Double C(sp^3) dehydrogenation as a route to coordinated Arduengo carbenes: experiment and computation on comparative π-acidity†

Victoria M. Ho, Lori A. Watson, John C. Huffman and Kenneth G. Caulton*

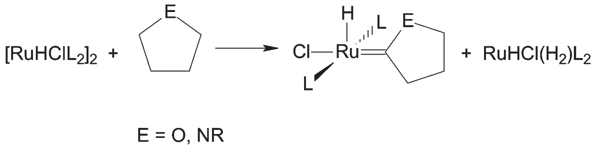
Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, IN 47405-7102

Received (in London, UK) 12th May 2003, Accepted 31st July 2003
First published as an Advance Article on the web 29th August 2003

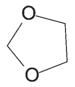
Reaction of $[RuHClL_2]_2$ (L = P^iPr_3) with the *C/C unsaturated* cyclic carbene:C(NMeCH)$_2$ produces the 16-electron square-pyramidal RuHCl[CNMeCH=CHNMe]L_2 by a chloride bridge-splitting reaction. Double $H_2C(sp^3)$ dehydrogenation of cyclic $H_2C(NMeCH_2)_2$ is successful for producing the *C/C saturated* carbene (bound to Ru); the two hydrogens removed are found as $RuHCl(H_2)L_2$. In this case, the free carbene is unstable with respect to dimerization to the olefin. The ^{13}C chemical shifts of the carbene carbons of these two complexes, the Ru/C distance, the N–C(carbene) distance, and a variety of reaction energies (from DFT calculations) and calculated atomic charges are generally consistent with these two carbenes, aromatic and non-aromatic, both binding similarly, and with little back donation from this electron-rich center. The ^{13}C chemical shifts are perhaps the most sensitive parameter. Collectively, these results suggest that, if the C/C unsaturated and the C/C saturated Arduengo carbenes differ in their binding to this electron-rich metal center, the difference is at or below detection limits.

Introduction

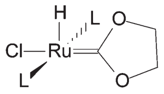
We have reported[1] that $[RuH(\mu\text{-}Cl)L_2]_2$, a precursor to the 14-electron fragment $RuHClL_2$ (L = P^iPr_3), has the ability to doubly dehydrogenate an sp^3 carbon alpha to a cyclic ether or amine heteroatom (eqn. 1). The two removed H are found as the dihydrogen molecule attached to a second metal center, in $RuHCl(H_2)L_2$. The doubly-activated CH_2 group in dioxolane, **1**, is converted analogously to **2** and $RuHCl(H_2)L_2$.



(1)

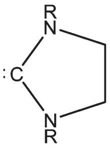


1

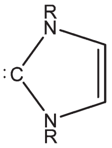


2

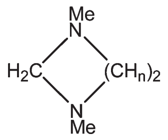
Given the wide interest[2] in "Arduengo carbenes", **3** and **3^U**,[3] we were interested in evaluating the reactivity of the methylene species **4** (n = 1 or 2) towards the very electron-rich metal center[4] in $[RuHClL_2]_2$. Both kinetic and thermodynamic questions are of interest for such a dehydrogenation. (Complexes of Arduengo carbenes have *not* been previously made by dehydrogenation of **4**, but rather from the preformed free carbene, as in eqn. 2. Alternatively, synthesis of these carbenes is often based upon deprotonation of the vinyl carbon of the related imidazolium cation.[5–8]). It has been established, both experimentally and computationally, that the C/C unsaturated Arduengo carbenes are primarily σ-donor ligands; there is little evidence for their being π acceptors.[9–16] In addition, we are interested in the stereoelectronic factors that dictate the orientation of the plane of the Arduengo carbene in product **5**, and the character of the Ru–C bond, as well as the influence of aromaticity (n = 1) *vs.* non-aromaticity (n = 2) in the five-membered ring[17] of analogous complexes on all of the above factors. For example, it was reasoned recently that for n = 2, "…due to the lack of carbene stabilization provided by the absence of π interactions, these saturated imidazole ligands might be more basic than their unsaturated analogs.[18] We report here answers to some of these questions.



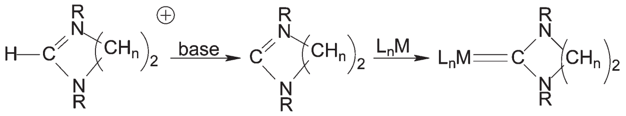
3



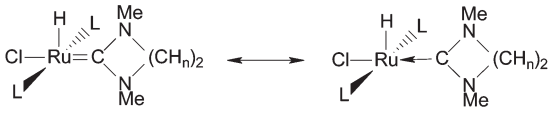
3^U



4



(2)



5

Results

C/C unsaturated carbene complex from the carbene

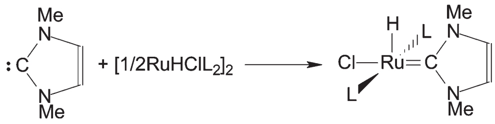
a) Synthesis. Reaction of **3^u** with $[RuHClL_2]_2$ in benzene gives, within 20 min at 25 °C, clean and complete conversion

---

† Electronic supplementary information (ESI) available: crystallographic data. See http://www.rsc.org/suppdata/nj/b3/b305249d/

DOI: 10.1039/b305249d

to **6**. NMR spectroscopic data completely define product stoichiometry and also certain structural features. The integration of the ^1H NMR spectrum shows that only one carbene ligand is bound to Ru, and a hydride-coupled ^{31}P NMR spectrum shows equivalent phosphines as a doublet, confirming the presence of one hydride ligand. The hydride signal is a triplet (hence, equivalent phosphines) at very high field (-29.25 ppm), indicating the absence of a ligand *trans* to hydride. Of special interest is the fact that two N methyl proton chemical shifts and two vinyl proton chemical shifts are detected. This requires a) the five-membered ring must not be oriented eclipsing the Ru–P bonds, but instead lie essentially in the molecular mirror plane defined by Ru, H and Cl and b) any rotation around the Ru–C bond is slow on the ^1H NMR timescale.



3^u **6**

b) Structure. An X-ray crystal structure determination (Fig. 1) confirms that the product is not a dimer, but rather an unsaturated monomer, and reveals a square-pyramidal geometry with a hydride in the apical site. There are no agostic interactions. The five-membered ring eclipses the Ru–H bond, accounting for the inequivalent N–Me and C–H groups detected spectroscopically. The Ru–Cl (2.452(27) Å) and Ru–P (2.347(27) Å) distances are very similar to those (2.422(2) and 2.379(0) Å, respectively)[19] in $RuHCl(CO)(P^iPr_3)_2$. The Ru–C distance, 1.967(5) Å, is ~0.15 Å shorter than the numerous[20] Ru–C (imidazolin-2-ylidene) distances reported recently, but it is longer than the corresponding distance in **7** (1.88 Å),[21] 1.90 Å in **8**, as well as the Ru–C distance (1.91 Å) calculated in $RuHCl[C(Me)(OMe)](PH_3)_2$.[21] The shorter Ru–C distance in **6** than to imidazolin-2-ylidenes can be attributed partly to the carbon location *trans* to a chloride (others used in the comparison are *trans* to phosphine), but primarily to the fact that all those *also* contain a non-heteroatom-stabilized carbene co-ligand. This non-heteroatom-stabilized carbene is a strong π-acid, and it effectively prevents any back-bonding (π-basicity) from the metal to the Arduengo carbene. For comparison, a typical[22] Ru^{II}-pyridine bond length is 2.06 Å.

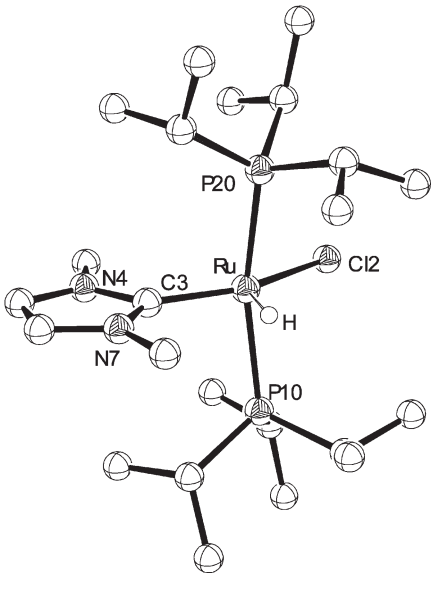
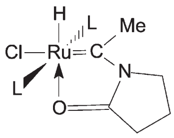
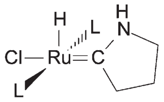


Fig. 1 Molecular structure of $RuHCl(P^iPr_3)_2(=C(NMeCH)_2)$ showing only the hydride hydrogen and selected atom labeling. Selected distances and angles: Ru–C, 1.967(5) Å; Ru–H, 1.45(5) Å, Ru–Cl, 2.452(2) Å; C–N, 1.382(6), 1.380(6) Å; Ru–P10, 2.346(2); Ru–P20, 2.348(2). ∠P–Ru–P, 163.28(8)°; ∠H–Ru–C, 81(2)°; ∠H–Ru–Cl, 123(2)°.



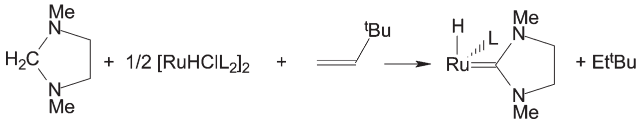
7



8

C–C saturated carbene complex by $H_2C(sp^3)$ dehydrogenation

The *saturated* heterocycle **3** can be dehydrogenated (< 20 min, 1 : 1 **3** : Ru ratio, 25 °C, benzene) by $[RuHClL_2]_2$ to produce equimolar carbene complex and H_2, trapped as $RuHCl(H_2)L_2$. The same carbene complex can be obtained without co-product $RuHCl(H_2)L_2$ by adding an equivalent of *tert*-butyl ethylene to the reaction mixture (eqn. 3). The neohexane that results from the hydrogenation of this sacrificial olefin can be removed *in vacuo*, allowing easy isolation of $RuHCl(P^iPr_3)_2(=C(NMeCH_2)_2)$ as a yellow–orange powder. The carbene complex **9** shows equivalent P nuclei; a hydride coupled ^{31}P NMR spectrum shows the equivalent phosphines as a doublet, indicating the presence of only one hydride ligand. The hydride itself appears as a triplet at $\delta = -24.30$ ppm, confirming both the presence of two equivalent phosphines and the lack of a ligand *trans* to hydride. Two NCH_3 proton NMR signals again indicate slow rotation around the Ru–C bond. The carbene carbon NMR signal is found at $\delta = 202.8$ ppm, 8 ppm downfield of that of $RuHCl(P^iPr_3)_2(=C(NMeCH)_2)$. The difference in ^{13}C NMR chemical shifts of the carbene carbon for the N-heterocyclic carbene in the free state relative to that when coordinated to $RuHCl(P^iPr_3)_2$, the "coordination chemical shift", is larger for the C–C saturated carbene (42 ppm) than for the aromatic cycle (17 ppm). Since this carbon is bonded to the metal, it is expected to be sensitive to bonding changes. We suggest that the larger coordination chemical shift is diagnostic of greater back donation to the C–C saturated carbene.



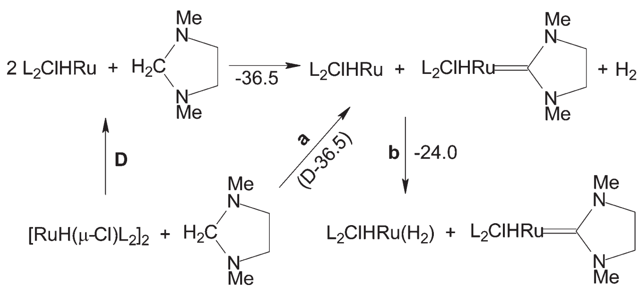
3 **9**

(3)

The Ru carbene is stable to the extent of being unchanged after 24 h at 60 °C in benzene.

Computational study of dehydrogenation thermodynamics

DFT calculations were carried out for the reactions shown in Scheme 1. The reactions shown are for the saturated heterocycle, which is the more difficult to dehydrogenate, and the



Scheme 1

one which was actually dehydrogenated experimentally. The dimer scission energy D was not calculated since the PH_3 phosphine fails to model important *cis* $(PR_3)_2$ steric interactions in the dimer.[23] Nevertheless, the reaction energy for transformation **a**, D-36.5 kcal, is likely to be positive, even after correction for a $T\Delta S$ term of about[24] 8 kcal mol^{-1} at 300 K. Thus, the binding energy of H_2 to $RuHClL_2$ (**b**), −24.0 kcal mol^{-1}, is essential to the overall reaction accomplished here, even with the entropy penalty involved. The energy of hydrogenation of *tert*-butyl ethylene plays a similar role in eqn. 3.

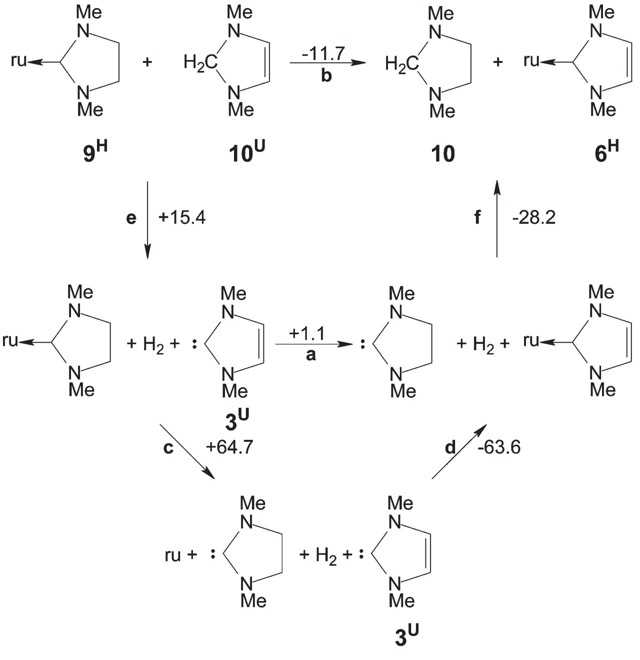
Calculated (DFT) reaction energies: do these carbenes exhibit π-acidity and does aromaticity affect the Ru–C bond?

Calculated reaction energies, idealized only to the extent that P^iPr_3 was replaced by PH_3, are shown in Scheme 2. Reaction **a** might have been expected to significantly favor the reactant side, reasoning solely from the anticipated higher stability of the (aromatic) ring $\mathbf{3^U}$. Moreover, if the carbene π orbital of $\mathbf{3^U}$ is involved in aromatic delocalization, $\mathbf{3^U}$ might be a weaker π acid ligand (hence a poorer ligand), again favoring the reactant side. In fact, reaction **a** is essentially thermoneutral, which predicts that effecting this carbene exchange in experimental practice can only be accomplished by excess added carbene. *Why* is reaction **a** thermoneutral? Reaction **b** shows another comparison between the two different carbene complexes, but this time the waiting "candidate ligand" is that which is hydrogenated at the carbene carbon ($\mathbf{10^U}$ or **10**). This reaction is quite favorable thermodynamically. This change in reaction energy cannot be due to the greater stability of the carbene complex $\mathbf{6^H}$ *vs.* $\mathbf{9^H}$ because this pair of compounds appears in *both* reactions **a** and **b**. The unsaturated, aromatic cyclic carbene does not more effectively stabilize the $RuHCl(PH_3)_2$ fragment: reactions **c** and **d** compare the binding energies of each carbene to $RuHCl(PH_3)_2$, and they differ insignificantly. Thus, neither cyclic carbene is *much more* effective in forming an Ru–C bond, a result which is best rationalized by the conclusion that *each carbene is bound to* $RuHCl(PH_3)_2$ *primarily by a sigma bond*. As mentioned above, if there were significant Ru–C π bonding, the aromatic carbene $\mathbf{3^U}$ should have a smaller reaction energy (**d**), since the carbene carbon p_π orbital would be less available for Ru–C π bonding. The similarity of reaction energies for **c** and **d** are more consistent with neither carbene having a greater π-acidity. Since the exothermic character of eq. **b** is not due primarily to the difference in stability of $\mathbf{6^H}$ *vs.* $\mathbf{9^H}$, we evaluated the hypothesis that it is due to the difference between $\mathbf{10^U}$ and **10**. Reaction **e** *vs.* **f** shows that it is much easier to dehydrogenate $\mathbf{10^U}$ than it is **10**, and this difference (∼13 kcal mol^{-1}) is the determining contribution to the exothermic character of eq. **b**. The smaller magnitude for the reaction energy **e** (*vs.* **f**) has been attributed[27] to the aromaticity of the carbene $\mathbf{3^U}$. It is therefore the lower energy cost of breaking two C–H bonds in $\mathbf{10^U}$, which makes reaction **b** exothermic. Reaction **a** is thus thermoneutral because no C–H bonds are broken.

Scheme 3 shows another means of establishing the effect of $RuHClL_2$ on the carbene. Eq. **a** shows the energy of hydrogenation of the C–C π bond; this is considerably smaller than that of ethylene (−32.2 kcal mol^{-1}), or of the diaminoolefin **12** (reaction **c**), which is further evidence for the aromaticity of **11**. The fact that the energies of reactions **a** and **b** in Scheme 3 are comparable indicates that there is no energetically significant difference in degree of delocalization of the π electrons of **11** when it is attached to $RuHClL_2$; if there were such delocalization, *i.e.*, significant back bonding from the metal to **11**, the reaction energy of eq. **b** would differ more from that of eq. **a**.

Bond lengths in the optimized geometries also permit some conclusions (Scheme 4; $n = 1$ data, $n = 2$ in parentheses). The C–N bonds in both carbenes lengthen (only) slightly on coordination to Ru, and the increase is slightly larger for the saturated carbene. Such lengthening is consistent with some back-bonding from Ru, and this being more for the saturated carbene. Note, however, that any change in Ru–C bonding between $n = 1$ and $n = 2$ has virtually no *trans*-effect on the Ru–Cl distance, but the Ru–C distance does shorten (only 0.018 Å) on going to the saturated carbene.

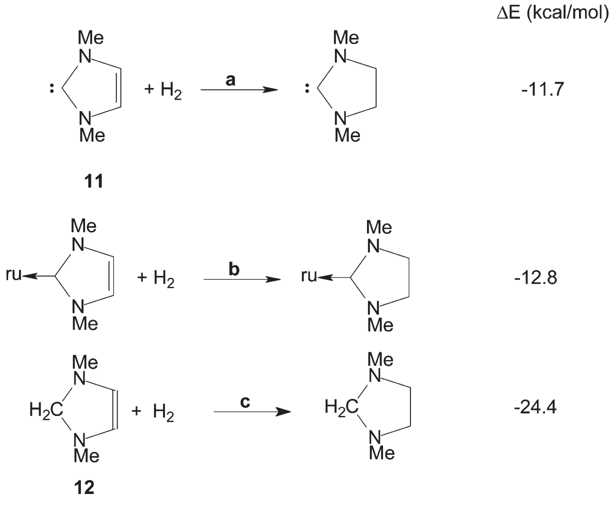
Table 1 shows the results of a natural bond orbital[25] population analysis of **3** and $\mathbf{3^U}$ in both free and coordinated states. On coordination, the population of all three sigma orbitals (lone pair and two C–N bonds) decreases and the population of the π orbital increases, the latter a symptom of back bonding (small, but not zero). The natural charge on the carbene carbon shows that the cyclic carbenes lose more electron density than they gain on binding to $RuHCl(PH_3)_2$. The difference between $\mathbf{3^U}$ and **3** is at the threshold of reliability, but consistent with the non-aromatic cycle being slightly more π-acidic.



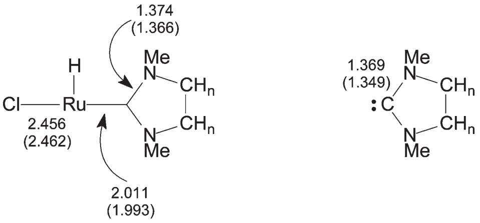
Scheme 2 Energies in kcal mol^{-1}; ru = $RuHCl(PH_3)_2$

Conclusions

In summary, all evidence supports the view that *both* carbene ligands are indeed primarily σ-donors towards the metal,



Scheme 3



Scheme 4

and that the Ru–C bond is best represented as it is in Schemes 2 and 3. The significant rotational barrier observed experimentally in both RuHCl[C(NMeCH$_n$)$_2$](P^{i}Pr$_3$)$_2$ complexes must thus arise mainly from steric repulsion between the N–Me groups and the two P^{i}Pr$_3$ groups when the ring eclipses the Ru–P bonds. The only caution to this conclusion is that, to a very electron-rich metal such as Ru in RuHClL$_2$, small variations in calculated bond lengths, together with the experimental bond lengths, suggest that back bonding to both cyclic carbenes is not "zero". These carbenes can perhaps be π acids but, on a less electron-rich metal, the evidence shows[26] that they certainly do not *need* back donation for strong binding to a metal.[27]

We have been conservative in interpreting the small difference in energies of reactions **c** *vs.* **d** (Scheme 2). Even if we take the calculated 1 kcal mol^{-1} difference in Ru–carbene bond dissociation energy as real, the calorimetric studies of BDE of Nolan show[2] variations of 14 kcal mol^{-1} simply on changing the N substituents from cyclohexyl to adamantyl. It is thus justifiable to conclude that any variation in back donation to C–C saturated *vs.* unsaturated Arduengo carbenes varies by less than that induced by steric repulsion.

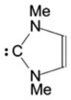
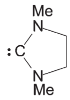
Experimental details

General considerations

All manipulations were performed using standard Schlenk techniques or in an argon filled glovebox unless otherwise noted. Solvents were distilled from Na–benzophenone or CaH$_2$, degassed prior to use, and stored in air-tight vessels. C(NMeCH)$_2$,[28] H$_2$C(NMeCH$_2$)$_2$,[29] and [RuHCl(P^{i}Pr$_3$)$_2$]$_2$,[21] were prepared according to published procedures. All other reagents were used as received from commercial vendors. ^{1}H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterated solvents. ^{31}P spectra are referenced to an external standard of 85% H$_3$PO$_4$ (at 0 ppm). NMR spectra were recorded with a Varian Gemini 2000 (300 MHz ^{1}H; 121 MHz ^{31}P; 75 MHz ^{13}C) or a Varian Unity Inova instrument (400 MHz ^{1}H; 162 MHz ^{31}P; 101 MHz ^{13}C).

Synthesis of RuHCl(P^{i}Pr$_3$)$_2$[=C(NMeCH)$_2$], 6. Under argon, 500.7 mg (0.5466 mmol) of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in 40 mL of toluene and 4.70 mL of 0.2325 M (THF; 1.09 mmol). :C(NMeCH)$_2$ was added dropwise over 10 min to the stirred solution. Stirring was continued for 19 h and the volatiles removed *in vacuo*. The resulting reddish brown solid was washed with 2 × 20 mL of cold (0 °C) pentane and dried *in vacuo*. Yield: 331 mg (54.7%). ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 5.99 (d, $J_{H-H} = 2.1$ Hz, 1H; [=C(NMeC*H*)$_2$]), 5.96 (d, $J_{H-H} = 2.1$ Hz, 1H; [=C(NMeC*H*)$_2$]), 3.50 (s, 3H; [=C(N*Me*CH)$_2$]), 2.99 (s, 3H; [=C(N*Me*CH)$_2$]), 2.35 (m, 6H; PC*H*(CH$_3$)$_2$), 1.34 (dvt, $J_{H-H} = 6$ Hz; $J_{P-H} = 7$ Hz, 18H; PCH(C*H*$_3$)$_2$), 1.13 (dvt, $J_{H-H} = 6$ Hz; $J_{P-H} = 7$ Hz, 18H; PCH(C*H*$_3$)$_2$), −29.25 (t, $J_{P-H} = 21.9$ Hz, 1H; (Ru*H*)); ^{31}P NMR (300 MHz, C$_6$D$_6$, 20 °C): $\delta = 53.0$ (s; *P*^{i}Pr$_3$). ^{13}C NMR (400 MHz, C$_6$D$_6$, 20 °C): $\delta = 194.8$ (s; [=*C*(NMeCH)$_2$]), 120.0 (s; [=C(NMe*C*H)$_2$]), 119.3 (s; [=C(NMe*C*H)$_2$]), 36.8 (s; [=C(N*Me*CH)$_2$]), 36.6 (s; [=C(N*Me*CH)$_2$]), 26.0 (vt, $J_{P-C} = 34$ Hz; P*C*H(CH$_3$)$_2$), 21.1 (s; PCH(*C*H$_3$)$_2$), 19.7 (s; PCH(*C*H$_3$)$_2$).

Table 1 Natural bond orbital populations of carbene carbon ($n(\sigma)$) and Ru($n(\pi)$) orbitals, and carbene carbon charge, q

		free	on RuHCl(PH$_3$)$_2$	coord-free
 **3^u**	q(carbene)	+0.106	+0.311	+0.21
	$n(\sigma)$	3.20	2.83	−0.37
	$n(\pi)$	0.66	0.81	+0.15
 **3**	q(carbene)	+0.190	+0.376	+0.19
	$n(\sigma)$	3.22	2.86	−0.36
	$n(\pi)$	0.55	0.72	+0.17

Synthesis of RuHCl(P^{i}Pr$_3$)$_2$(=C(NMeCH$_2$)$_2$), 9. Under argon, 11.1 mg (0.0121 mmol) of [RuHCl(P^{i}Pr$_3$)$_2$]$_2$ was dissolved in approximately 0.5 ml of C$_6$D$_6$ in an air tight NMR tube. 2.4 mg (0.0240 mmol) of 1,3-dimethyl-1,3-diazolidine was added at room temperature. The formation of RuHCl(P^{i}Pr$_3$)$_2$(H$_2$) was confirmed by comparison to literature values.[30] *RuHCl(P^{i}Pr$_3$)$_2$(=CNMeCH$_2$CH$_2$NMe)*: ^{1}H NMR (300 MHz, C$_6$D$_6$, 20 °C): δ 2.51 (m, 10 H; [=C(NMeC*H*$_2$)$_2$] and PC*H*(CH$_3$)$_2$), 1.98 (s, 3H; [=C(N*Me*CH$_2$)$_2$]), 1.84 (s, 3H; [=C(N*Me*CH$_2$)$_2$]), 1.25 (dvt, $J_{H-H} = 6$ Hz; $J_{P-H} = 7$ Hz, 18H; PCH(C*H*$_3$)$_2$), 1.21 (dvt, $J_{H-H} = 6$ Hz; $J_{P-H} = 7$ Hz, 18H; PCH(C*H*$_3$)$_2$), $\delta = -23.47$ (t, $J_{P-H} = 18$ Hz, 1H; (Ru*H*Cl(P^{i}Pr$_3$)$_2$)); ^{31}P NMR (300 MHz, C$_6$D$_6$, 20 °C): $\delta = 57.29$(s; (*P*^{i}Pr$_3$)); ^{13}C NMR (400 MHz, C$_6$D$_6$, 20 °C): $\delta = 202.83$ (t, $J_{P-C} = 14$ Hz; [=*C*(NMeCH$_2$)$_2$]), 30.76 (s; [=C(NMe*C*H$_2$)$_2$]), 29.24 (s; [=C(NMe*C*H$_2$)$_2$]), 25.03 (vt, $J_{P-C} = 11$ Hz; P*C*H(CH$_3$)$_2$), 24.09 (s; [=C(N*Me*CH$_2$)$_2$]), 23.28 (s; [=C(N*Me*CH$_2$)$_2$]), 20.58 (s; PCH(*C*H$_3$)$_2$), 19.78 (s; PCH(*C*H$_3$)$_2$).

Computational details

All calculations were performed with the Gaussian 98 package.[31] Geometry optimizations of all species were performed with the B3PW91[32] functional. Basis sets used included LANL2DZ for Ru, Cl, and P, 6-31G* for C and N, and 6-31G** for all hydrogens.[33] The basis set LANL2DZ is the Los Alamos National Laboratory ECP plus a double zeta valence on Ru, Cl, and P;[34] additional d polarization functions[35] were added to all phosphorus and chlorine atoms in DFT calculations. All optimizations were performed with C$_1$ symmetry and all minima were confirmed by analytical calculation of frequencies, which were also used to compute zero point energy corrections without scaling. All energies discussed include this ZPE correction.

Crystal structure determination of RuHCl(P^{i}Pr$_3$)$_2$(=C(NMeCH)$_2$)

Crystals suitable for X-ray diffraction were obtained from a saturated C$_6$D$_6$ solution of RuHClL$_2$(=C(NMeCMe$_2$). A typical orange crystal was removed from the tube and affixed under N$_2$ to a glass fiber using silicone grease and transferred to the Bruker SMART6000 CCD system where it was cooled to −160 °C using a gas-flow cooling system of local design. The data were collected (Table 2) using 30-second frames with an omega scan of 0.30 degrees. Data were corrected for Lorentz and polarization effects and equivalent reflections averaged using the Bruker SAINT software as well as utility programs from the XTEL library. The structure was solved using SHELXTL and Fourier techniques. In addition to the Ru complex, two C$_6$D$_6$ solvent molecules were present in the

Table 2 Crystallographic data for $RuHCl[C(NMeCH)_2](P^iPr_3)_2$

Formula	$C_{35}H_{63}ClN_2P_2Ru$	Space group	*Pbca*
a, Å	18.8912(6)	T, °C	−160
b, Å	19.2995(6)	λ, Å	0.71073
c, Å	20.7963(7)	ρ_{calc}, g cm^{-3}	1.245
V, Å^3	7582.14 Å^3	$\mu(MoK_a)$, cm^{-1}	5.929
Z	8	R	0.0296
formula weight	710.37	R_w	0.0286

[a] Graphite monochromator. [b] $R = \Sigma \quad F_o| - |F_c/\Sigma|F_o|$ [c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$ where $w = 1/\sigma^2(|F_o|)$.

lattice. As the refinement of the model progressed, it was observed that there were several large peaks that did not lie in chemically reasonable positions. Examination of the residual peaks revealed that there was a disorder present in which the Cl atom was located approximately 180° from the position shown in the figures. It was possible to model the disorder using partial occupancy Ru, Cl, and P atoms. The occupancy converged to 0.125 for the secondary position. After the disorder was properly modeled, it was possible to locate and refine all hydrogen atoms associated with the major position. A final difference Fourier was essentially featureless, with the largest peak being 0.55 e Å^{-3}.

Acknowledgements

VMH was a summer NSF-REU researcher during which time this project was executed. LAW thanks the NSF for a graduate fellowship. This research was supported by an NSF research grant to KGC. We thank Dr Joseph N. Coalter, III, for stimulating suggestions and discussion during this project.

References

1 J. N. Coalter, III, G. Ferrando and K. G. Caulton, *New J. Chem.*, 2000, **24**, 835.
2 D. Bourissou, O. Guerret, P. Gabbai and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39; M. Regitz, *Angew. Chem.*, 1996, **35**, 725; L. Jafarpour and S. P. Nolan, *Adv. Organomet. Chem.*, 2000, **46**, 181; M. S. Viciu, G. A. Grasa and S. P. Nolan, *Organometallics*, 2001, **20**, 3607; L. R. Titcomb, S. Caddick, F. G. N. Cloke, D. J. Wilson and D. McKerrecher, *Chem. Commun.*, 2001, 1388; P. L. Arnold, F. G. N. Cloke, T. Geldbach and P. B. Hitchcock, *Organometallics*, 1999, **18**, 3228; R. A. Michelin, A. J. L. Pombeiro and M. F. C. Guedes da Silva, *Coord. Chem. Rev.*, 2001, **218**, 75.
3 These are now frequently called N-heterocyclic carbenes.
4 K. G. Caulton, *J. Organometal. Chem.*, 2001, **617–618**, 56.
5 M. S. Viciu, R. A. Kelly, E. D. Stevens, F. Naud, M. Studer and S. P. Nolan, *Org. Lett.*, 2003, **5**, 1479.
6 L. Jafarpour, A. C. Hillier and S. P. Nolan, *Organometallics*, 2002, **21**, 442.
7 M. Poyatos, J. A. Mata, E. Falomir, R. H. Crabtree and E. Peris, *Organometallics*, 2003, **22**, 1110.
8 T. M. Trnka, J. P. Morgan, M. S. Sanford, T. E. Wilhelm, M. Scholl, T.-L. Choi, S. G. Ding, M. W. Day and R. H. Grubbs, *J. Am. Chem. Soc.*, 2003, **125**, 2546.
9 W. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162.
10 C.-Y. Liu, D.-Y. Chen, G.-H. Lee, S.-M. Peng and S.-T. Liu, *Organometallics*, 1996, **15**, 1055.
11 W. A. Herrmann, M. Elison, J. Fischer, C. Köcher and G. R. J. Artus, *Chem.-Eur. J.*, 1996, **2**, 772.
12 W. A. Herrmann, C. Köcher, L. J. Goossen and G. R. J. Artus, *Chem.-Eur. J.*, 1996, **2**, 1627.
13 W. A. Herrmann, L. J. Goossen, G. R. J. Artus and C. Koecher, *Organometallics*, 1997, **16**, 2472.
14 W. A. Herrmann, J. Fischer, K. Oefele and G. R. J. Artus, *J. Organomet. Chem.*, 1997, **530**, 259.
15 W. A. Herrmann, J. Schwarz and M. G. Gardiner, *Organometallics*, 1999, **18**, 4082.
16 G. Boehme and G. Frenking, *J. Am. Chem. Soc.*, 1996, **118**, 2039.
17 A. J. Arduengo III, J. R. Goerlich and W. J. Marshall, *J. Am. Chem. Soc.*, 1995, **117**, 11 027.
18 M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, **1**, 953; see also A. K. Chatterjee, J. P. Morgan, M. Scholl and R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, **122**, 3783.
19 D. Huang, W. E. Streib, J. C. Bollinger, K. G. Caulton, R. F. Winter and T. Scheiring, *J. Am. Chem. Soc.*, 1999, **121**, 8087.
20 J. Huang, L. Jafarpour, A. C. Hillier, E. D. Stevens and S. P. Nolan, *Organometallics*, 2001, **20**, 2878; H. M. Lee, D. C. Smith, Jr., Z. He, E. D. Stevens, C. S. Yi and S. P. Nolan, *Organometallics*, 2001, **20**, 794; J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5375; L. Jafarpour, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 5416; L. Jafarpour, J. Huang, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 3760; J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, **18**, 2370.
21 J. N. Coalter, J. C. Bollinger, J. C. Huffman, U. Werner-Zwanziger, K. G. Caulton, E. R. Davidson, H. Gérard, E. Clot and O. Eisenstein, *New J. Chem.*, 2000, **24**, 9.
22 G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, 1989, S1.
23 See also M. Czerw, T. K. Whittingham and K. Krogh-Jespersen, in *Computational Organometallic Chemistry*, ed. T. Cundari, Dekker, New York, 2001.
24 M. E. Minas de Piedade and J. A. M. Simoes, *J. Organometal. Chem.*, 1996, **518**, 167.
25 *NBO 4.M*. E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, 1999.
26 W. J. Oldham, Jr., S. M. Oldham, B. L. Scott, K. D. Abney, W. H. Smith and D. A. Costa, *Chem. Commun.*, 2001, 1348.
27 C. Boehme and G. Frenking, *Organometallics*, 1998, **17**, 5801.
28 (*a*) A. J. Arduengo, M. Harlow and J. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361; (*b*) A. J. Arduengo, H. V. Rasika Dias, M. Harlow and J. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530.
29 A. A. Castolo, V. I. Bakhmutov, R. Contreras, M. Guizado-Rodriguez, G. Merino, H. Noth and A. Vela, *Inorg. Chem.*, in press.
30 (*a*) T. Burrow, S. Sabo-Etienne and B. Chaudret, *Inorg. Chem.*, 1995, **34**, 2470; (*b*) J. Wolf, W. Steuer, C. Gruenwald, O. Gervert, M. Laubender and H. Werner, *Eur. J. Inorg. Chem.*, 1998, 1827.
31 *Gaussian 98 (Revision A.7)*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Milliam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavavhari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1998.
32 A. D. Becke, *Phys. Rev.*, 1988, **A38**, 3098; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372; A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; J. P. Perdue and Y. Wang, *Phys. Rev. B*, 1991, **45**, 13 244.
33 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213.
34 P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284; P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299.
35 A. Höllwarth, M. Böhme, S. Dapprich, A. W. Ehlers, A. Gobbi, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp and G. Frenking, *Chem. Phys. Lett.*, 1993, **208**, 237.