Carbene Complexes from Olefins, Using $RuHCl(P^iPr_3)_2$. Influence of the Olefin Substituent

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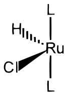
Unsaturated hydrido/halide compounds[1−4] have special potential since they are multifunctional: a 16-electron configuration permits substrate binding with negligible activation energy, a π-donor halide or pseudohalide ligand delivers a stabilizing effect of controlled variable degree, and the hydride is the transferable ligand (reducing equivalents). Tetracoordinated d^6 complexes[2,4] offer additional advantages: the 14-electron configuration, with the resulting *two* empty valence orbitals, offers either the potential for binding two substrates (four-electron total substrate donor power) *or* sufficient electrophilicity to bind even very weak substrates. For example, the 14-electron configuration catalyzes olefin polymerization.[5] We report here, using a 14-electron d^6 moiety, an unusual direct synthesis of coordinated carbenes from olefins, without need of alkali metal or Grignard reagents, and without alkyl α-H abstraction to liberate alkane.[6]

Dehydrohalogenation of $Ru(H)_2Cl_2L_2$ ($L = P^iPr_3$) with 1 equiv of lithium 2,2,6,6-tetramethylpiperide in benzene gives $RuHClL_2$, the first uncharged d^6 species with a 14-valence electron configuration. This molecule shows diastereotopic methyl protons, which is only consistent with a "saw horse" structure, **1**, as found for $Ir(H)_2L_2^+$ and $RuX(CO)L_2^+$ ($X = H$, Ph) and as calculated for $RuHCl(PH_3)_2$.[2−4,7] Additionally, this structure of a "*cis*-divacant octahedron" must *not* invert rapidly to form **1′**, since that would effect NMR coalescence of the diastereotopic methyl groups. We continue to struggle with crystal twinning, which has frustrated our attempts to ascertain whether this structure achieves light stabilization by one or more agostic interactions. The ^1H and $^{31}P\{^1H\}$ NMR spectra of $RuHClL_2$ show only broadening at −95 °C in d_8-toluene, but provide no clear answer to the question of agostic interactions. However, $RuDClL_2$, synthesized in either of two different ways, shows >90% exchange of D selectively into the ^{i}Pr methyl groups within 2 h at 25 °C. This is consistent with participation of agostic interactions. Because $RuHClL_2$ reacts immediately with many donors, including N_2, by adduct formation, any such agostic interactions have negligible (e.g., inhibiting) influence on reaction chemistry.



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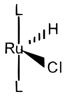
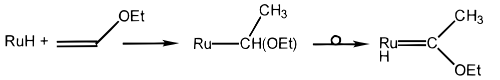


1′

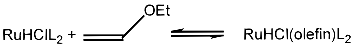
Reaction of $RuHClL_2$ with vinyl ethyl ether at 25 °C gives immediate formation of $RuHCl[C(Me)OEt]L_2$. This rearrangement is very rare.[6,8] "...the spontaneous isomerization of an alkene complex to an alkylidene has not to our knowledge been explicitly observed."[9] This is a new member of the class of molecules $RuX_2(carbene)L_2$, distinguished however by the presence of two inequivalent anionic ligands on Ru.[10]

The product $RuHCl[C(Me)(OEt)]L_2$ would appear to be formed "merely" by addition of the Ru−H bond across the C═C bond, but in an unconventional direction (eq 1), with Ru going to the relatively uncharged internal carbon (cf. the terminal sp^2 carbon).[11] The alternative regiochemistry of Ru−H addition would form the unobserved species $L_2HClRu{=}C(H)(CH_2OEt)$. Certainly the result we report here suggests that the hydrido carbene complex is more stable than any 14-electron alkyl RuCl(alkyl)L_2.



(1)

Regarding the mechanism, the reaction of equimolar $RuHClL_2$ with ethyl vinyl ether is immediate at −65 °C in toluene-d_8 to give a primary product whose ^{31}P and ^1H NMR are consistent with a 1:1 adduct of intact olefin, **I**. At this temperature, there is no sign of uncomplexed $RuHClL_2$ and there is no sign (e.g., line broadening) of rapid exchange of free and coordinated olefin. The $^{31}P\{^1H\}$ NMR of **I** is especially diagnostic of structure because it is an AB pattern ($J(P_A{-}P_B) = 300$ Hz), indicative of binding the unsymmetrical olefin substituents in a manner that leaves the phosphines inequivalent (but transoid).[12] As the temperature is raised, eq 2 shifts detectably to the left but, by 0 °C, adduct is still present in large amounts as $RuHCl[C(CH_3)(OEt)]L_2$ begins to form.



I

(2)

When $RuHClL_2$ and $H_2C{=}CD(OEt)$ are combined at −40 °C and observed by ^2H NMR beginning at −20 °C, one sees immediately $RuDCl(olefin)L_2$ in which there is also D in the phosphine methyl groups, and some free $HDC{=}CH(OEt)$. These indicate reversible olefin binding to Ru and reversible migration

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† Indiana University.

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(1) Caulton, K. G. *New J. Chem.* **1994**, *18*, 25.

(2) Cooper, A. C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*, 9069.

(3) Huang, D.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2004.

(4) Huang, D.; Huffman, J. C.; Bollinger, J. C.; Eisenstein, O.; Caulton K. G. *J. Am. Chem. Soc.* **1997**, *119*, 7398.

(5) (a) Jordan, R. F. *Adv. Organomet. Chem.* **1991**, *32*, 325. (b) Killian, C. M.; Johnson, L. K.; Brookhart, M. *Organometallics* **1997**, *16*, 2005.

(6) A referee asserts that the formation of a coordinated vinylidene from a terminal acetylene represents "a fairly close precedent". We will report separately why vinylidene from alkynes is thermodynamically more accessible than carbenes, C(Me)R, from olefins. Moreover, the reactivity of C(sp)−H and C(sp^2)−H bonds toward transition metals is very different. (a) de los Rios, I.; Tenorio, M. J.; Puerta, M. C.; Valevga, P. *J. Am. Chem. Soc.* **1997**, *119*, 6529. (b) Slugovc, C.; Sapunov, V. N.; Wiede, P.; Schmid, R.; Kirchner, K. *J. Chem. Soc., Dalton Trans.* **1997**, 4209. (c) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091.

(7) Oliván, M.; Clot, E.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 3091.

(8) An α-agostic interaction apparently makes ethylidene more stable than ethylene, on the highly reducing, but unsaturated $(Me_3SiNC_2H_4)_3NTa$ fragment: Freundlich, J. S.; Schrock, R. R.; Cummins, C. C.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 6476.

(9) Roger, C.; Bodner, G. S.; Hatton, W. G.; Gladysz, J. A. *Organometallics* **1991**, *10*, 3266.

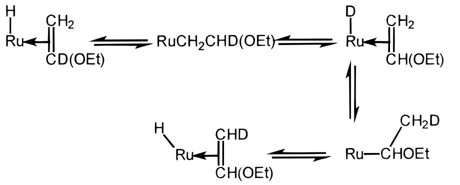
(10) (a) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 100. (b) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974. (c) Wu, Z.; Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 5503. (d) Schwab, P.; France, M. B.; Ziller, J. W.; Grubbs, R. H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2039.

(11) Similar regiochemistry was proposed to rationalize the production of $L_2Cl_2Ru[{=}C(H)CH_3]$ from $RuHCl(H_2)L_2$ and $HClC{=}CH_2$: Wilhelm, T. E.; Belderrain, T. R.; Brown, S. R.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.

(12) Slower rearrangement to the carbene with $H_2C{=}CD(OEt)$ permits observation of this AB NMR pattern even at 25 °C.

S0002-7863(98)00518-6 CCC: $15.00

of H (or D) from Ru to *both* olefinic carbons (eq 3). The



(3)

scrambling of D into the phosphine methyls was already established as a characteristic of $RuDClL_2$ itself. It is thus clear that Ru−H adds in both directions to the olefin, but only one of these leads to carbene product; the regiochemistry of carbene production is *not* caused by selectivity in the initial H migration step. By 0 °C, carbene product grows in, with D both at Ru (minor population) and at the carbene methyl (major population).[13] The significantly *slower* reaction rate observed using $H_2C{=}CD(OEt)$ establishes that C−D cleavage occurs before or at the rate determining step.

Since this is a rare case where free olefin is a source of carbene ligand,[14] it is of interest to know why these reactions give the carbene $RuHCl(C(Me)X)L_2$, with the isomeric olefin complex $RuHCl(H_2C{=}CHX)L_2$ as only an intermediate.[15] We have therefore carried out ab initio calculations on $RuHCl[C(Me)X](PH_3)_2$ and $RuHCl[H_2C{=}CH(X)](PH_3)_2$, and to evaluate the thermodynamic impact of the π-donor OMe substituent, we have compared the cases X = OMe to X = H. Full geometry optimizations within the framework of DFT (B3LYP) calculations[16,17] have been carried out.[18] The olefin complexes have a square-pyramidal geometry with apical hydride and the C═C bond eclipsing the cis Ru−H bond (**I**). For X = OMe, the olefin complex with the CH(OMe) end closer to the hydride is less stable by only 1.2 $kcal\cdot mol^{-1}$ than the other isomer. This may suggest little regiochemical preference for a given insertion into Ru−H, in agreement with the experimental lack of selectivity for this step. For X = H, the carbene isomer is calculated to be 14 $kcal\cdot mol^{-1}$ *higher* and the carbene group eclipses P−Ru−P. For X = OMe, the carbene group prefers to be perpendicular to P−Ru−P and the two resulting conformations (OMe anti or syn to hydride) are respectively *only* 0.1 and 0.2 $kcal\cdot mol^{-1}$ above the more stable olefin complex. These varied carbene rotational conformer electronic preferences for the sterically small PH_3 species serve to explain why the *four* observed[10] structures of $RuCl_2(carbene)(PR_3)_2$ molecules show a wide variation in carbene rotational conformation.

The presence of an empty site on Ru and a lone pair on the oxygen does NOT result in an energy minimum in which the CH(OMe) group bonds to the metal through C and O simultaneously (i.e., η^2-carbene group): bonding through only carbon is preferred. However, the OMe group has a dominant influence in making the isomerization from the olefin to the carbene complex thermodynamically feasible as summarized by the isodesmic eq 4, where each species has its optimal geometry. The calculated energy difference of −13.9 kcal/mol favors OMe being on the carbene ligand and not on the olefinic ligand. The influence of the heteroatomic group thus supports the idea that

$$(H_3P)_2HClRu(CH_2{=}C(OMe)H) + (H_3P)_2HClRu{=}C(H)Me \rightarrow (H_3P)_2HClRu{=}C(OMe)Me + (H_3P)_2HClRu(CH_2{=}CH_2) \quad (4)$$

the 14-electron fragment $RuHCl(PH_3)_2$ is not a sufficiently strong electron donor to stabilize an unsubstituted carbene. However, there is almost no difference of binding energy of C_2H_4 and $CH_2{=}C(H)(OMe)$ to the 14-e Ru fragment as illustrated by the very small difference in energy between the two sides of the isodesmic eq 5 (1.6 $kcal\cdot mol^{-1}$ in favor of the ethylene complex). The lack

$$(H_3P)_2HClRu(CH_2{=}C(OMe)H) + H_2C{=}CH_2 \rightleftharpoons (H_3P)_2HClRu(CH_2{=}CH_2) + H_2C{=}C(OMe)H \quad (5)$$

of transformation of the C_2H_4 into the carbene complex is thus NOT due to a lack of pre-coordination of the C_2H_4. Consistent with the calculated preference for coordinated olefin, not carbene, for X = H, we find experimentally that ethylene simply forms an adduct with $RuHClL_2$, which persists for 2 h at 25 °C, with no formation of the isomeric carbene complex.

In the results reported here, the hydride ligand of $RuHClL_2$ is not a net reducing agent, but instead is merely a catalyst for H migration (i.e., to C_β, but then back to Ru from C_α). The question remains: *why*, in contrast to elsewhere among the transition metals,[8] is the carbene thermodynamically accessible from the olefin isomer on $RuHClL_2$? The origin of this thermodynamic difference lies in the cumulative effect of the Ru fragment and of X in stabilization of the Ru═C(X)Me double bond when X = OR. The isodesmic reaction in eq 6 (all singlet states employed[19])

$$C(Me)H + H_2C{=}C(OMe)H \xrightarrow{\Delta E = -29.9\ \text{kcal/mol}} H_2C{=}CH_2 + C(OMe)Me \quad (6)$$

reveals the large effect of OMe on the free carbene in lowering the calculated[18] endothermicity of the free olefin to free carbene isomerization by 29.9 kcal/mol. Likewise, coordination to $RuHCl(PH_3)_2$ also lowers the endothermicity of the isomerization by a large amount (e.g., 50 kcal/mol for X = OMe). The fact that the full 30 kcal/mol stabilization of eq 6 is *not* realized in eq 4 suggests that Ru and the OR group compete for the empty p_π orbital on the carbene carbon. In sum, both Ru and the OR groups are necessary to make the isomerization possible.

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Supporting Information Available: Details of reactivity studies, spectroscopic data, and calculated energies of all species used in isodesmic reactions (2 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[13] Even if $H_2C{=}CD(OEt)$ is reacted with $RuHClL_2$ (2:1 mole ratio) at 25 °C, to minimize the time spent as the olefin adduct, D is found statistically in RuD, $Ru{=}CC(H, D)_3(OEt)$, and all three vinylic positions of free ethyl vinyl ether; this procedure only serves to decrease the deuteration in the phosphine methyl groups.

[14] Spivak, G. J.; Coalter, J. N.; Oliván, M.; Eisenstein, O.; Caulton, K. G. *Organometallics* **1998**, *17*, 999.

[15] For examples of opposite carbene/olefin stability, see: (a) Heinekey, D. M.; Radzewich, C. E. *Organometallics* **1998**, *17*, 51. (b) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1997**, *99*, 22533. (c) Casey, C. P.; Polichnowski, S. W.; Shusterman, A. J.; Jones, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 7282. (d) Brookhart, M.; Tucker, J. R.; Husk, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 258.

[16] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

[17] Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *B37*, 785.

[18] (a) The calculations were carried out with the Gaussian 94 set of programs. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Ciolowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombre, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1995, Gaussian 94, Revision B3. ECP have been used for Ru, Cl, and P with their associated double ζ basis set,[b] augmented by a d function for Cl and P.[c] The other atoms were represented by a 6-31G(d,p) basis set,[d] except for C and H of Me and $H(PH_3)$ which were represented by a STO-3G basis set.[e] (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (c) Höllwarth, A.; Böhme, M.; Dapprich, S.; Ehlers, A. W.; Gobbi, A.; Jonas, V.; Köhler, K.; Stegmann, R.; Veldkamp, A.; Frenking, G. *Chem. Phys. Lett.* **1993**, *208*, 237. (d) Harihan, P. C.; Pople, J. *Theor. Chim. Acta* **1973**, *28*, 213. (e) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

[19] Triplet CHMe lies only 3−5 kcal/mol lower. See: Ma, B.; Schaeffer, H. F., III *J. Am. Chem. Soc.* **1994**, *116*, 3539.