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Ruthenium Hydride Complexes of 1,2-Dicyclohexylimidazol-2-ylidene

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The mono and bis N-heterocyclic carbene (NHC) complexes $Ru(ICy)(PPh_3)_2(CO)H_2$ (**1**) and $Ru(ICy)_2(PPh_3)(CO)H_2$ (**2**) (ICy = 1,2-dicyclohexylimidazol-2-ylidene) were isolated from the reaction of $Ru(PPh_3)_3(CO)H_2$ with ICy at elevated temperature. X-ray crystallography revealed that **1** contains a trans arrangement of the PPh_3 ligands with the ICy trans to hydride; in complex **2**, the two ICy ligands are cis to one another. Both **1** and **2** undergo H/D exchange with D_2, as well as reacting rapidly with CO to give $Ru(ICy)(PPh_3)(CO)_3$ (**3**) and $Ru(ICy)_2(CO)_3$ (**4**). Addition of CO_2 to solutions of **2** resulted in insertion into one of the Ru−H bonds to afford both the κ^1- and κ^2-formate complexes $Ru(ICy)_2(PPh_3)(CO)(\kappa^1\text{-}OCHO)H$ (**5**) and $Ru(ICy)_2(CO)(\kappa^2\text{-}OCHO)H$ (**6**). Addition of CO_2 to **1** gave solely $Ru(ICy)(PPh_3)(CO)(\kappa^2\text{-}OCHO)H$ (**7**). The product from reaction of ICy with $Ru(PPh_3)_3HCl$ proves to be solvent dependent, generating two isomers of the mono-NHC complex $Ru(ICy)(PPh_3)_2HCl$ (**8a**,**b**) in dichloromethane but the bis-NHC species $Ru(ICy)_2(PPh_3)HCl$ (**10**) in THF. An agostic interaction between Ru and a β-CH_2 hydrogen of the ICy ligand is apparent both in the X-ray crystal structure of **8a** and also in solution. This interaction is broken upon addition of CO, which yields $Ru(ICy)(PPh_3)_2(CO)HCl$ (**9**). The molecular structure of the coordinatively unsaturated species **10** is devoid of any agostic bonding.

Introduction

Ruthenium complexes have played a pivotal role in the elevation of N-heterocyclic carbene (NHC) ligands to the ubiquitous position that they now occupy in organometallic chemistry, most spectacularly in their applications in metathesis reactions.[1] However, NHC-supported Ru hydride complexes constitute only a relatively small proportion of this group, which is perhaps somewhat surprising, given the high catalytic activity (especially for the hydrogenation of $C{=}C/C{=}O$ bonds)[2] that is associated with tertiary phosphine "analogues" (note that there is now ample evidence to show that NHCs are not simply phosphine mimics, as previously proposed). The research groups of Yi and Nolan,[3] Caulton,[4] Leitner,[5] Morris[6], Chaudret and Sabo-Etienne,[7] and Fogg,[8] along with our group, have prepared mono- and dihydride Ru NHC complexes via substitution of phosphine precursors, while the monocarbene complex $Ru(SIPr)(PCy_3)(CO)HCl$ (SIPr = 1,3-bis(2,6-diisopropylphenyl)-4,5-dihydroimidazol-2-ylidene) is formed upon the decomposition of $Ru(SIPr)(PCy_3)(=CHPh)Cl_2$ in the presence of primary alcohols.[9] C−H bond activation of the coordinated carbene has been established in the N-aryl carbene hydride complexes $Ru(IMes)'(PPh_3)_2(CO)H$ (**A**),[10,11] $Ru(IMes)'(PPh_3)_2H$ (**B**),[6] $Ru(SIMes)'(PPh_3)_2H$,[6] and $Ru(IMes)'(P{-}E)(CO)H$ (P−E = dppp, arphos)[12] and implicated in H/D exchange reactions of $Ru(IMes)(PCy_3)(\eta^2\text{-}H_2)_2H_2$ (**C**) (IMes = 1,2-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene)[5] (Chart 1). Similarly, while we have shown that the N-alkyl com-

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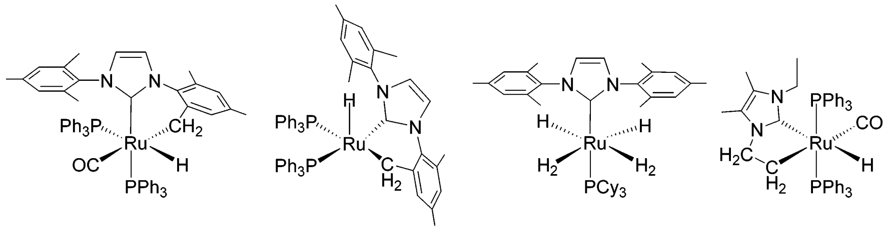
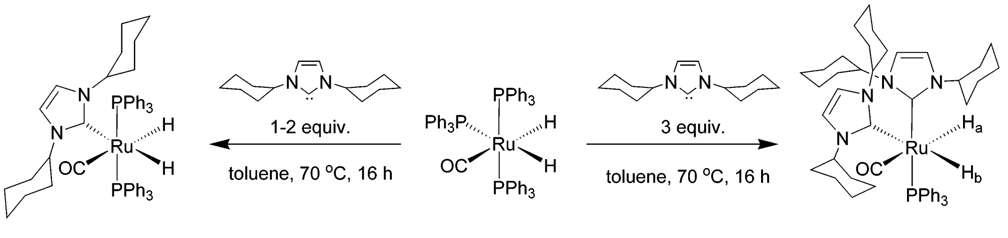
10.1021/om050600c CCC: $30.25

Chart 1



A **B** **C** **D**

Scheme 1



1 **2**

plex $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (IEt_2Me_2 = 1,3-diethyl-4,5-dimethylimidazol-2-ylidene) behaves like the IMes derivative **A**, undergoing facile C−H bond activation to afford $Ru(IEt_2Me_2)'(PPh_3)_2(CO)H$ (**D**) upon addition of a hydrogen acceptor,[13] Morris has found that the more electron rich system $Ru(I^tBu)(PPh_3)_2H_2$ (I^tBu = 1,3-di-*tert*-butylimidazol-2-ylidene) shows no propensity for intramolecular C−H activation.[6,14] This formally 16-electron species is stabilized by a Ru···I^tBu agostic interaction both in solution and in the solid state. Moreover, despite the fact that replacement of two phosphine ligands by bulky IMes groups affords bis-NHC ruthenium complexes such as $Ru(IMes)_2(CO)_2(OH)H$[15] and $Ru(IMes)_2(N_2)(\eta^2\text{-}H_2)H_2$,[5] a second I^tBu cannot be incorporated into $Ru(I^tBu)(PPh_3)_2H_2$.

We now report our studies on the coordination of the less sterically demanding and more flexible ICy ligand (ICy = 1,2-dicyclohexylimidazol-2-ylidene) to $Ru(PPh_3)_3(CO)H_2$ and $Ru(PPh_3)_3HCl$, which generates mono- and bis-ICy complexes in both cases. X-ray crystallography reveals that $Ru(ICy)(PPh_3)_2HCl$ contains a Ru···H−C agostic interaction with a cyclohexyl group of the carbene, whereas the structure of $Ru(ICy)_2(PPh_3)HCl$ shows no agostic bond.

Results and Discussion

Formation of $Ru(ICy)(PPh_3)_2(CO)H_2$ (1) and $Ru(ICy)_2(PPh_3)(CO)H_2$ (2). The reaction of $Ru(PPh_3)_3(CO)H_2$ with 1, 2, 4 or 8 equiv of ICy in toluene at 70 °C produced, in all cases, a mixture of $Ru(ICy)_{3-x}(PPh_3)_x(CO)H_2$ ($x = 0{-}2$). Employing 2 equiv of ICy gave the optimum yield of the monocarbene complex $Ru(ICy)(PPh_3)_2(CO)H_2$ (**1**), which was isolated as a white microcrystalline solid in 29% yield (Scheme 1).[16] Multinuclear NMR spectral data are consistent with a stereochemistry in which the ICy ligand has been incorporated into an equatorial position, trans to the hydride. Thus, in the hydride region of the ^1H NMR spectrum (C_6D_6), two doublets of triplets at δ −5.93 ($J_{HP} = 26.3$, $J_{HH} = 6.0$ Hz) and −9.49 ($J_{HP} = 26.9$, $J_{HH} = 6.0$ Hz) indicate the presence of two trans PPh_3 ligands, both situated cis to the hydrides. The equivalence of the phosphines was further apparent by the appearance of just a single resonance in the $^{31}P\{^1H\}$ NMR spectrum. The geometry in **1** is common to the products formed by other N-alkyl-substituted carbenes (IEt_2Me_2, $I^iPr_2Me_2$, I^iPr_2, I^nPr_2, IMe_4)[13,17] with $Ru(PPh_3)_3(CO)H_2$ and contrasts with the incorporation of the aryl-substituted carbene IMes into an axial position, trans to phosphine as found in $Ru(IMes)(PPh_3)_2(CO)H_2$.[10,18] This difference presumably reflects steric effects; the bulky, rigid IMes ligand can only go cis to one PPh_3, while the alkyl arms of ICy are more “floppy”, enabling it to flex and fit between two cis phosphine ligands.[19,20]

When 3 equiv of ICy was reacted with $Ru(PPh_3)_3(CO)H_2$, the bis- and tris-NHC complexes $Ru(ICy)_2(PPh_3)(CO)H_2$ (**2**) and $Ru(ICy)_3(CO)H_2$ were formed in a ratio

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[13] Burling, S.; Mahon, M. F.; Paine, B. M.; Whittlesey, M. K.; Williams, J. M. J. *Organometallics* **2004**, *23*, 4537.

[14] Examples of C−H activation of I^tBu have been described at low-valent Rh and Ir metal centers. (a) Dorta, R.; Stevens, E. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2004**, *126*, 5054. (b) Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516. (c) Scott, N. M.; Pons, V.; Stevens, E. D.; Heinekey, D. M.; Nolan, S. P. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 2512. There is also a very rare case of C−N bond cleavage in an NHC following reaction of $Ni(cod)_2$ with I^tBu in THF. Caddick, S.; Cloke, F. G. N.; Hitchcock, P. B.; de K. Lewis, A. K. *Angew. Chem., Int. Ed.* **2004**, *43*, 5824.

[15] Jazzar, R. F. R.; Bhatia, P. H.; Mahon, M. F.; Whittlesey, M. K. *Organometallics* **2003**, *22*, 670.

[16] Despite careful stoichiometries being employed in the preparation of **1**, the reaction always resulted in a mixture of **1** and **2**. Separation of the two compounds required multiple recrystallizations, resulting in substantial losses of material. An isolable yield of 29% was typical for **1**, although on occasion, yields of over 40% were achieved.

[17] Abbreviations: $I^iPr_2Me_2$ = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene; I^iPr_2 = 1,3-diisopropyl-imidazol-2-ylidene; I^nPr_2 = 1,3-di-*n*-propylimidazol-2-ylidene; IMe_4 = 1,3,4,5-tetramethylimidazol-2-ylidene. Burling, S.; Mahon, M. F.; Paine, B. M.; Whittlesey, M. K.; Williams, J. M. J. Unpublished results.

[18] Small amounts (ca. 5%) of the “IMes” isomer with the carbene trans to phosphine are observed during the formation of **1**.

[19] Scott, N. M.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2005**, 1815.

[20] Nolan and co-workers have proposed the concept of percentage buried volume ($\%V_{Bur}$) to afford some measure of the steric demands of NHC ligands. ICy is one of the least bulky NHCs and has a $\%V_{Bur}$ value similar to that of PPh_3. (a) Hillier, A. C.; Sommer, W. J.; Yong, B. S.; Petersen, J. L.; Cavallo, L.; Nolan, S. P. *Organometallics* **2003**, *22*, 4322. (b) Dorta, R.; Stevens, E. D.; Scott, N. M.; Costabile, C.; Cavallo, L.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 2485.

of 1.8:1. The latter species proved to be alkane soluble and was readily separated from **2** by washing with hexane,[21] allowing **2** to be isolated as a cream-colored solid in good yield (62%) (Scheme 1). The presence of only one phosphine ligand in **2** was immediately obvious from the appearance of two hydridic doublets of doublets at δ −5.39 (H_a, J_{HP} = 40.1, J_{HH} = 4.4 Hz) and −9.10 (H_b, J_{HP} = 30.2, J_{HH} = 4.4 Hz) in the proton NMR spectrum; the magnitude of the couplings to ^{31}P shows that both hydrides are cis to the PPh_3 ligand, necessitating a cis arrangement of the two ICy groups. Consequently, one of the carbene ligands has restricted rotation, as evidenced by ^1H NMR with three backbone NCH signals observed in a 2:1:1 ratio. Similarly, the cyclohexyl NC*H* signals are observed as two multiplets (δ 5.48, 5.28) and one very broad singlet (δ 5.93), which sharpens into two resonances at δ 6.98 and δ 4.91 at −40 °C. By comparison with the ^1H NMR data for **1**, which also contains two separate imidazole backbone and cyclohexyl NCH signals, this suggests that it is the ICy ligand positioned trans to hydride that shows restricted motion.[22] A comparison of the IR data for the mono- (1922 cm^{-1}) and bis-ICy (1885 cm^{-1}) species reveals a significant enhancement of back-donation to the carbonyl group on incorporation of the second carbene ligand. Experimentally determined and calculated IR data for Cr, Co, Rh, Ir, and Ni NHC complexes have conclusively shown that NHCs are significantly better σ-donors than phosphines, although there are some contradictions within these data as to whether N-alkyl substituents strengthen or weaken the donor power of the carbene relative to N-aryl groups.[19,23]

Structural Characterization of 1 and 2. The X-ray crystal structures of **1** and **2** were established by X-ray crystallography, as shown in Figures 1 and 2, respectively, with pertinent bond angles and distances reported in Tables 1 and 2. Both structures are distorted away from regular octahedral geometries, presumably due to the steric constraints of having both ICy and PPh_3 ligands in their coordination geometries. Thus, in **1**, the trans P(1)−Ru−P(2) angle is compressed to 157.59(6)°, while in **2**, the trans ICy−Ru−PPh_3 angle is similarly constrained (C(17)−Ru−P(1), 161.75(13)°). Of most interest is the comparison of Ru−NHC bond lengths. For the ICy ligand trans to hydride, the Ru−C bond lengths in **1** and **2** are identical (**1**, 2.140(4) Å; **2**, 2.147(3) Å), but the latter is significantly longer than the Ru−ICy distance trans to phosphine in **2** (2.099(3) Å). While steric factors are likely to play some role in explaining these differences, presumably the positioning of a carbene trans to a labilizing hydride group is also important.

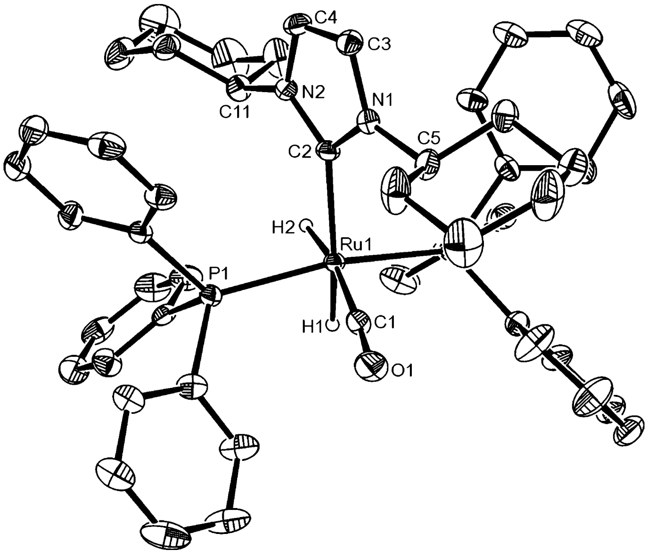

Figure 1. Molecular structure of $Ru(ICy)(PPh_3)_2(CO)H_2$ (**1**). Thermal ellipsoids are shown at the 30% probability level for the major disordered component. Hydrogens attached to carbons are omitted for clarity.

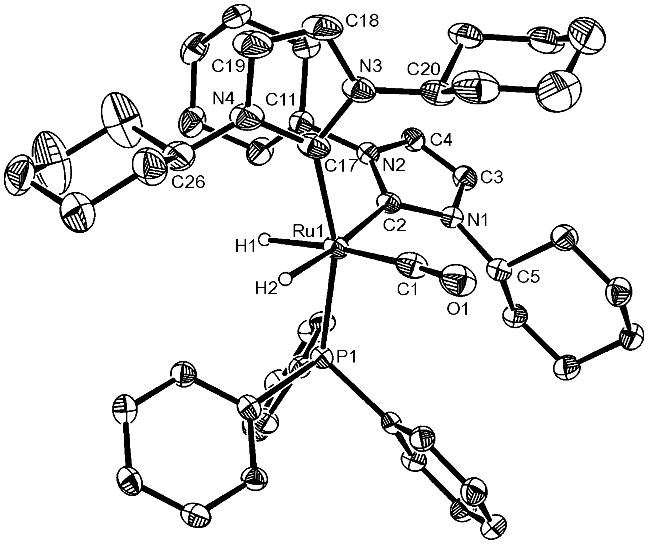

Figure 2. Molecular structure of $Ru(ICy)_2(PPh_3)(CO)H_2$ (**2**). Thermal ellipsoids are shown at the 30% probability level. Hydrogens attached to carbons are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for $Ru(ICy)(PPh_3)_2(CO)H_2$ (1)

Ru(1)−C(1)	1.883(6)	Ru(1)−P(2)	2.3348(14)
Ru(1)−C(2)	2.140(4)	O(1)−C(1)	1.174(7)
Ru(1)−P(1)	2.2889(14)		
C(1)−Ru(1)−C(2)	100.8(2)	C(2)−Ru(1)−P(2)	97.40(13)
C(1)−Ru(1)−P(1)	91.28(18)	P(1)−Ru(1)−P(2)	157.59(6)
C(2)−Ru(1)−P(1)	99.45(13)	O(1)−C(1)−Ru(1)	175.7(5)
C(1)−Ru(1)−P(2)	99.98(19)		

Reactivity of 1 and 2 toward D_2, CO, and CO_2. Both **1** and **2** react with D_2 at elevated temperature via H/D exchange. Thus, the ^1H NMR spectrum of a sample of **1** heated at 50 °C under 1 atm of D_2 for 16 h showed the appearance of two broad triplet hydride resonances, indicating formation of the two isotopomers of Ru(ICy)-

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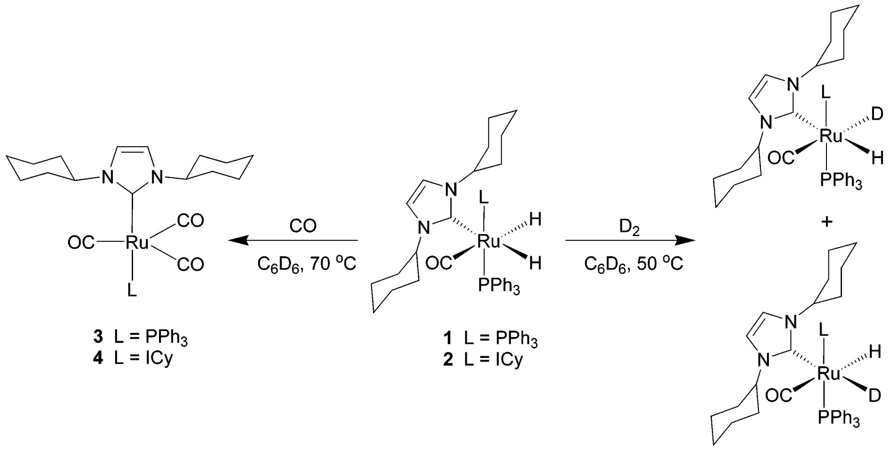
[21] Attempts to separate $Ru(ICy)_3(CO)H_2$ from free PPh_3 in the hexane washings were unsuccessful, preventing isolation of the complex.

[22] Restricted rotation of the NHC was reported in $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$.[13]

[23] For example, ν_{CO} occurs at 1937 cm^{-1} for $CpCo(PPh_3)(CO)$ and 1921 cm^{-1} for CpCo(IPr)(CO) (IPr = 1,2-bis(2,6-diisopropylphenyl)-imidazol-2-ylidene). Simms, R. W.; Drewitt, M. J.; Baird, M. C. *Organometallics* **2002**, *21*, 2958. IR studies on $Ni(NHC)(CO)_3$ afford IR data consistent with alkyl substituens, making the NHC ligand more donating (e.g. $Ni(IMes)(CO)_3$: 2050.7, 1969.8 cm^{-1}; $Ni(ICy)(CO)_3$; 2049.6, 1964.6 cm^{-1}). Dorta, R.; Stevens, E. D.; Hoff, C. D.; Nolan, S. P. *J. Am. Chem. Soc.* **2003**, *125*, 10490. However, in *cis*-$Rh(NHC)(CO)_2Cl$ (Doyle, M. J.; Lappert, M. F.; Pye, P. L.; Terreros, P. *J. Chem. Soc., Dalton Trans.* **1984**, 2355), *cis*-$Ir(NHC)(CO)_2Cl$ (Chianese, A. R.; Li, X.; Janzen, M. C.; Faller, J. W.; Crabtree, R. H. *Organometallics* **2003**, *22*, 1663), *trans*-$Rh(NHC)_2(CO)I$ (Martin, H.; James, N. H.; Aitken, J.; Gaunt, J. A.; Adams, H.; Haynes, A. *Organometallics* **2003**, *22*, 4451), and $Cr(NHC)(CO)_5$ (Lee, M.-T.; Hu, C.-H. *Organometallics* **2004**, *23*, 976), this trend is not always obeyed (e.g.: *trans*-$Rh(IMes)_2(CO)I$, 1937 cm^{-1}; *trans*-$Rh(IMe)_2(CO)I$, 1943 cm^{-1}).

Scheme 2



3 L = PPh$_3$
4 L = ICy

1 L = PPh$_3$
2 L = ICy

L = PPh$_3$ or ICy

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ru(ICy)$_2$(PPh$_3$)(CO)H$_2$ (2)

Ru(1)−C(1)	1.865(4)	Ru(1)−P(1)	2.3035(8)
Ru(1)−C(2)	2.147(3)	C(1)−O(1)	1.160(4)
Ru(1)−C(17)	2.099(3)		
C(1)−Ru(1)−C(2)	101.00(14)	C(17)−Ru(1)−P(1)	161.75(13)
C(17)−Ru(1)−C(2)	91.06(13)	C(2)−Ru(1)−P(1)	99.45(9)
C(1)−Ru(1)−P(1)	98.81(12)	O(1)−C(1)−Ru(1)	174.7(3)

(PPh$_3$)$_2$(CO)HD (Scheme 2).[24] The reaction was complete after heating for a further 3 days. The rate of reaction for the bis-ICy species **2** proved to be much slower than that of **1**, requiring 2 days of heating at 50 °C to produce only minor deuterium exchange; the reaction was still not complete after 1 week of heating.

Complexes **1** and **2** react with CO to produce the corresponding five-coordinate tricarbonyl complexes Ru(ICy)(PPh$_3$)(CO)$_3$ (**3**) and Ru(ICy)$_2$(CO)$_3$ (**4**), respectively (Scheme 2). Both complexes show spectroscopic features similar to those reported for Ru(IMes)(PPh$_3$)(CO)$_3$ and Ru(IMes)$_2$(CO)$_3$.[6,15] Thus, the $^{13}C\{^1H\}$ NMR spectrum of **3** displays a doublet carbonyl resonance at δ 211.7 ($J_{CP} = 15.5$ Hz) comparable to that for the IMes species (δ 211.4, $J_{CP} = 12.6$ Hz). The IR spectrum (recorded in C_6D_6) contained a single broad band at 1873 cm^{-1}.

As in the case of reactions with D_2, the reaction of complex **2** with CO is considerably slower than for **1**; attempts to drive conversion to **4** through to completion, by heating, led to the appearance of additional products, including complex **3** and Ru(PPh$_3$)$_3$(CO)H$_2$. As a consequence, **4** could not be isolated in sufficient purity to allow structural characterization or elemental analysis. However, NMR spectroscopy shows that the compound clearly contains two *trans*-ICy ligands by the appearance of only one set of NHC resonances. Repeated attempts to record solution IR data consistently afforded a spectrum containing four ν_{CO} bands (2009, 1930, 1870, and 1839 cm^{-1}), perhaps suggesting the existence of more than one conformer of the complex in solution.

Addition of CO_2 to a benzene solution of **2** generated a mixture of the κ^1- and κ^2-formate species Ru(ICy)$_2$(PPh$_3$)(CO)(κ^1-OCHO)H (**5**) and Ru(ICy)$_2$(CO)(κ^2-OCHO)H (**6**) (Scheme 3) as a result of insertion into one of the Ru−H bonds. The former, which proved to be insoluble in C_6D_6 and only partially soluble in THF-d_8, showed a significantly lower field hydride signal (δ −6.90, $J_{HP} = 27.9$ Hz) in the proton NMR spectrum, consistent with (i) a coordinatively saturated ruthenium complex and (ii) the hydride ligand being situated trans to CO[25] (the magnitude of J_{PH} implies a *cis*-P−Ru−H geometry and, thus, a *trans*-H−Ru−CO arrangement). In the IR spectrum, an absorption band at 1618 cm^{-1} confirmed the monodentate coordination mode of the Ru−OC(O)H moiety.[26] Upon heating **5** in THF-d_8 to aid dissolution, complete conversion to **6** took place within 30 min. Complex **6** was characterized through the appearance of high-field (δ −18.35) and low-field (δ 8.19) singlets in the ^1H NMR spectrum for the hydride and formate groups, respectively. Use of $^{13}CO_2$ led to splitting of the formate into a doublet with $J_{CH} = 195.0$ Hz. A change in relative disposition of the two ICy ligands takes place upon conversion of **5** to **6**, as indicated by the NCH backbone resonances. In **5**, the two doublets and a multiplet (integrating as 1:1:2) implies a cis arrangement of the two NHCs, while the appearance of just a singlet in the spectrum of **6** is consistent with the carbenes being trans to one another. Confirmation of the κ^2 coordination mode in **6** was provided by IR spectroscopy, which revealed a band for $\nu(^{12}CO_2)_{asym}$ at 1566 cm^{-1}, much lower in frequency than that associated with **5**.[27]

Due to the difficulty associated with synthesising **1** in large quantities, only a preliminary study was carried out on its reactivity toward CO_2 (Scheme 4). Insertion of CO_2 into a Ru−H bond gives Ru(ICy)(PPh$_3$)(CO)(κ^2-OCHO)H (**7**), although in contrast to **2**, elevated temperatures and longer reaction times are required,

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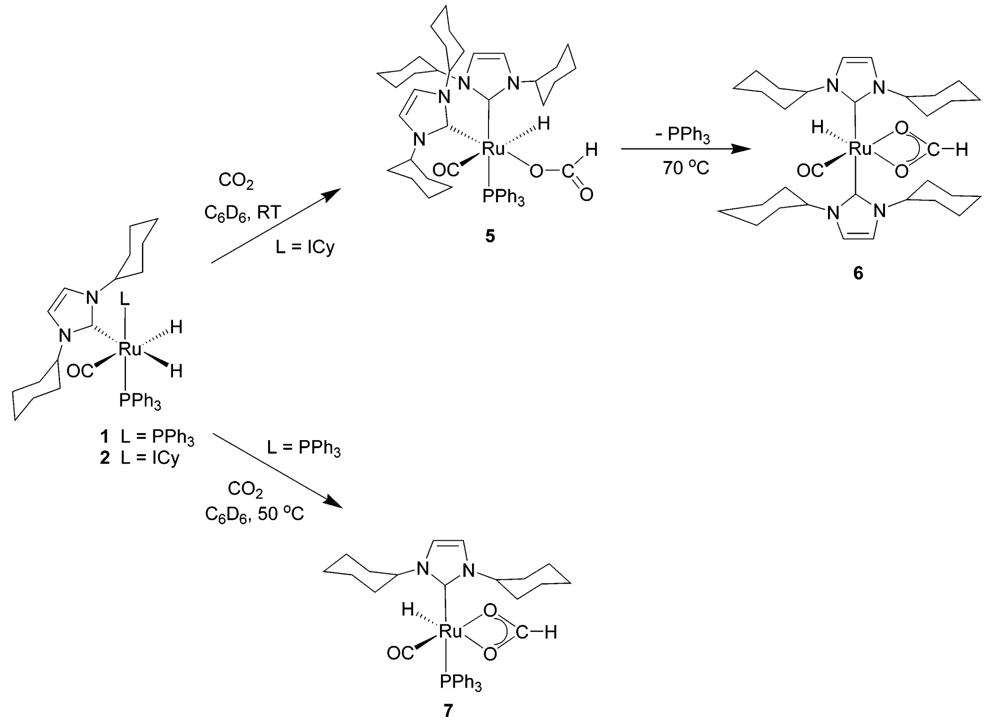
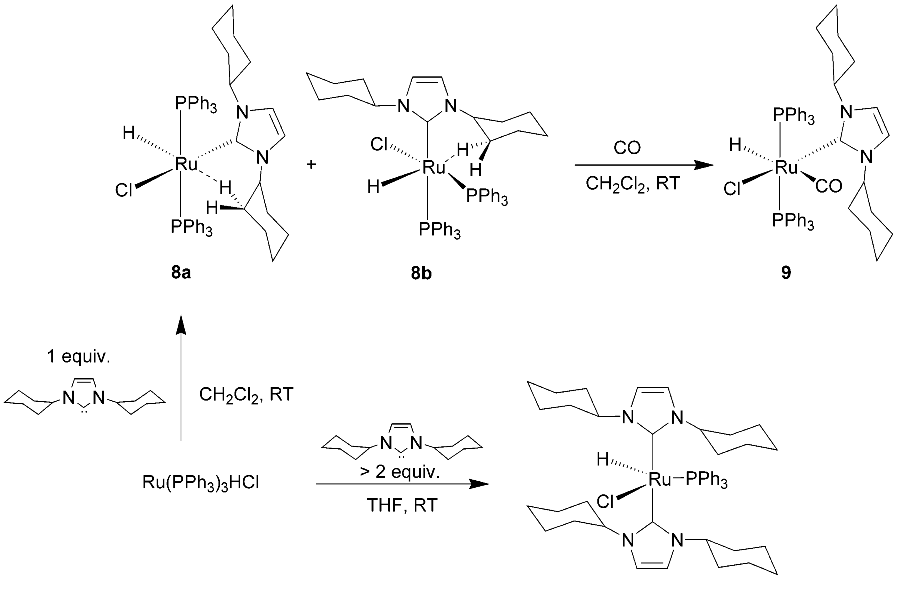
Scheme 3



Scheme 4



precluding any observation of a κ^1 species on the reaction pathway. The proton NMR data for **7** (Ru−H, δ −17.05, $J_{\mathrm{HP}} = 23.1$ Hz; Ru−O^{13}C(O)H, δ 7.87, $J_{\mathrm{HC}} = 199.0$ Hz) are comparable to those for **6**, apart from the additional coupling to phosphorus on the hydride. The appearance of one set of ICy resonances indicates that the carbene is free to rotate and suggests that it is situated in an axial position, trans to phosphine. The IR spectrum displays an absorption band at 1560 cm^{-1}, supporting a κ^2 binding mode for the formate group.

Synthesis and Structural Characterization of Ru(ICy)(PPh$_3$)$_2$HCl (8). We have extended our studies on the coordination chemistry of ICy by probing reactions with the hydride chloride complex Ru(PPh$_3$)$_3$HCl, which as described earlier has been used by Morris and co-workers as a precursor for mono-IMes, -SIMes, and -I^{t}Bu complexes.[6] They have shown that, in refluxing THF, 2 equiv of I^{t}Bu generates the coordinatively unsaturated and highly reactive fragment “Ru(I^{t}Bu)(PPh$_3$)$_2$”, which undergoes facile oxidative addition of H$_2$ to yield two isomers of the agostic complex Ru(I^{t}Bu)(PPh$_3$)$_2$H$_2$. We have found that elevated temperatures are not required for reaction of Ru(PPh$_3$)$_3$HCl with ICy; thus, addition of 1 equiv of ICy to Ru(PPh$_3$)$_3$HCl in CH$_2$Cl$_2$ at room temperature resulted in the rapid formation of Ru(ICy)(PPh$_3$)$_2$HCl, which exists as a mixture of isomers (**8a**,**b**) (Scheme 4).[28] The structure of **8a**, determined by X-ray crystallography, was found to have a distorted-octahedral geometry (P(1)−Ru(1)−P(2), 161.68(3)°) in which the sixth coordination site at

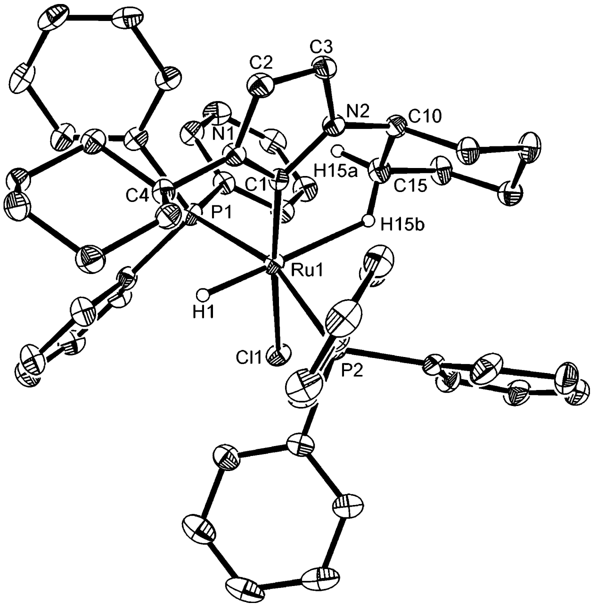


Figure 3. Molecular structure of Ru(ICy)$(PPh_3)_2$HCl (**8a**). Thermal ellipsoids are shown at the 30% probability level. Hydrogens attached to carbons, other than those illustrated, are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Ru(ICy)$(PPh_3)_2$HCl (8a)

Ru(1)−C(1)	2.003(3)	Ru(1)−P(2)	2.3135(9)
Ru(1)−P(1)	2.3360(9)	Ru(1)−Cl(1)	2.4607(8)
Ru(1)−H(15B)	2.072(5)	Ru(1)−C(15)	2.808(5)
C(1)−Ru(1)−P(2)	95.34(10)	C(1)−Ru(1)−P(1)	97.47(10)
P(2)−Ru(1)−P(1)	161.68(3)	C(1)−Ru(1)−Cl(1)	173.77(9)
P(2)−Ru(1)−Cl(1)	86.07(3)	P(1)−Ru(1)−Cl(1)	82.62(3)

the metal is filled by an agostic C−H interaction with a β-CH_2 group of one of the cyclohexyl arms (Figure 3). Selected bond distances and angles are given in Table 3. In comparison to the Ru−ICy bond lengths in **1** and **2**, the distance in **8a** is significantly shorter (Ru(1)−C(1), 2.003(3) Å), presumably reflecting not only the strong donor characteristics and low steric demands of the ICy ligand but also simply the availability of more space at the metal center. The agostic Ru−C distance (Ru(1)−C(15), 2.808(5) Å) is more than 1.3 Å shorter than the next nearest interaction with a cyclohexyl CH_2 group (Ru(1)−C(14), 4.113(5) Å), while both the Ru(1)····H(15B) distance (2.072(5) Å) and Ru(1)····H(15B)−C(15) angle (129.6(3)°) are consistent with other data in the literature.[29] The relative orientations of the cyclohexyl groups with respect to the imidazole ring in the carbene merit note, in that the angles between the latter and the least-squares planes subtended by atom sets C5, C6, C8, C9 and C11, C12, C14, C15 are 89 and 50°, respectively. The latter 50° angle reflects rotation of the cyclohexyl ring implicated in the agostic interaction around the N2−C10 vector, such that the hydrogen on the α-carbon (C10) is cis to that on imidazole C3. This is unique as, in the absence of agostic interactions, the α-cyclohexyl hydrogen atoms are always trans to those on imidazole, thus affording the least sterically demanding orientation for the pendant rings on the carbene as a whole, with respect to the metal center.

Examples involving agostic interactions to the cyclohexyl groups of phosphines are not particularly common,[30] and certainly in ruthenium chemistry, activation/dehydrogenation of the cyclohexyl ring is a more documented reaction.[31] Interestingly, with respect to reactions of the ICy ligand, Herrmann and co-workers have shown that protonation of Cp*Ir(ICy)Me_2 also leads to dehydrogenation of one of the cyclohexyl rings,[32] whereas Cp*Ru(ICy)Cl is stable to any form of activation of the carbene, even though it is coordinatively unsaturated.[33]

Both **8a** and **8b** are detectable in solution at room temperature through the appearance of two high-field hydride resonances in the ^{1}H NMR spectrum, represented by a triplet at δ −26.50 (J_{HP} = 23.1 Hz) and a "flattened" triplet at δ −26.76, respectively (Figure 4). At −20 °C, this latter resonance sharpens to a doublet of doublets (J_{HP} = 35.1, 23.1 Hz). Both high-field chemical shifts are consistent with the hydride being trans to the agostic C−H bond in the two isomers, while the coupling constants for **8b** indicates a *cis*-$(PPh_3)_2$ geometry, as shown in Scheme 4. Proton NMR spec-

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[28] A reviewer has raised a point about performing reactions with NHCs in chlorinated solvents. The fact that **8a/b** is formed quickly (within 1 h) implies that any incompatibility of ICy with CH_2Cl_2 that leads to NHC degradation should not be problematic. In fact, we see no evidence by ^{1}H NMR spectroscopy for any reaction of ICy with CH_2Cl_2 (ICy dissolved in C_6D_6 in the presence of 10 equiv of CH_2Cl_2) after 2 h at room temperature, although after 16 h, the spectrum had changed significantly, with several low-field resonances present above δ 9. Others have noted previously that chlorinated solvents will react with both aryl- and alkyl-substituted NHCs. (a) Arduengo, A. J., III; Davidson, F.; Dias, H. V. R.; Goerlich, J. R.; Khasnis, D.; Marshall, W. J.; Prakasha, T. K. *J. Am. Chem. Soc.* **1997**, *19*, 12742. (b) Kuhn, N.; Fahl, J.; Fawzi, R.; Maichle-Mossmer, C.; Steimann, M. *Z. Naturforsch., B* **1998**, *53*, 720. (c) Cole, M. L.; Jones, C.; Junk, P. C. *New J. Chem.* **2002**, *262*, 1296.

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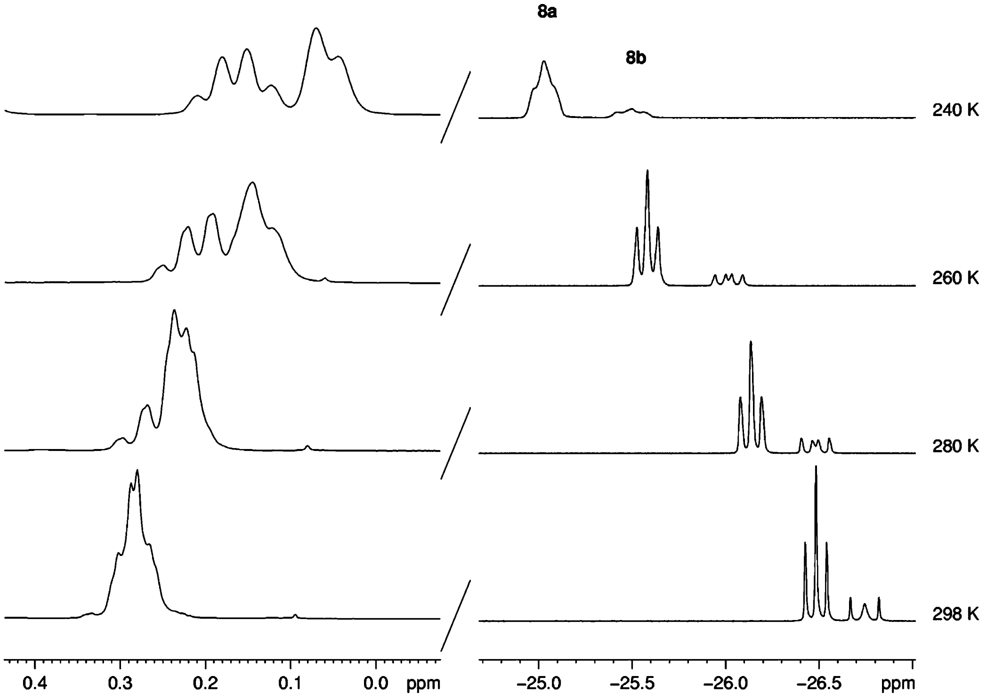

Figure 4. Variable-temperature ^1H NMR spectra (400 MHz, CD_2Cl_2), showing the agostic cyclohexyl and hydride regions of a mixture of **8a** and **8b**.

troscopy also indicates that the agostic interaction in **8a** is retained in solution. An unusual broad multiplet signal at δ 0.28 in the ^1H NMR spectrum at room temperature was assigned to the agostic protons of **8a** (Figure 4). A 2D NOESY experiment confirmed that this signal showed contacts with the ruthenium hydride at δ −26.50, as well as with the neighboring CH of the cyclohexyl group at δ 3.77. The feature at δ 0.28 shows some dynamic behavior upon cooling to −30 °C (a temperature at which the hydride signals begin to broaden), clearly resolving into more than one signal; these features are still quite broad and most probably still highly coupled to other cyclohexyl protons. We propose that the broadness could arise from exchange of the two methylene protons on the cyclohexyl group.

The two isomers appear in a ratio of ca. 1:0.4 at room temperature and undergo interconversion, as demonstrated conclusively by 2D EXSY NMR. Upon cooling to −30 °C, the ratio alters further in favor of **8a** (1:0.25), although **8a** is never obtained as the sole product; warming to 50 °C resulted in the appearance of a new low-field singlet resonance at δ 10.81, consistent with the formation of the dicyclohexylimidazolium chloride salt[34] via reductive elimination from the metal center.[35]

Addition of 1 atm of CO to a solution of **8a/8b** in CH_2Cl_2 breaks the agostic interaction to afford the six-coordinate carbonyl complex $Ru(ICy)(PPh_3)_2(CO)HCl$ (**9**), as a yellow microcrystalline solid in moderate yield (Scheme 4). The hydride resonance for **9** is shifted significantly downfield to δ −2.37, in line with it now being positioned trans to the carbonyl. Crystals of complex **9** suitable for X-ray crystallography were grown from benzene/pentane. The molecular structure, shown in Figure 5, confirms the loss of the agostic cyclohexyl interaction and incorporation of the CO trans to hydride. As one goes from **8a** to **9**, the P−Ru−P angle increases to 168.619(17)° and the Ru−ICy bond lengthens to 2.0779(16) Å (Table 4), although it is worth noting that the change in Ru−carbene bond length is not accompanied by any change in the Ru−Cl distances (**8a**, 2.4607(8) Å; **9**, 2.4670(4) Å).

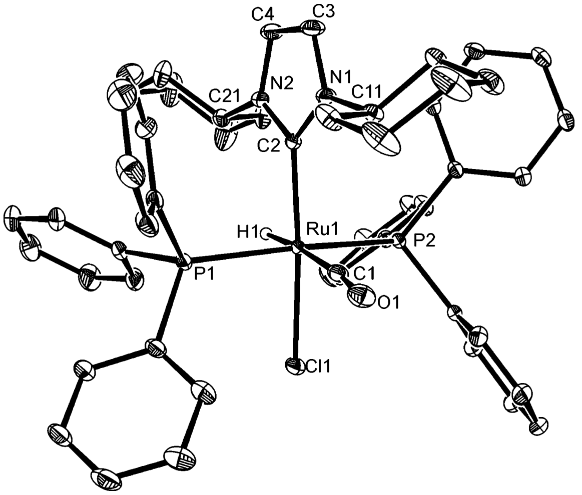

Figure 5. Molecular structure of $Ru(ICy)(PPh_3)_2(CO)HCl$ (**9**). Thermal ellipsoids are shown at the 30% probability level. Hydrogens attached to carbons are omitted for clarity.

Synthesis and Structural Characterization of $Ru(ICy)_2(PPh_3)HCl$ (10). The reaction of ICy with $Ru(PPh_3)_3HCl$ followed a different route upon changing the solvent from CH_2Cl_2 to THF. Addition of 1 equiv of ICy to a THF solution of $Ru(PPh_3)_3HCl$ at room temperature gave a mixture of starting material, **8a,b**, and the bis-ICy complex $Ru(ICy)_2(PPh_3)HCl$ (**10**) in a ratio of ca. 2.1:2.1:1:6.7. Upon addition of a second equivalent of carbene, there was complete conversion through to **10**

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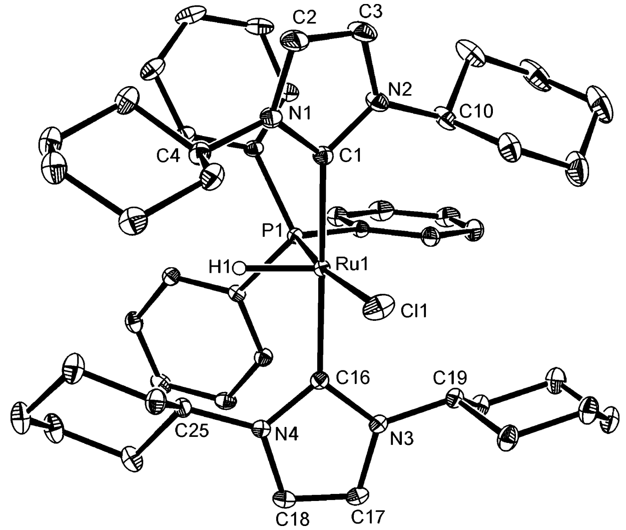

Figure 6. Molecular structure of Ru(ICy)$_2$(PPh$_3$)HCl (**10**). Thermal ellipsoids are shown at the 30% probability level. Hydrogens attached to carbons are omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Ru(ICy)(PPh$_3$)$_2$(CO)HCl (9)

Ru−C(4)	1.916(2)	Ru−C(1)	2.0779(16)
Ru−P(1)	2.3466(4)	Ru−P(2)	2.3622(4)
Ru−Cl(1)	2.4670(4)	C(4)−O	1.131(2)
C(4)−Ru−C(1)	100.89(7)	C(4)−Ru−P(1)	92.15(5)
C(1)−Ru−P(1)	92.37(4)	C(4)−Ru−P(2)	97.62(5)
C(1)−Ru−P(2)	91.50(4)	P(1)−Ru−P(2)	168.619(17)
C(4)−Ru−Cl(1)	91.41(5)	C(1)−Ru−Cl(1)	167.67(5)
P(1)−Ru−Cl(1)	88.018(15)	P(2)−Ru−Cl(1)	85.933(15)

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Ru(ICy)$_2$(PPh$_3$)HCl (10)

Ru−C(1)	2.1044(17)	Ru−C(16)	2.0752(16)
Ru−P(1)	2.1944(4)	Ru−Cl(1)	2.4516(5)
C(16)−Ru−C(1)	171.82(6)	C(16)−Ru−P(1)	93.91(5)
C(1)−Ru−P(1)	93.91(5)	C(16)−Ru−Cl(1)	86.21(5)
C(1)−Ru−Cl(1)	86.50(5)	P(1)−Ru−Cl(1)	170.275(18)

(Scheme 4).[36] As expected, the ^{1}H NMR spectrum of **10** displayed a very high field doublet hydride signal at δ −31.23[37] and one set of ICy resonances integrating in a ratio of 2:1 to the hydride.

Unequivocal evidence for the structure and stereochemistry of **10** was provided by X-ray crystallography. The molecular structure (Figure 6, Table 5) reveals a five-coordinate square-pyramidal geometry at ruthenium, with the hydride ligand in the apical site. It is noteworthy that the phosphorus atom is located 0.45 Å out of the least-squares plane of the remaining atoms (Ru1, C1, Cl1, and C16) forming the pyramid base. This distortion may be attributed, in part, to steric considerations. In particular, collision between the phenyl rings based on C31 and C43 with the cyclohexyl moieties based on C4 and C25 is prevented, while the aryl ring based on C37 is concomitantly oriented such that it utilizes the cleft between the cyclohexyl rings based on C10 and C19. The closest Ru···CH$_2$ distance is 3.878(5) Å, beyond the range for any agostic interaction.

Conclusions

The substitution of one or two PPh$_3$ ligands in Ru(PPh$_3$)$_3$(CO)H$_2$ and Ru(PPh$_3$)$_3$HCl by the alkyl substituted N-heterocyclic carbene ICy has allowed the isolation and full characterization of 16- and 18-electron mono- and bis-ICy complexes. In the case of Ru(ICy)$_2$(PPh$_3$)(CO)H$_2$ (**2**), the carbenes adopt a cis configuration, which we assume to arise from the ability of the cyclohexyl rings to flex their shape. Both Ru(ICy)(PPh$_3$)$_2$(CO)H$_2$ (**1**) and **2** react with D$_2$, CO, and CO$_2$; insertion of CO$_2$ into the Ru−H bonds affords κ^2-formate complexes as the ultimate products.

Of most interest is the reactivity of ICy with Ru(PPh$_3$)$_3$HCl, which yields mono- and bis-ICy complexes, but only upon variation of the solvent. We are currently trying to elucidate the role that the solvent plays in dictating these products. In comparison to the work of Morris on Ru(I^{t}Bu)(PPh$_3$)$_2$H$_2$, which is stabilized by an agostic interaction to a *tert*-butyl methyl group on the NHC, we find that Ru(ICy)(PPh$_3$)$_2$HCl (**8a**,**b**) is also stabilized by agostic bonding, in this case through a β-CH$_2$ group on a cyclohexyl arm. In contrast, the more electron rich species Ru(ICy)$_2$(PPh$_3$)HCl (**10**) shows no evidence for an agostic interaction, nor indeed any willingness to undergo intramolecular bond activation. This is relevant in light of the work from Nolan's group indicating that the isoelectronic Rh(III) species Rh(I^{t}Bu)(I^{t}Bu)′HCl contains not only a C−H activated NHC but also a second agostically bound carbene and is, moreover, subject to further C−H activation chemistry.[14a,b] While any differences may simply be due to the different steric bulks of I^{t}Bu and ICy, it suggests that further developments are likely in the activation of NHCs by low-valent metal complexes.

Experimental Section

General Comments. All manipulations were carried out using standard Schlenk, high-vacuum, and glovebox techniques. Solvents were purified using an MBraun SPS solvent system (toluene, THF, pentane) or under a nitrogen atmosphere from purple solutions of sodium benzophenone ketyl (benzene, hexane), Mg/I$_2$ (ethanol, methanol), or calcium hydride (dichloromethane). Deuterated solvents (Aldrich) were vacuum-transferred from potassium (C$_6$D$_6$, C$_6$D$_5$CD$_3$, and THF-d_8) or calcium hydride (CD$_2$Cl$_2$). Deuterium gas (Isotec, 99.8%), CO (BOC, 99.9%), CO$_2$, and ^{13}CO$_2$ (both Aldrich) were used as received. Ru(PPh$_3$)$_3$(CO)H$_2$ and Ru(PPh$_3$)$_3$HCl were prepared according to the literature.[38,39] ICy was prepared according to a method described by Nolan. NMR spectra were recorded on Bruker Avance 300 and 400 MHz NMR spectrometers and referenced (^{1}H; ^{13}C{^{1}H}) as follows: benzene (δ 7.15; δ 128.0), toluene (δ 2.09; δ 21.3), THF (δ 3.58), dichloromethane (δ 5.32; δ 53.7). ^{31}P{^{1}H} NMR chemical shifts were referenced externally to 85% H$_3$PO$_4$ (δ 0.0). 2D experiments (^{1}H COSY, ^{1}H−X (X = ^{13}C, ^{31}P) HMQC/HMBC, EXSY, NOESY) were performed using standard Bruker pulse sequences. IR spectra were recorded either as solutions in C$_6$D$_6$ or as Nujol mulls on a Nicolet Protégé 460 FTIR spectrometer. Elemental analyses were performed either at the University of Bath or by Elemental Microanalysis Ltd, Okehampton, Devon, U.K.

Ru(ICy)(PPh$_3$)$_2$(CO)H$_2$ (1). A toluene solution (10 mL) of ICy (153 mg, 0.66 mmol) and Ru(PPh$_3$)$_3$(CO)H$_2$ (300 mg, 0.33

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[36] Compound **10** is not observed at all upon reaction of Ru(PPh$_3$)$_3$HCl with ICy (even with >1 equiv) in CH$_2$Cl$_2$.

[37] Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2000**, *19*, 3429.

[38] Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 48.

[39] Schunn, R. A.; Wonchoba, E. R.; Wilkinson, G. *Inorg. Synth.* **1971**, *13*, 131.

mmol) was heated with stirring (70 °C, 16 h) in a Schlenk flask under argon. The volatiles were removed in vacuo, and the residue was washed with ethanol (2 × 10 mL) and filtered. The resulting cream-colored solid was dissolved in benzene and layered with ethanol, affording $Ru(ICy)(PPh_3)_2(CO)H_2$ as fine cream-colored crystals. Yield: 85 mg (29%). Anal. Found (calcd) for $C_{52}H_{56}N_2OP_2Ru$: C, 70.3 (70.33); H, 6.30 (6.36); N, 3.32 (3.15). ^1H NMR (C_6D_6, 298 K): δ 7.85−7.80 (m, 12H, PPh_3), 7.09−6.99 (m, 18H, PPh_3), 6.58 (d, J_{HH} = 1.6 Hz, 1H, im C*H*), 6.38 (d, J_{HH} = 1.6 Hz, 1H, im C*H*), 5.18 (m, 1H, Cy C*H*), 4.80 (m, 1H, Cy C*H*), 1.73 (m, 2H, Cy C*H*$_2$), 1.49−0.57 (m, 18H, Cy), −5.93 (dt, J_{HP} = 26.3, J_{HH} = 6.0 Hz, 1H, Ru−*H*), −9.49 (dt, J_{HP} = 26.9, J_{HH} = 6.0 Hz, 1H, Ru−*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 62.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 206.6 (t, J_{CP} = 9.5 Hz, Ru−*C*O), 193.1 (t, J_{CP} = 7.8 Hz, Ru−C_{ICy}), 140.5 (virtual triplet (vt), J = 19.8 Hz, PPh_3), 133.4 (vt, J = 6.0 Hz, PPh_3), 127.6 (s, PPh_3), 126.7 (vt, J = 4.3 Hz, PPh_3), 116.0 (s, im *C*H), 115.4 (s, im *C*H), 58.5 (s, *C*H, Cy), 58.2 (s, *C*H, Cy), 33.3 (s, *C*H$_2$), 32.0 (s, *C*H$_2$), 25.1 (s, *C*H$_2$), 25.0 (s, *C*H$_2$), 24.9 (s, *C*H$_2$), 24.7 (s, *C*H$_2$). IR (C_6D_6, cm^{-1}): 1922 (ν_{CO}).

$Ru(ICy)_2(PPh_3)(CO)H_2$ (2). A toluene (20 mL) solution of ICy (230 mg, 1.0 mmol) and $Ru(PPh_3)_3(CO)H_2$ (300 mg, 0.33 mmol) was heated with stirring (70 °C, 16 h) in a Schlenk flask under argon. The mixture was heated. The volatiles were removed in vacuo, and the residue was washed with hexane (3 × 10 mL) and filtered. The resulting cream-colored solid was dissolved in the minimum amount of THF and layered with hexane, affording $Ru(ICy)_2(PPh_3)(CO)H_2$ as small cream-colored crystals. Yield: 175 mg (62%). Anal. Found (calcd) for $C_{49}H_{65}N_4OPRu$: C, 68.2 (68.58); H, 7.53 (7.63); N, 6.28 (6.53). ^1H NMR (C_6D_6, 298 K): δ 7.88 (m, 6H, PPh_3), 7.12 (m, 6H, PPh_3), 7.04 (m, 3H, PPh_3), 6.63 (br s, 2H, im C*H*), 6.59 (d, J_{HH} = 2.2 Hz, 1H, im C*H*), 6.56 (d, J_{HH} = 2.2 Hz, 1H, im C*H*), 5.93 (br s, 2H, Cy C*H*), 5.48 (m, 1H, Cy C*H*), 5.28 (m, 1H, Cy C*H*), 2.91 (m, 1H, Cy C*H*$_2$), 2.37 (m, 2H, Cy C*H*$_2$), 1.87−0.77 (m, 37H, Cy), −5.39 (dd, J_{HP} = 40.1, J_{HH} = 4.4 Hz, 1H, Ru−*H*), −9.10 (dd, J_{HP} = 30.2, J_{HH} = 4.4 Hz, 1H, Ru−*H*). $^{31}P\{^1H\}$ (C_6D_6, 298K): δ 60.8 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 207.3 (d, J_{CP} = 8.6 Hz, Ru−*C*O), 197.7 (d, J_{CP} = 6.9 Hz, Ru−C_{ICy}), 192.4 (d, J_{CP} = 82.8 Hz, Ru−C_{ICy}), 144.0 (d, J_{CP} = 34.5 Hz, PPh_3), 134.0 (d, J_{CP} = 11.2 Hz, PPh_3), 127.6 (s, PPh_3), 127.1 (d, J_{CP} = 8.6 Hz, PPh_3), 116.1 (s, im *C*H), 116.0 (s, im *C*H), 59.3 (s, Cy *C*H), 59.2 (s, Cy *C*H), 58.0 (s, Cy *C*H), 36.1 (s, Cy *C*H$_2$), 34.0 (s, Cy *C*H$_2$), 33.1 (s, Cy *C*H$_2$), 32.4 (s, Cy *C*H$_2$), 25.7−25.4 (7 × Cy *C*H$_2$). IR (C_6D_6, cm^{-1}): 1885 (ν_{CO}).

Reaction of 1 with D_2. A sample of **1** (5.4 mg, 6.1 μmol) in C_6D_6 (0.6 mL) in a NMR tube fitted with a resealable PTFE tap was degassed (freeze−pump−thaw ×3) before 1 atm of D_2 was added. The sample was then heated for 16 h at 50 °C. ^1H NMR spectroscopy indicated incomplete H/D exchange into both Ru−H resonances at δ − 5.93 and − 9.49. Continued heating at 50 °C for a further 3 days completed the H/D exchange.

Reaction of 2 with D_2. The above experiment was repeated using the bis-ICy complex $Ru(ICy)_2(PPh_3)(CO)H_2$ (**2**; 4.3 mg, 5.0 μmol). The sample was heated in C_6D_6 under D_2 for 48 h at 50 °C, leading to H/D exchange into both Ru−H resonances at δ − 5.39 and − 9.10 of the starting material, but at a significantly slower rate than found for **1**.

$Ru(ICy)(PPh_3)(CO)_3$ (3). A sample of $Ru(ICy)(PPh_3)_2(CO)(H)_2$ (**1**; 18.0 mg, 20.3 μmol) was dissolved in C_6D_6 (0.6 mL) in a NMR tube fitted with a J. Young PTFE tap. The contents of the tube were freeze−pump−thaw (×3) degassed and then placed under 1 atm of CO. The sample was heated for 3 h at 70 °C and then examined by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, which indicated complete conversion to **3**. ^1H NMR (C_6D_6, 298 K): δ 7.96 (m, 4H, PPh_3), 7.08−7.01 (m, 11H, PPh_3), 6.59 (s, 2H, im C*H*), 5.74 (tt, J_{HH} = 12.1, 3.3 Hz, 2H, Cy C*H*), 2.13 (m, 4H, Cy C*H*$_2$), 1.65−1.46 (m, 10H, Cy C*H*$_2$), 1.26−1.16 (m, 4H, Cy C*H*$_2$), 0.95 (m, 2H, Cy C*H*$_2$). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 59.7 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 211.7 (d, J_{CP} = 15.5 Hz, Ru−*C*O), 177.6 (d, J_{CP} = 61.6 Hz, Ru−C_{ICy}), 137.7 (d, J_{CP} = 45.0 Hz, PPh_3), 133.8 (d, J_{CP} = 8.3 Hz, PPh_3), 129.4 (d, J_{CP} = 1.8 Hz, PPh_3), 128.5 (d, J_{CP} = 8.3 Hz, PPh_3), 118.0 (s, im *C*H), 60.3 (s, *C*H, Cy), 33.8 (s, Cy *C*H$_2$), 25.8 (s, Cy *C*H$_2$), 25.5 (s, Cy *C*H$_2$). IR (C_6D_6, cm^{-1}): 1873 (ν_{CO}).

$Ru(ICy)_2(CO)_3$ (4). $Ru(ICy)_2(PPh_3)(CO)H_2$ (**2**; 17.6 mg, 20.5 μmol) was dissolved in C_6D_6 (0.6 mL) in a NMR tube fitted with a Teflon tap. The tube was freeze−pump−thaw (×3) degassed and 1 atm of CO added. The sample was heated for 24 h at 70 °C and then examined by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, which indicated conversion to $Ru(ICy)_2(CO)_3$ (**4**). ^1H NMR (C_6D_6, 298 K): δ 6.64 (s, 4H, im C*H*), 5.89 (m, 4H, Cy C*H*), 2.24 (m, 8H, Cy C*H*$_2$), 1.77−1.54 (m, 24H, Cy C*H*$_2$), 1.29−1.15 (m, 8H, Cy C*H*$_2$). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 216.0 (s, Ru−*C*O), 181.9 (s, Ru−C_{ICy}), 117.7 (s, im *C*H), 59.8 (s, Cy *C*H), 33.9 (s, Cy *C*H$_2$), 26.0 (s, Cy *C*H$_2$), 25.6 (s, Cy *C*H$_2$). IR (C_6D_6, cm^{-1}): 2009, 1930, 1870, 1839 (ν_{CO}).

$Ru(ICy)_2(PPh_3)(CO)(\kappa^1$-OCHO)H (5). A benzene (3 mL) solution of **2** (45 mg, 52 μmol) in a resealable ampule was freeze−pump−thaw (×3) degassed before the addition of 1 atm of CO_2. The solution was stirred for 16 h at room temperature, during which time a white precipitate appeared. This was isolated by filtration and washed with pentane, affording **5** as a white solid. Yield: 22 mg (47%). Anal. Found (calcd) for $C_{50}H_{65}N_4O_3PRu$: C, 66.34 (66.57); H, 7.70 (7.26); N, 6.38 (6.21). ^1H NMR (THF-d_8, 298 K): δ 7.78 (s, 1H, Ru−OC(O)*H*), 7.66 (br, 6H, PPh_3), 7.27 (br, 12H, PPh_3), 7.22 (d, 1H, J_{HH} = 1.6 Hz, im C*H*), 7.17 (d, 1H, J_{HH} = 1.6 Hz, im C*H*), 7.08 (m, 2H, im C*H*), 5.78 (m, 1H, Cy C*H*), 4.97 (m, 1H, Cy C*H*), 4.52 (m, 1H, Cy C*H*), 4.41 (m, 1H, Cy C*H*), 2.22−0.84 (m, 40H, Cy C*H*$_2$), −6.90 (br d, J_{HP} = 27.9 Hz, Ru−*H*).$^{31}P\{^1H\}$ NMR (THF-d_8, 298 K): δ 41.4 (br). IR (Nujol, cm^{-1}): 1891 (ν_{CO}), 1618 ($\nu_{OCO,asym}$).

$Ru(ICy)_2(CO)(\kappa^2$-OCHO)H (6). A sample of **2** (40 mg, 47 μmol) in benzene (3 mL) was placed into an ampule fitted with a resealable PTFE valve and subjected to three freeze−pump−thaw degassing cycles. The solution was then placed under 1 atm of CO_2 (repetition with $^{13}CO_2$ afforded the J_{HC} couplings given below) and heated at 70 °C for 3 h. The mixture was cooled to room temperature and filtered and the filtrate reduced in vacuo. The resulting residue was stirred in ethanol (3 mL), producing a bright yellow solid. After filtration the solid was washed with pentane, affording **6** as a yellow solid. Yield: 17 mg (57%). ^1H NMR (C_6D_6, 298 K): δ 8.19 (d, 1H, J_{HC} = 195.0 Hz, Ru−OC*H*O), 6.62 (s, 4H, im C*H*), 5.71 (m, 4H, Cy C*H*), 2.47 (m, 4H, Cy C*H*$_2$), 2.28 (m, 4H, Cy C*H*$_2$), 1.83−1.67 (m, 20H, Cy CH$_2$), 1.43−1.28 (m, 8H, Cy C*H*$_2$), 1.10 (m, 4H, Cy C*H*$_2$), −18.35 (s, Ru−*H*). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 208.2 (s, Ru−*C*O), 190.9 (s, Ru−C_{ICy}), 171.5 (s, Ru−O*C*HO), 116.6 (s, im *C*H), 59.8 (s, Cy *C*H), 34.8 (s, Cy *C*H$_2$), 26.8 (s, Cy *C*H$_2$), 26.1 (s, Cy *C*H$_2$). IR (C_6D_6, cm^{-1}): 1884 (ν_{CO}), 1566 ($\nu_{OCO,asym}$).

$Ru(ICy)(PPh_3)(CO)(\kappa^2$-OCHO)H (7). $Ru(ICy)(PPh_3)_2(CO)H_2$ (**1**; 80 mg, 90 μmol) was dissolved in benzene (5 mL) in an ampule fitted with a J. Young resealable PTFE tap. The mixture was freeze−pump−thaw (×3) degassed and 1 atm of CO_2 added (repetition with $^{13}CO_2$ afforded the J_{HC} couplings given below). The mixture was heated at 50 °C for 40 h, at which time a sample examined by ^1H NMR spectroscopy indicated >95% conversion to **7**. ^1H NMR (C_6D_6, 298 K): δ 7.90 (m, 6H, PPh_3), 7.87 (d, 1H, J_{HC} = 199.0 Hz, Ru−OC*H*O), 7.44 (m, 2H, PPh_3), 7.22−7.11 (m, 7H, PPh_3) 6.55 (s, 2H, im C*H*), 5.39 (m, 2H, Cy C*H*), 2.47 (m, 2H, Cy C*H*$_2$), 2.28 (m, 2H, Cy C*H*$_2$), 1.89−1.05 (m, 18H, Cy C*H*$_2$), −17.05 (d, J_{HP} = 23.1 Hz, Ru−*H*). $^{31}P\{^1H\}$ NMR (C_6D_6, 298 K): δ 47.0 (s). $^{13}C\{^1H\}$ NMR (C_6D_6, 298 K): δ 200.1 (d, J_{CP} = 11.0 Hz, Ru−*C*O), 184.9 (d, J_{CP} = 97.3 Hz, Ru−C_{ICy}), 172.4 (s, Ru−O*C*HO), 135.9 (d, J_{CP} = 37.3 Hz, PPh_3), 134.7 (d, J_{CP} = 11.7 Hz, PPh_3), 134.1 (d, J_{CP} = 19.0 Hz, PPh_3), 128.1 (s, PPh_3), 117.1 (s, im *C*H), 60.0 (s, *C*H, Cy), 34.8 (s, Cy *C*H$_2$), 26.1 (s, Cy *C*H$_2$), 25.8 (s, Cy *C*H$_2$). IR (C_6D_6, cm^{-1}): 1911 (ν_{CO}), 1560 ($\nu_{OCO,asym}$).

Table 6. Crystal Data and Structure Refinement Details for Compounds 1, 2, 8a, 9, and 10

	1	**2**	**8a**	**9**	**10**
empirical formula	$C_{52}H_{56}N_2OP_2Ru$	$C_{49}H_{65}N_4OPRu$	$C_{51}H_{55}ClN_2P_2Ru$	$C_{53}H_{57}Cl_3N_2OP_2Ru$	$C_{48}H_{64}ClN_4PRu$
formula wt	888.00	858.09	894.43	1007.37	864.52
cryst syst	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_12_12_1$	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a/Å	9.09300(10)	9.7180(1)	9.7370(2)	12.4520(1)	15.7080(1)
b/Å	23.9540(3)	19.7080(3)	13.1000(4)	22.0150(1)	11.1880(1)
c/Å	20.5920(3)	22.8730(4)	19.0750(5)	18.4720(1)	24.8340(2)
α/deg			75.405(1)		
β/deg	91.258(1)		86.082(1)	108.387(1)	90.417(1)
γ/deg			69.051(1)		
U/Å^3	4484.14(10)	4380.69(11)	2198.31(10)	4805.23(5)	4364.24(6)
Z	4	4	2	4	4
D_c/g cm^{-3}	1.315	1.301	1.351	1.392	1.316
μ/mm^{-1}	0.461	0.435	0.527	0.600	0.495
F(000)	1856	1816	932	2088	1824
cryst size/mm	0.10 × 0.05 × 0.05	0.17 × 0.15 × 0.10	0.15 × 0.15 × 0.15	0.40 × 0.25 × 0.10	0.25 × 0.20 × 0.10
θ range for data collecn/deg	3.76−28.00	3.71−27.48	4.04−27.57	3.57−27.47	3.52−30.04
Index ranges	$-12 \le h \le +12$	$-12 \le h \le +12$	$-12 \le h \le +12$	$-16 \le h \le +16$	$-22 \le h \le +22$
	$-31 \le k \le +31$	$-25 \le k \le +25$	$-17 \le k \le +17$	$-28 \le k \le +28$	$-15 \le k \le +15$
	$-27 \le l \le +27$	$-29 \le l \le +29$	$-24 \le l \le +24$	$-23 \le l \le +23$	$-34 \le l \le +34$
no. of rflns collected	21 109	72 630	41 598	79 867	76 684
no. of indep rflns, R(int)	10 716, 0.0789	10 001, 0.0925	9978, 0.0696	10 957, 0.0452	12 721, 0.0531
no. of rflns obsd (>2σ)	6508	7887	7375	9865	10812
data completeness	0.991	0.994	0.982	0.996	0.996
abs cor	none	multiscan	multiscan	multiscan	multiscan
Max., min transmission factors	0.83, 0.94	0.92, 0.88	0.93, 0.82	0.92, 0.76	0.95, 0.91
no. of data/restraints/params	10 716/3/564	10 001/2/514	9978/1/515	10 957/1/581	12 721/1/498
goodness of fit on F^2	1.107	1.028	1.051	1.067	1.040
R1, wR2 ($I > 2\sigma(I)$)	0.0742, 0.1360	0.0444, 0.0770	0.0495, 0.1087	0.0307, 0.0683	0.0336, 0.0683
R1, wR2 (all data)	0.1381, 0.1531	0.0709, 0.0851	0.0801, 0.1239	0.0370, 0.0707	0.0451, 0.0725
largest diff peak, hole/e Å^{-3}	0.613, −0.614	0.347, −0.644	1.978, −1.737	0.467, −0.603	1.174, −0.947

Ru(ICy)(PPh$_3$)$_2$HCl (8a,b). A solution of ICy (88 mg, 0.38 mmol) and Ru(PPh$_3$)$_3$HCl (320 mg, 0.35 mmol) in CH_2Cl_2 (8 mL) was stirred under argon at room temperature for 1 h. The volatiles were removed in vacuo, and the residue was washed with hexane (2 × 5 mL) and filtered. The resulting brown solid was dissolved in CH_2Cl_2 and layered with ethanol, affording Ru(ICy)(PPh$_3$)$_2$HCl (**8**) as orange crystals. Yield: 187 mg (60%). Anal. Found (calcd) for $C_{51}H_{55}ClN_2P_2Ru$: C, 68.20 (68.48); H, 6.17 (6.20); N, 3.30 (3.13). NMR data for **8a**: ^{1}H NMR (CD_2Cl_2, 298 K) δ 7.41−7.34 (m, 12H, PPh$_3$), 7.30−7.21 (m, 18H, PPh$_3$), 6.83 (d, J_{HH} = 1.8 Hz, 1H, im C*H*), 6.42 (d, J_{HH} = 1.8 Hz, 1H, im C*H*), 3.77 (m, 1H, Cy C*H*), 3.33 (m, 1H, Cy C*H*), 2.19 (m, 1H, Cy), 1.91 (m, 1H, Cy), 1.80−0.70 (m, 16H, Cy C*H$_2$*), 0.28 (m, 2H, C*H*$_2$, agostic), −26.50 (t, J_{HP} = 23.1 Hz, 1H, Ru−*H*); ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K) δ 48.4 (s); ^{13}C{^{1}H} NMR (CD_2Cl_2, 298 K) δ 191.1 (t, J_{CP} = 12.4 Hz, Ru−C_{ICy}), 138.3 (t, J_{CP} = 17.1 Hz, PPh$_3$), 134.6 (t, J_{CP} = 6.0 Hz, PPh$_3$), 128.8 (s, PPh$_3$), 127.9 (t, J_{CP} = 4.4 Hz, PPh$_3$), 117.0 (s, im *C*H), 115.9 (s, im *C*H), 59.8 (s, Cy *C*H), 58.5 (s, Cy *C*H), 31.9 (s, *C*H$_2$, agostic), 31.2 (s, *C*H$_2$), 26.2 (s, *C*H$_2$), 25.2 (s, *C*H$_2$), 18.6 (s, *C*H$_2$). Selected NMR data for **8b**: ^{1}H NMR (CD_2Cl_2, 253 K) δ 6.79 (s, 1H, im C*H*), 6.66 (s, 1H, im C*H*), 4.66 (m, 1H, Cy C*H*), 3.33 (m, 1H, Cy C*H*), 0.19 (m, 2H, C*H*$_2$, agostic), −26.01 (dd, J_{HP} = 23.1, 35.1 Hz, 1H, Ru−*H*); ^{31}P{^{1}H} NMR (CD_2Cl_2, 298 K) δ 75.1 (d, J_{PP} = 24.5 Hz), 49.6 (d, J_{PP} = 24.5 Hz).

Ru(ICy)(PPh$_3$)$_2$(CO)HCl (9). A mixture of **8a** and **8b** (38 mg, 42.5 μmol) was dissolved in CH_2Cl_2 (3 mL) in an ampule fitted with a J. Young PTFE tap. The flask was freeze−pump−thaw (×3) degassed and 1 atm of CO added. An immediate color change to yellow occurred upon stirring. Stirring was continued for 1 h at room temperature, at which point the volatiles were removed to leave a yellow residue. This was washed with hexane (2 × 3 mL) and dried in vacuo. Recrystallization from benzene/pentane afforded yellow crystals of **9** suitable for X-ray crystallography. Yield: 15 mg (39%). Anal. Found (calcd) for $RuC_{52}H_{55}ClN_2OP_2$: C, 68.39 (67.70); H, 6.16 (6.01); N, 3.00 (3.04). ^{1}H NMR (C_6D_6, 298 K): δ 8.04 (br m, 12H, PPh$_3$), 7.03 (br m, 18H, PPh$_3$), 6.30 (d, J_{HH} = 2.0 Hz, 1H, im C*H*), 6.23 (d, J_{HH} = 2.0 Hz, 1H, im C*H*), 5.05 (m, 1H, Cy C*H*), 4.83 (m, 1H, Cy C*H*), 1.52−0.65 (m, 20H, Cy), −2.37 (t, J_{HP} = 21.6, 1H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 50.6 (s). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 204.3 (t, J_{CP} = 8.3 Hz, Ru−*C*O), 185. 1 (t, J_{CP} = 11.9 Hz, Ru−C_{ICy}), 139.2 (vt, J_{CP} = 19.6 Hz, PPh$_3$), 134.7 (m, PPh$_3$), 133.4 (vt, J_{CP} = 5.5 Hz, PPh$_3$), 131.4 (s, PPh$_3$), 117.6 (s, im *C*H), 117.1 (s, im *C*H), 60.5 (s, Cy *C*H), 58.9 (s, Cy *C*H), 33.6 (s, Cy *C*H$_2$), 33.5 (s, *C*H$_2$), 26.2 (s, *C*H$_2$), 26.0 (s, *C*H$_2$), 25.9 (s, *C*H$_2$), 25.7 (s, *C*H$_2$). IR (Nujol, cm^{-1}): 1972 (ν_{CO}).

Ru(ICy)$_2$(PPh$_3$)HCl (10). THF (5 mL) was added to a mixture of ICy (150 mg, 0.65 mmol) and Ru(PPh$_3$)$_3$HCl (300 mg, 0.32 mmol) under argon. The mixture was stirred at room temperature for 2 h and then filtered. The volatiles were removed in vacuo, and the residue was washed with pentane (3 × 5 mL) and filtered. The resulting orange solid was dissolved in benzene and layered with pentane to afford **10** as dark orange crystals. Yield: 90 mg (32%). Anal. Found (calcd) for $C_{48}H_{64}ClN_4PRu$: C, 66.58 (66.68); H, 7.49 (7.46); N, 6.32 (6.48). ^{1}H NMR (C_6D_6, 298 K): δ 7.48 (m, 6H, PPh$_3$), 7.02−6.95 (m, 9H, PPh$_3$), 6.61 (d, J_{HH} = 1.8 Hz, 1H, im C*H*), 6.50 (d, J_{HH} = 1.8 Hz, 1H, im C*H*), 5.29 (m, 2H, Cy C*H*), 4.73 (m, 2H, Cy C*H*), 3.21 (m, 2H, Cy C*H$_2$*), 3.06 (m, 2H, Cy C*H$_2$*), 1.79−0.90 (m, 36H, Cy C*H$_2$*), −31.23 (d, J_{HP} = 51.8 Hz, 1H, Ru−*H*). ^{31}P{^{1}H} NMR (C_6D_6, 298 K): δ 75.7 (s). ^{13}C{^{1}H} NMR (C_6D_6, 298 K): δ 198.7 (d, J_{CP} = 13.0 Hz, Ru−C_{ICy}), 143.0 (d, J_{CP} = 36.9 Hz, PPh$_3$), 134.7 (d, J_{CP} = 5.6 Hz, PPh$_3$), 133.1 (d, J_{CP} = 10.2 Hz, PPh$_3$), 126.9 (d, J_{CP} = 8.4 Hz, PPh$_3$), 116.0 (s, im *C*H), 115.1 (s, im *C*H), 58.4 (s, *C*H), 58.0 (s, *C*H), 35.4 (s, *C*H$_2$), 35.2 (s, *C*H$_2$), 33.1 (s, *C*H$_2$), 32.2 (s, *C*H$_2$), 26.3 (s, *C*H$_2$), 26.2 (s, *C*H$_2$), 26.1 (s, *C*H$_2$), 26.0 (s, *C*H$_2$), 25.9 (s, *C*H$_2$), 25.7 (s, *C*H$_2$).

X-ray Crystallography. Single crystals of compounds **1**, **2**, **8a**, **9**, and **10** were analyzed at 150 K using a Nonius Kappa CCD diffractometer and Mo Kα radiation (λ = 0.710 73 Å). Details of the data collections, solutions, and refinements are given in Table 6. The structures were universally solved using SHELXS-97[40] and refined using full-matrix least squares in

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[40] Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, *467−473*, A46. Sheldrick, G. M, SHELXL-97, a Computer Program for Crystal Structure Refinement; University of Göttingen, Göttingen, Germany, 1997.

SHELXL-97.[40] Convergence was uneventful, with the following exceptions and points of note. In **1**, the atoms Ru1, C1, O1, and H2 were disordered in an 80:20 ratio with their primed labeled counterparts. H1 (trans to carbene) was readily located and refined as having a similar distance to each ruthenium fragment. Partial hydrogen atoms H2/H2A were refined at 1.6 Å from the parent metal. The hydride ligands were located and refined subject to a Ru1−H1 distance of 1.65 Å in **2** and 1.60 Å in compounds **8a**, **9**, and **10**. Additionally, in **9**, refinement revealed the presence of one molecule of dichloromethane within the asymmetric unit, disordered over two sites in a 40:60 ratio, with one common chlorine atom (Cl3). The absolute structure parameter for **2** was refined to a value of 0.46(2).

Crystallographic data for compounds **1**, **2**, **8a**, **9**, and **10** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 278383−278387. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

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Supporting Information Available: CIF files giving X-ray crystallographic data for **1**, **2**, **8a**, **9**, and **10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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