2$), 26.3 (*C*H$_2$), 27.5 (*C*H$_2$), 29.9 (C(*C*H$_3$)$_3$), 31.0 (*C*H$_2$), 31.5 (C(*C*H$_3$)$_3$), 31.7 (*C*H$_2$), 32.3 (*C*H$_2$), 34.0 (*C*(CH$_3$)$_3$), 34.3(*C*H$_2$), 35.0 (*C*H$_2$), 35.4 (*C*(CH$_3$)$_3$), 54.9 (N*C*H(CH$_3$)$_2$), 63.2($^{\text{c-hex}}$*C*H$_{\text{NHC}}$), 67.8 ($^{\text{COD}}$*C*H), 70.3 ($^{\text{COD}}$*C*H), 71.3($^{\text{c-hex}}$*C*H$_{\text{imine}}$), 97.0 ($^{\text{COD}}$*C*H), 97.4 ($^{\text{COD}}$*C*H), 113.8 (N*C*HCPh)), 119.1 (NCH*C*Ph), 126.5, 127.3, 128.9, 129.5, 129.9 ($^{\text{Ph}}$*C*H), 130.1, 132.5, 136.5, 139.9 ($^{\text{Ph}}$*C*$_{\text{ipso}}$), 158.6 (*C*OH), 168.7 ($^{\text{imine}}$*C*H), 183.3 (d, $^1J_{\text{Rh-C}}$ = 52 Hz, Rh*C*). MS (ESI): *m/z* 710 ([M − Cl]$^+$, 100%). Anal. [Found (calc)] for C$_{41}$H$_{58}$N$_3$ClORh: C 66.05 (65.90); H 7.70 (7.82); N 5.58 (5.62).

Synthesis of [Rh(κ^2-*C*NO(H))][B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (7). To a dichloromethane solution (10 mL) of **6** (152 mg, 0.200 mmol) was added solid Na[B{3,5-(CF$_3$)$_2$C$_6$H$_3$}$_4$] (260 mg, 0.290 mmol), and the mixture was stirred for 15 min at 20 °C. The mixture was then washed with water (2 × 15 mL) and the organic layer retained and dried over MgSO$_4$. On filtration the volatiles were removed from the filtrate under reduced pressure to give **7** as a yellow solid. Yield = 309 mg, 98%. ^{1}H NMR (CDCl$_3$, 700 MHz): δ 1.38 (6 H, d, ^3J = 7 Hz, CH(C*H*$_3$)$_2$), 1.40 (6 H, d, ^3J = 7 Hz, CH(C*H*$_3$)$_2$), 1.44 (9 H, s, C(C*H*$_3$)$_3$), 1.49 (9 H, s, C(C*H*$_3$)$_3$), 1.82–2.45 (12 H, m, $^{c\text{-hex}}$C*H*$_2$ + $^{\text{COD}}$C*H*$_2$), 3.41 (1 H, m, $^{c\text{-hex}}$C*H*$_{\text{imine}}$), 3.76 (1 H, m, $^{\text{COD}}$C*H*), 4.08 (1 H, m, $^{\text{COD}}$C*H*), 4.27 (1 H, m, $^{\text{COD}}$C*H*), 4.77 (1 H, m, $^{\text{COD}}$C*H*), 4.93 (1 H, m, NC*H*(CH$_3$)$_2$), 6.22 (1 H, m, $^{c\text{-hex}}$C*H*$_{\text{NHC}}$), 6.57 (1 H, s, 1 H, s, O*H*), 6.74 (1 H, s, NC*H*CPhN), 7.25–8.08 (12 H, m, $^{\text{Ph}}$C*H*), 8.71 ($^{\text{imine}}$C*H*). ^{13}C{^{1}H} NMR (CDCl$_3$, 175 MHz): δ 23.3 (CH(*C*H$_3$)$_2$), 24.5 (*C*H$_2$), 24.9 (*C*H$_2$), 25.7 (CH(*C*H$_3$)$_2$), 27.9 (*C*H$_2$), 28.7 (*C*H$_2$), 29.3 (*C*H$_2$), 29.5 (*C*H$_2$), 30.1 (C(*C*H$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 32.9 (*C*H$_2$), 34.4 (*C*(CH$_3$)$_3$), 34.6 (*C*(CH$_3$)$_3$), 35.3 (*C*H$_2$),

52.1 (N*C*H(CH$_3$)$_2$), 68.1 ($^{\text{c-hex}}$C*H*$_{\text{NHC}}$), 71.8 ($^{\text{COD}}$*C*H), 71.9 ($^{\text{COD}}$*C*H), 73.2 ($^{\text{c-hex}}$CHH$_{\text{imine}}$), 96.9 ($^{\text{COD}}$*C*H), 99.8 ($^{\text{COD}}$*C*H), 117.0 (N*C*HCPh), 117.5 ($^{\text{BArF}}$*C*H$_{\text{para}}$), 118.9 (NCH*C*Ph), 120.1 ($^{\text{Ph}}$*C*H), 123.2 ($^{\text{Ph}}$*C*$_{\text{ipso}}$), 124.5 (q, $^2J = 273$ Hz, $^{\text{BArF}}$*C*F$_3$), 128.9 (m, $^{\text{BArF}}$F$_3$C*C*$_{\text{ipso}}$), 129.7, 130.1, 130.5, 130.8 ($^{\text{Ph}}$*C*H) 134.8 ($^{\text{BArF}}$*C*H$_{\text{ortho}}$), 135.2, 136.8, 143.2 ($^{\text{Ph}}$*C*$_{\text{ipso}}$) 155.8 (*C*OH), 161.7 (q, $^2J = 51$ Hz, $^{\text{BArF}}$B*C*$_{\text{ipso}}$), 168.6 ($^{\text{imine}}$*C*H), 174.9 (d, $^1J = 51$ Hz, Rh*C*). MS (FAB): *m/z* 710 ([M − BArF]$^+$), 100%. Anal. [Found (calc)] for $C_{73}H_{69}N_3BF_{24}ORh$: C 55.88 (55.70), H, 4.56 (4.42), N 2.72 (2.67).

Synthesis of [Fe(κ^2-C(AgBr)*NO*)$_2$] (8). To a tetrahydrofuran (30 mL) solution of [Fe(II){N(SiMe$_3$)$_2$}$_2$] (82 mg, 0.22 mmol) cooled to −78 °C was added a tetrahydrofuran (20 mL) suspension of **5a** (300 mg, 0.44 mmol) cooled to −78 °C. The mixture was allowed to warm to room temperature over 3 h, giving an orange solution, which was stirred for a further 16 h. The volatiles were removed under reduced pressure, and the resulting red-orange solid was washed with hexane (2 × 10 mL) to give **8** as a red-orange powder. Yield: 256 mg, 81%. M/S (ESI): *m/z* 500 [M − FeAg$_2$Br$_2$]$^+$ 100%, 1133 [M −Ag$_2$Br]$^+$ 55%. Anal. [Found (calc)] $C_{66}H_{88}N_6Ag_2Br_2O_2$: C 56.00 (55.48), H 6.27 (6.21), N 5.80 (5.88).

Catalytic Hydroamination. To a toluene solution (0.5 mL) of piperidine (0.04 mL, 0.5 mmol) and methacrylonitrile (0.135 mL, 2.0 mmol) was added **4** (17.3 mg, 10 μmol). The mixture was then stirred at 40 °C for 12 h. After cooling, toluene (1 mL) was added and the mixture passed through a silica plug, followed by addition of diethylene glycol dibutyl ether (internal standard, 1.123 mL, 0.5 mmol). Yield of 3-(piperidin-1-yl)butanenitrile was determined using GC. Enantiomer separation was achieved on a Cyclosil-B column at 115 °C iso, $t_R = 37.6$ and 38.9 min.

Catalytic Conjugate Addition. To a 10:1 dioxane/water (5 mL) solution of **7** (9.8 mg, 6.24 μmol) was added boronic acid (0.41 mmol), enone (0.21 mmol), and triethyl amine (42 mg, 0.41 mmol) and the solution refluxed for 3 h. After cooling, ethyl acetate (3 mL) was added and the solution washed with water (2 × 5 mL). The organic layer was collected and dried over magnesium sulfate, and the volatiles were removed under reduced pressure to give a pale yellow solid or oil. The solid/oil was subsequently dissolved in 1:1 dichloromethane/hexane solution (3 mL) and passed through a silica plug, and enantioselectivity was determined by chiral HPLC using a Chiralcel OD column, at a flow of 1.0 mL/min (98% hexane, 2% 2-propanol) at 20 °C. $t_R = 8.5$ min 3-phenylcyclopentanone (*S*), 10.8 3-phenylcyclopentanone (*R*); 25.0 3-phenylcyclohexanone (*S*), 26.9 3-phenylcyclohexanone (*R*); 28.4 3-(4-methoxy)phenylcyclopentanone (*S*), 30.1 3-phenylcyclopentanone (*R*); 27.6 3-(4-methoxy)phenylcyclohexanone (*S*), 28.5 3-(4-methoxy) phenylcyclohexanone (*R*); 8.3 4-phenylnonenone (*S*), 8.7 4-phenylnonenone (*R*).

Crystallographic Studies. [Pd(κ^3-*CNO*)Br] (3), [Rh(κ^1-*C*NO-(H))Cl] (6), and [Fe(κ^2-C(AgBr)*NO*)$_2$] (8). Single crystals of **3** and **6** were grown from vapor diffusion of pentane into a benzene solution of the complex. Single crystals of **8** were grown by cooling a hexane/toluene solution of **8** to −40 °C. Crystals were mounted on glass fibers with STP oil and immediately cooled to 110 K in a dinitrogen gas stream on the diffractometer. Data were collected on a Bruker Smart 6000 diffractometer equipped with a molybdenum source with a CCD detector. Structures were solved and refined by full-matrix least-squares on F^2 using SHELX programs.[22] All hydrogen atoms, except H(1) for complex **6**, were placed in calculated positions using a riding model. Atom H(1) was found in a difference map. For complex **8** the toluene of crystallization exhibits some disorder in position. However, attempts to model using two positions failed; hence the single-position model used has large and prolate anisotropic displacement parameters. Atom C(62) was restrained to be more isotropic to prevent a nonpositive definite.

Acknowledgment. The authors thank EPSRC for financial support (G.D. and J.C.F.), Johnson Matthey PLC for palladium and rhodium salts, and Dr. Gideon Grogan for chiral GC analysis of 3-(piperidin-1-yl)butanenitrile.

Supporting Information Available: X-ray crystallographic files in CIF format for complexes **3**, **6**, and **8**. This information is available free of charge via the Internet at http://pubs.acs.org.

OM7009478

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(22) Sheldrick, G. A. *SHELX*; University of Göttingen: Göttingen, Germany, 1997.