Letter

R-Group reversal of isomer stability for $RuH(X)L_2(CCHR)$ *vs.* $Ru(X)L_2(CCH_2R)$: access to four-coordinate ruthenium carbenes and carbynes†

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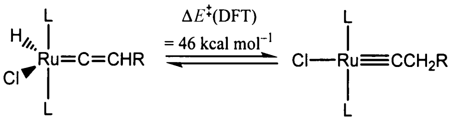
NaOPh converts equimolar $RuHClL_2(=C=CHR)$ ($L = PPr^i_3$ and PCy_3) first to $RuH(OPh)L_2(=C=CHR)$, but then, only for $R = H$, these isomerize to the more stable carbynes $Ru(OPh)L_2(C–CH_3)$; the rate of isomerization is slowed considerably by THF. $RuH(OPh)L_2(=C=CHR)$ can also be synthesized by reaction of $RuCl_2L_2[=CH(CH_2R)]$ with 2 NaOPh; again, only when $R = H$ does the hydrido vinylidene isomerize to the carbyne. While *phenoxide* converts $RuCl_2L_2(=CHPh)$ to $Ru(OPh)L_2(CPh)$, *via* the observable intermediates $RuCl_{2-n}(OPh)_nL_2(=CHPh)$, *alkoxides* OBu^t and OAdamantyl cause phosphine displacement to give the four-coordinate carbenes $Ru(OR)_2L(=CHPh)$. DFT (B3PW91) calculations show these d^6 species have a traditional *cis*-divacant octahedral structure with *trans* OR groups.

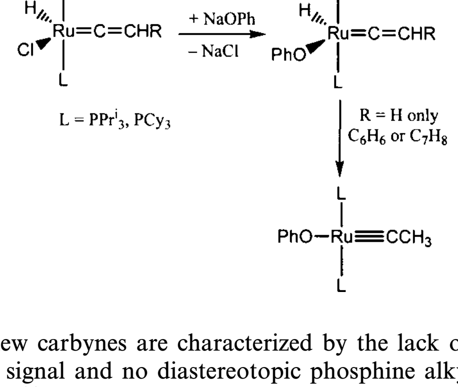
For more than a decade, five-coordinate vinylidene complexes of the type $Ru(X)(Y)L_2(=C=CRR')$ (L = phosphine) have been proposed as intermediates in or used as catalyst precursors for many useful organometallic transformations, though isomeric four-coordinate carbynes $Ru(X)L_2(C–C(Y)RR')$ remained unknown.[1] A recent study investigated the possibility that such isomers, which were shown through DFT calculations to be of similar (within ± 3 kcal mol^{-1}) energy, might exist in rapid ($t_{1/2} \sim 1$ s) equilibrium through 1,3-H shifts ($Y = H$); this was proven to be false [see eqn. (1), which gives the activation energy for unimolecular hydrogen migration].[2] We now detail the synthesis and characterization of such unsaturated four-coordinate carbynes, $Ru(X)L_2(C–CH_2R)$, and illustrate the influence of X and R in determining the thermodynamic preference over a hydrido vinylidene. A corollary study of X ligand replacement in $RuCl_2(=CHPh)L_2$ reveals unprecedented phosphine loss behavior, yielding a four-coordinate carbene $Ru(=CHPh)(OR)_2L$.



(1)

Hydrido vinylidene complexes $RuHClL_2(=C=CHR)$ ($L = PPr^i_3$, PCy_3; $R = H$, Ph)[3,4] react cleanly with NaOPh in toluene or THF at room temperature to first form simple halide-metathesis products $RuH(OPh)L_2(=C=CHR)$. These species are characterized by ^1H NMR hydride resonances in the range -14 to -17 ppm, shifted slightly from those of the parent chloride compound and displaying similar J_{PH} values. Aromatic signals for the new phenoxide ligand are present, and the characteristic vinylidene and ^{31}P resonances are seen.

Remarkably, when $R = H$ (and $L = PPr^i_3$ or PCy_3), the new complexes spontaneously isomerize within <1 h in *arene* solvents to four-coordinate carbynes $Ru(OPh)L_2(C–CH_3)$; *no* such rearrangement for the $R = Ph$ complexes is seen at room or higher temperatures or in the presence of added NEt_3 [eqn. (2)]. The parent chlorides ($R = H$ or Ph) also show *no* tendency to isomerize to carbyne. For example, immediate NMR observation of samples of $RuHClL_2(CCH_2)$ that were treated with NaOPh in C_6D_6 ($L = PPr^i_3$; a drop of THF-d_8 was added for rapid NaOPh solubility) showed the major ($>90\%$) product was $RuH(OPh)L_2(CCH_2)$, but isomerization to carbyne quickly ensued. The isomerization *does* proceed in THF, but at a *much* slower rate ($t_{1/2} \approx$ days).



(2)

The new carbynes are characterized by the lack of a high-field ^1H signal and no diastereotopic phosphine alkyl signals by ^1H or ^{13}C NMR, suggesting a planar structure, and only three aromatic ^1H NMR signals are observed for the OPh unit. The $RuCCH_3$ protons appear in the characteristic region of 0.0 to -0.5 ppm[5] with resolved $^4J_{PH}$ values of 3 or 4 Hz; ^{13}C NMR shows the α and β carbons of the ethylidyne moiety at 261 ($J_{PC} = 21$ Hz) and 28 ppm, respectively ($L = PCy_3$). The ^{31}P NMR spectra shows singlets at 55 and 46 ppm for $L = PPr^i_3$ and PCy_3, respectively.

During the course of our investigation, we reasoned that vinylidenes $RuH(OPh)L_2(=C=CHR)$ should be accessible by dehydrohalogenation of the carbenes $RuCl_2L_2[=CH(CH_2R)]$ since treatment of the former with HCl readily generates the carbenes.[4] Addition [eqn. (3)] of NaOPh to THF solutions of $RuCl_2L_2(=CHCH_3)$ (2 : 1 mole ratio),[6] with $L = PPr^i_3$, generates free phenol and the vinylidene complex

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† Electronic supplementary information (ESI) available: complete experimental and computational details. See http://www.rsc.org/suppdata/nj/b0/b006971j/

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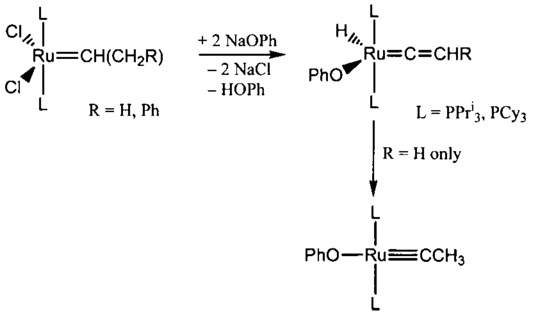
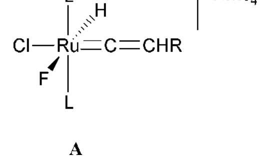
$RuH(OPh)L_2(CCH_2)$ within 1 h at 25 °C, which persists, in agreement with the above observations for isomerization in *THF*. However, when $RuCl_2L_2(=CHCH_3)$ was mixed with NaOPh (1 : 2 mole ratio) in C_6D_6, the isomeric carbyne $Ru(OPh)L_2(CCH_3)$ was formed after 12 h and only a trace amount of vinylidene was present. Consistent with the results above with R = Ph, treatment of the benzyl substituted carbene, $RuCl_2L_2[CH(CH_2Ph)]$, with NaOPh yields clean conversion to vinylidene complex $RuH(OPh)L_2(CCHPh)$ in either solvent, but *no* subsequent isomerization to carbyne. The presence of liberated HOPh when preparing the hydrido vinylidenes from carbenes [eqn. (3)] shows little effect on the rate of isomerization (with R = H).



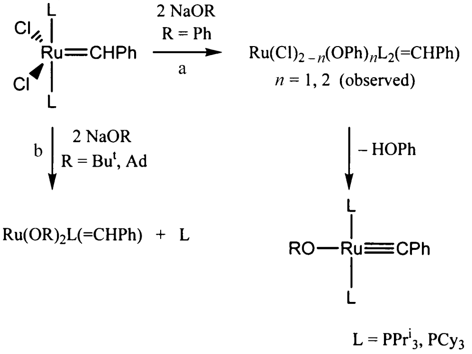
(3)

The dramatic rate decrease in the isomerization of $RuH(OPh)L_2(CCH_2)$ to $Ru(OPh)L_2(CCH_3)$ in THF solvent suggests that its donor potential might act to hinder the H exchange. When $L = PPr^i_3$ and R = Ph, evidence for this is seen in the preparation of $RuH(F)L_2(=C=CHR)$ by treatment of $RuHClL_2(=C=CHR)$ with NMe_4F. During the halide metathesis in C_6D_6, an intermediate is observed after 30 min; its NMR spectroscopy is consistent with six-coordinate $[RuH(F)ClL_2(=C=CHR)]NMe_4$, an adduct of the two reagents (**A**). Apparently this species is metastable because the cation in the fluoride source lacks the electrophilicity (*cf.* Na^+) to rapidly remove Cl^-. A *trans* disposition of the hydride and fluoride are suggested in **A** by the large J_{FH} of 80 Hz, and coordinative saturation is implied by the 4 ppm downfield shift of the ^1H resonance relative to the five-coordinate vinylidene. The triplet structure of the hydride signal establishes the retention of two phosphines. The $NMe_4{}^1H$ signal is observed at 2.8 ppm, and all other expected ^1H and ^{31}P resonances are seen displaced from those of the starting chloride. The ^{19}F signal for this adduct appears at −252 ppm, strongly shifted from that in the final product $RuH(F)L_2(C=CHPh)$ (−155 ppm), which forms within 12 h in C_6D_6. The fact that F^- binds strongly to the vacant site in $RuHClL_2(=C=CHR)$ suggests that the donation of THF in a *solvating environment* could indeed hinder the vinylidene-to-carbyne transformation if a flexible coordination sphere about Ru is required for isomerization.



A

Since the four-coordinate phenoxy ethylidynes were found to be stable and accessible from dichloro carbenes, we presumed that the analogous benzylidynes might also be accessible and resistant to isomerization due to their lack of β protons. Treatment of the benzylidenes $RuCl_2L_2(=CHPh)$[7] with 2 equiv. of NaOPh in THF [eqn. (4a)] leads within 3 h to the formation of carbynes $Ru(OPh)L_2(CPh)$, with $L = PPr^i_3$ or PCy_3, in good yields; the intermediates $RuCl(OPh)L_2(CHPh)$ and $Ru(OPh)_2L_2(CHPh)$ are detected. Free HOPh is observed by ^1H NMR, but free L is *absent*. Like their ethylidyne counterparts, these molecules are also characterized by NMR with the lack of a high-field ^1H signal, no diastereotopic ^1H or ^{13}C signals for the phosphine ligands, and aromatic resonances consistent with C_{2v} symmetry. Again, ^{31}P NMR shows only singlets at 55 and 44 ppm, and the Ru*C*Ph carbon ($L = PPr^i_3$) resonates at 248 ppm in ^{13}C NMR (t, J_{PC} = 20 Hz), again shifted *ca.* 40 ppm upfield with a large P–C coupling relative to other Ru carbynes.[8] To verify our proposed atom connectivity and planar geometry for these novel complexes, we determined the structure of $Ru(OPh)(PPr^i_3)_2(CPh)$ by X-ray crystallography (Fig. 1).[9]



(4)

Aliphatic alkoxides show remarkably different behavior [eqn. (4b)]. The carbenes $RuCl_2L_2(=CHPh)$, with $L = PPr^i_3$ or PCy_3, react (3 h, THF) with sodium alkoxides (NaOR; R = Bu^t or adamantyl) to form *four*-coordinate carbene complexes, $Ru(OR)_2L(=CHPh)$ with liberation of equimolar free phosphine. Solution NMR studies on these molecules at 25 °C show equivalent OR groups and diastereotopic CH_aH_b signals for the Ru–OAd protons γ to Ru.[10]

The structure of these molecules was established by DFT (B3PW91) geometry optimization of $Ru(OCH_3)_2(CH_2)(PH_3)$ as a model using effective core potential for Ru and P and a double ζ quality basis set with added polarization functions for all atoms but Ru (see Electronic supplementary information for details) with GAUSSIAN 98.[11] Various geometrical starting points differing in the coordination at the metal (*cis* or *trans* methoxy groups in particular) and orientation at the carbene all converged to the same "saw-horse" (*i.e.*, *cis*-divacant octahedron) geometry in which the two OMe ligands are mutually *transoid* and CH_2 and PH_3 are mutually *cis*. This is quite the same geometry as we have shown and analyzed earlier for the other d^6 species.[12–16] $RuH(CO)L_2{}^+$, $RuPh(CO)L_2{}^+$, $Ir(H)_2L_2{}^+$ and monomeric $RuHClL_2$. The

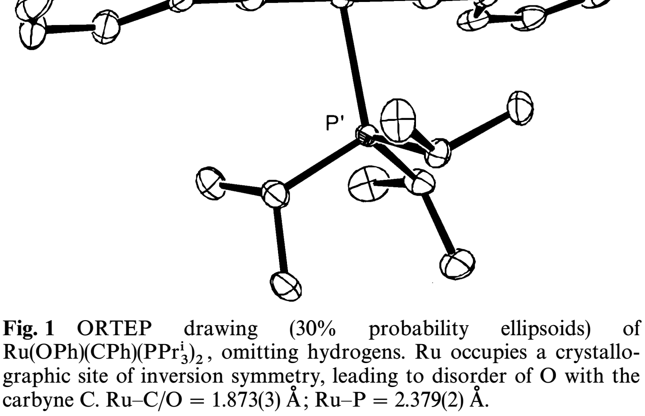
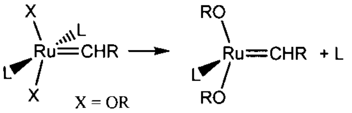


Fig. 1 ORTEP drawing (30% probability ellipsoids) of $Ru(OPh)(CPh)(PPr^i_3)_2$, omitting hydrogens. Ru occupies a crystallographic site of inversion symmetry, leading to disorder of O with the carbyne C. Ru–C/O = 1.873(3) Å; Ru–P = 2.379(2) Å.

π-acid carbene ligand is *trans* to an empty site (both ∠C–Ru–O = 111°) and the orientation of the OMe ligands are *transoid* (∠O–Ru–O = 134°), so that the Ru(carbene)(O)$_2$ substructure is nearly planar (sum of angles = 356°). The phosphorus lies 2.19 Å out of this plane with a P–Ru–C angle of 91°. In sum, this structure is that of $RuX_2L_2(CHR)$ (X = OR) with one L removed and with little modification of the remaining ligands [eqn. (5)].



(5)

These results of isomer stability reversal and phenol or phosphine loss show a subtle interplay of steric factors, X-group Brønsted basicity *vs.* nucleophilicity, and probably conjugative stabilization of Ru=C=CHR when R is phenyl. These effects, when employed judiciously, permit access to new classes of ruthenium reagents for further study.

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