Reactivity of $[RuHCl(P^iPr_3)_2]_2$ with Functionalized Vinyl Substrates. The H_2 Ligand as a Sensitive Probe of Electronic Structure

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Reaction of $[RuHClL_2]_2$ ($L = P^iPr_3$) with 2-vinylpyridine gives $L_2ClRu(\eta^2\text{-}CH{=}CHC_5H_4N)$ with liberation of H_2. Reaction of $[RuHClL_2]_2$ with a range of olefins D(H)C═CR(EWG) substituted by electron-donating (D) and -withdrawing (EWG) groups occurs by oxidative addition of a vinyl C−H bond to give the metallacycles $L_2ClH_nRu(\eta^2\text{-}^{\ddagger}C(D){=}CR(EWG))$. The ^{13}C chemical shift of $^{\ddagger}C$ and the fate of the "H_n" unit (decoordination, binding as H_2, or binding as two hydrides) are strongly correlated, depend on the donating and withdrawing power of D and EWG, and can be used to decide whether $^{\ddagger}C$ binds to Ru as a carbene or as a vinyl. These results emphasize the reducing power of Ru(II) when π-acid ligands such as CO are absent.

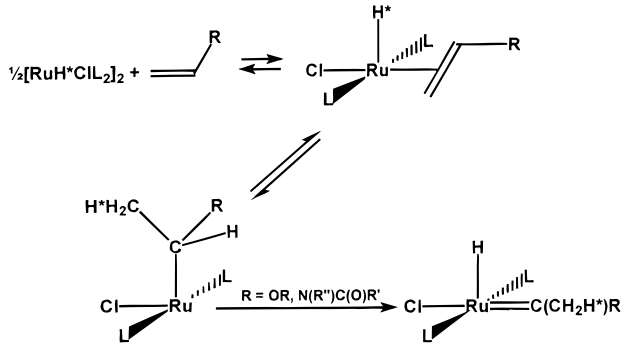
Introduction

The molecule $RuHClL_2$ ($L = P^iPr_3$), which exists as the chloro-bridged dimer $[RuH(\mu\text{-}Cl)L_2]_2$, reacts initially with ethylene, vinyl ethers, and vinyl amides to form an olefin adduct.[1] The latter two olefins, with electron-donating substituents, are then isomerized to coordinated carbenes, a reaction enabled by the hydride ligand on Ru (Scheme 1). We have analyzed why the carbene isomer is more stable for electron-donating R, but not for R = H.[1]

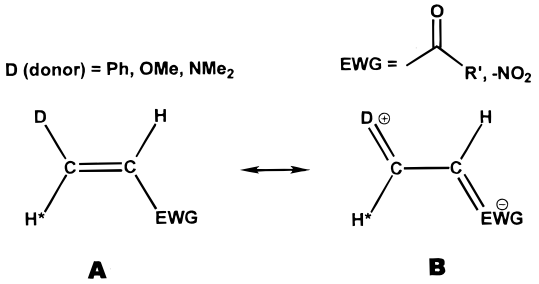
We examine here the result of "opposing" the electron-donating olefin substituent with an electron-withrawing substituent (Scheme 2). The push/pull interaction of these two has the effect of diminishing the double-bond character between the two vinylic carbons (**B**), but this does not suppress reactivity with $[RuHClL_2]_2$. The consequence of this change is to alter the mechanism of Scheme 1, from one of insertion and then α-H migration to one of vinylic C−H bond scission. As a consequence, the product of this reaction has two H on Ru, which becomes an indicator of the metal oxidation state. Three possible outcomes, $Ru(H)_2$, $Ru(H_2)$, or Ru + H_2, can be used to assess the bonding of the organic reagent to the metal. Henceforth, for simplicity, we will refer to the dimeric $[RuHClL_2]_2$ in monomeric form, $RuHClL_2$.

Insertion of olefins into the CH_2 bond of enones is promoted by $Ru(H)_2(CO)(PPh_3)_3$.[2] Metallacycles were proposed as intermediates. Ruthenium-catalyzed addition of the ortho C−H bond of *aromatic* ketones[3] and imines[4] has been developed in detail, including a computational mapping of one potential energy surface,[5] and *arene* ortho metalation is a mature field.[6,7]

Scheme 1



Scheme 2



Results

We begin with the reaction of an olefin which lacks push/pull substituents, but serves to introduce a mechanism which is an alternative to that in Scheme 1.

2-Vinylpyridine. Reaction of $RuHClL_2$ with this olefin was examined even though it does not have a heteroatom on an sp^2 carbon. We were interested here in the degree to which the nitrogen donor would bind to Ru, and whether such binding might assist conversion of *this* olefin to a carbene or give additional mechanistic insight into the previously reported conversions with vinyl ether and amides (Scheme 1). The

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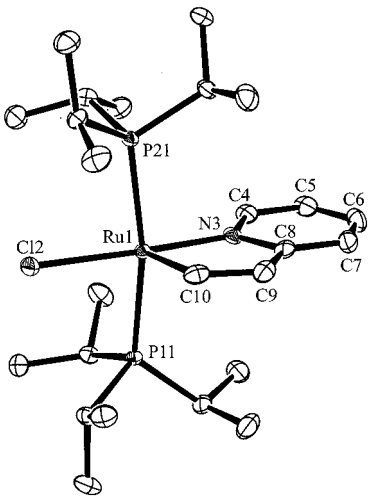
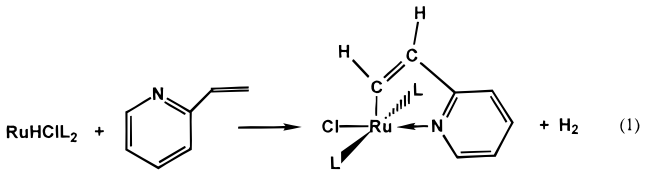
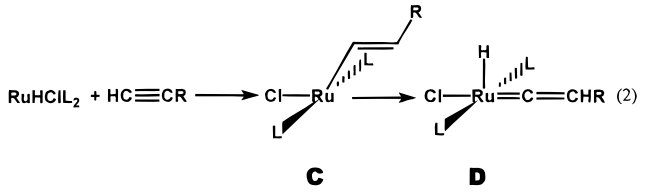


Figure 1. ORTEP drawing of the non-hydrogen atoms of $RuCl(P^iPr_3)_2(\eta^2\text{-}CH{=}CHC_5H_4N)$, showing selective atom labeling.

reaction is slow (overnight at 25 °C) but gives primarily one product. The product ultimately isolated is not a hydride or dihydrogen complex as no appropriate signal is seen in ^1H NMR, but it still contains two vinylic hydrogens (in addition to those of the pyridyl group), and two associated vinylic ^{13}C NMR signals. This product is thus (eq 1) an unsaturated σ vinyl



complex, which implies the loss of H_2. Dissolved H_2 was not observed, but evidence is seen for the formation of 2-ethylpyridine and for $RuH(H_2)ClL_2$, which represent alternate fates for lost H_2. In addition, this product is quantitatively generated in the time of mixing from reaction of $RuHCl(P^iPr_3)_2$ with 1 equiv of 2-ethynylpyridine in C_6D_6. This product is to be contrasted to the reaction of (eq 2) $RuHClL_2$ with RCCH, where



the vinyl intermediate **C** transforms to the vinylidene hydride **D**.[8] Because $RuHClL_2$ strongly coordinates pyridine,[9] its presence here allows chelation to stabilize the σ-bound vinyl isomer relative to that of hydrido vinylidene.

X-ray Structure Determination of $RuClL_2(-CH{=}CH-C_5H_4N)$. The molecule has effective C_s symmetry, and all the atoms of the vinylpyridyl ligand lie in the mirror plane, as do Ru and Cl (Figure 1). The phosphines are almost perfectly related by this idealized mirror plane (the Ru−P distances do not differ statistically), and they bend slightly away from both the Ru−N and the Ru−C bonds (Figure 2). Bond angles around square-pyramidal Ru are close to 90°, with the smallest one (77.9(1)°) involving the five-membered chelate ring. The vinyl carbon lies *trans* to the empty coordination site, and the Ru−C(10) distance, 1.943(3) Å, is short compared to 2.03−2.08 Å for vinyl carbons,[10] consistent with its strong *trans* influence. There is no evidence for agostic ^{i}Pr interactions with Ru; all ∠Ru−P−C are similar and greater than 108.9°. The Ru−Cl distance (2.4134(8) Å) is typical,[10] and the Ru−N distance (2.058 Å) is shorter than those[10] to pyridine in six-coordinate Ru(II) species (2.11−2.12 Å). The C(9)−C(10) distance, 1.306(5) Å, is typical for a double bond, and C(8)−C(9) is typical for an sp^2-sp^2 single bond. The two phosphines approximately eclipse each other (as indicated by their idealized mirror symmetry), and they are each approximately staggered with respect to the Ru−Cl and Ru−C bonds.

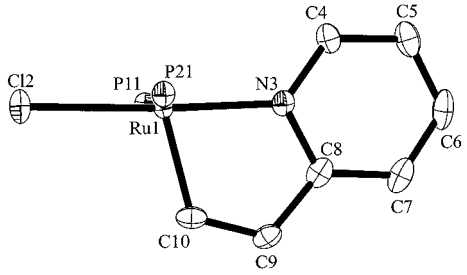
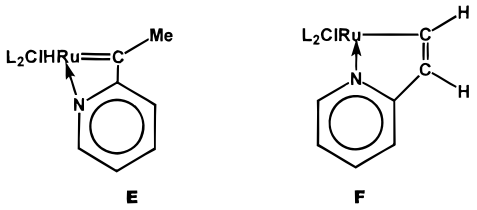


Figure 2. ORTEP drawing of $RuCl(P^iPr_3)_2(\eta^2\text{-}CH{=}CHC_5H_4N)$ showing the bending of the phosphorus away from the Ru−N and Ru−C bonds.

Mechanism of Formation. The surprising absence of **E** as a product leads to the corollary questions of why and how **F** is formed from 2-vinylpyridine. Monitoring of the reaction of



$RuHClL_2$ with 2-vinylpyridine at 25 °C in benzene-d_6 reveals the growth, then decay of an intermediate identified as $RuCl(H_2)(\eta^2\text{-}CH{=}CHNC_5H_4)L_2$ by spectroscopic methods. By ^1H NMR, signals for the substructure $RuCl(\eta^2\text{-}CH{=}CHNC_5H_4)L_2$ are seen, accompanied by a broad singlet at −8.8 ppm which integrates for two protons. In addition, this compound exhibits a $^{31}P\{^1H\}$ NMR singlet approximately 3 ppm displaced from that of the molecule with no metal-bound H's. The presence of a dihydrogen ligand instead of two classical hydrides is indicated by a short $T_{1(min)}$ time of 15 ms (400 MHz, −50 °C) for the upfield signal. Treatment of $RuClL_2(CH{=}CH-C_5H_4N)$ with 1 atm of H_2 in C_6D_6 generates the H_2 adduct (in the time of mixing), which persists for at least 3 h. This solution then slowly (>24 h) forms 2-ethylpyridine and $RuH(H_2)ClL_2$.We propose that the mechanism of the reaction in eq 1 begins with binding of the pyridine nitrogen (**G** in eq 3), thus allowing a close approach of the vinylic hydrogen to the unsaturated ruthenium center. Support for this proposal comes from a labeling study with enones (see below).

Substituted α,β-Unsaturated Ketones and Aldehydes. These reagents might have reacted with $RuHClL_2$ to give

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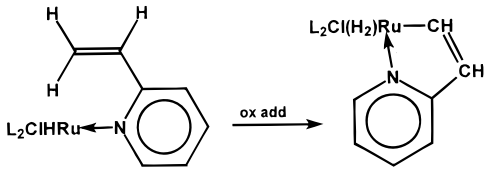
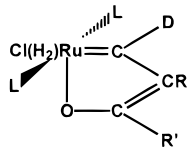


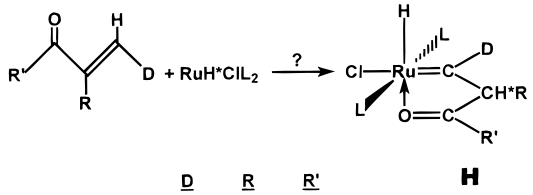
(3)

G

chelated carbene products (eq 4). In fact, this rapid reaction gives a product **I**. Species **I** *might* form from **H** by migration of the CHR hydrogen (anticipated to be acidic because it is α to both carbonyl and carbene) to the metal.



I



(4)

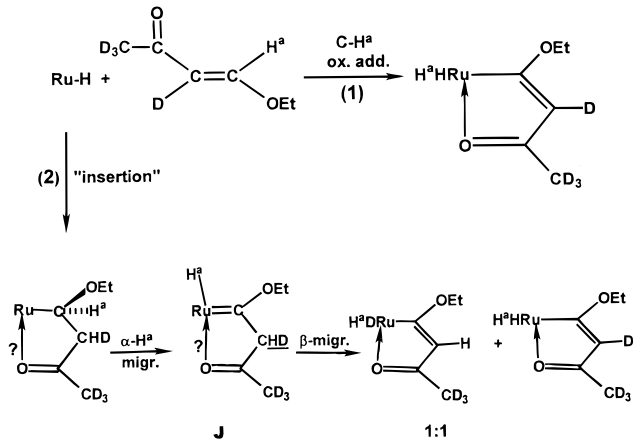
D	R	R'
OMe	H	Me
NMe_2	Me	H
Ph	H	Me

H

(a) With D = OMe, the reaction occurs in the time of mixing, although the location of H_2 with respect to the carbene is not established with certainty by the spectral data. The two metal-bound hydrogens are established as H_2 by the short $T_{1(min)}$ (16.6 ms at 400 MHz, −50 °C),[11,12] in spite of a somewhat uncharacteristically high field chemical shift (−11.4 ppm) and resolvable coupling (8.7 Hz) to two phosphines. Consistent with a saturated electron count, the (Ru=C) ^{13}C and the ^{31}P NMR chemical shifts differ strongly from those of five-coordinate carbene complexes derived from vinyl ethers,[9] and this compound is pale watermelon color, indicating a higher HOMO/LUMO gap. The H_2 ligand is not removed by the vacuum involved in solvent removal or when the solid is isolated and dried *in vacuo* for 4 h. Further study (see below) shows that the fate of these two H's varies considerably as D, R, and R′ are changed in eq 4.

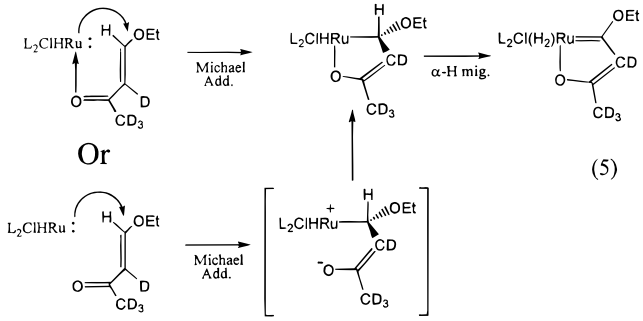
To test for the fate of individual hydrogens in the mechanism of formation of $L_2ClRu(H_2)(\eta^2\text{-}C(OMe)CH{=}C(O)Me)$, the reaction with D-labeled olefin *trans*-$D_3CC(O)CD{=}C(H)(OEt)$ was carried out. Scheme 3 shows how direct oxidative addition (path 1) leaves the D untouched, while "insertion", (path 2), the addition of Ru−H across the C=C bond and formation of a carbene transient **J**, creates a symmetric methylene group which leads to 50:50 distribution of deuterium population (i.e., ^2H NMR intensity) at the metal and at C_β. The actual outcome of this test was sought by ^1H and ^2H NMR assay of the reaction product, $L_2ClRu(HD_x)(\eta^2\text{-}C(OEt)C(H/D_y)C(O)CD_3)$ where $(x + y = 1)$, isolated after 3 h. Deuterium NMR showed no D on ruthenium (−11.4 ppm) but full retention of the original D content at C_β. The presence of the CD_3 group on the olefin gives an internal standard for quantitative monitoring of D at

Scheme 3



C_β. Proton NMR showed the full presence of two hydrogens (i.e., the original RuH and also H^a) on Ru and no H at C_β above the 7% H present in the original olefin (Figure 3). We therefore assign the mechanism of this reaction as involving direct C−H* oxidative addition (path 1); no deuterium scrambling from reversible or irreversible insertions occurs.

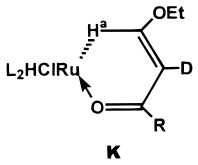
Also consistent with the labeling study above and very similar to direct oxidative addition is Michael addition to C_β, followed by α-H migration (eq 5). This process can be viewed as one



(5)

extreme of the C−H cleavage process where the ruthenium electron density acts more nucleophilic toward C_β than reducing toward the C−H bond. The actual mechanism in this addition may actually lie somewhere between these two extremes in the C−H cleavage process, though for simplicity we will label this mechanism as direct oxidative addition.

Since direct vinyl C−H oxidative addition represents a complete reversal of the mechanism deduced for vinyl ethers (Scheme 1), some comment is required. First, the olefin used here is better described as a highly polarized, conjugated olefin, and push/pull interaction in **B** shows that Ru−H addition is disfavored by diminished double-bond character between C_α and C_β. Perhaps more important is the fact that initial coordination of the keto oxygen (**K**) to $RuHClL_2$ would likely give an



K

agostic interaction favoring C−H^a bond cleavage in a way which is absent for vinyl ethers. Note that this directing effect to assist C−H^a cleavage also operates with 2-vinylpyridine (**G**) as proposed above.

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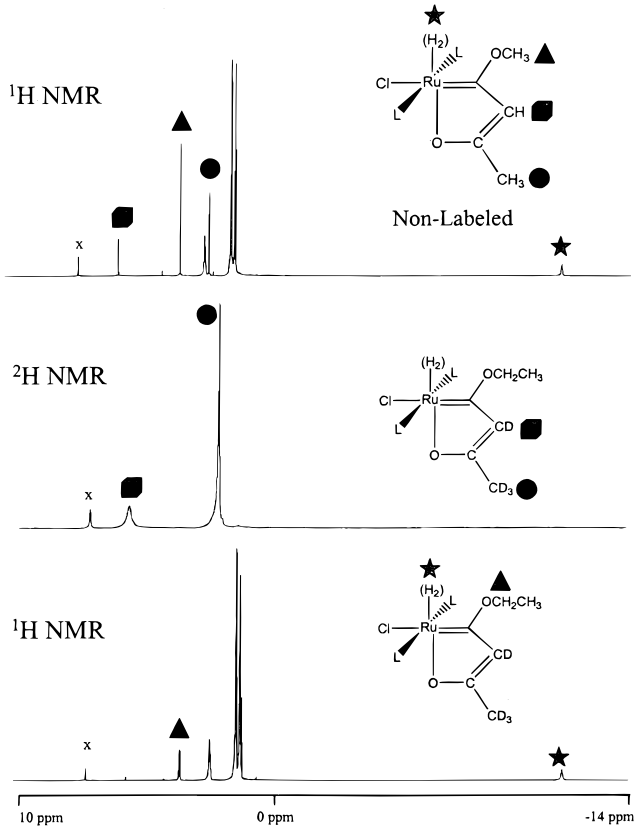
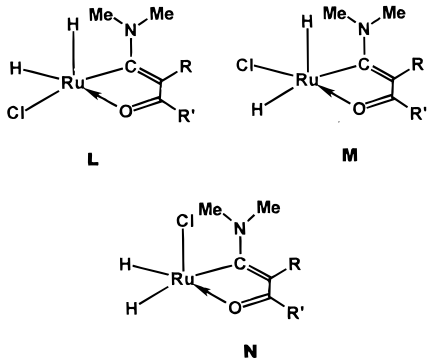


Figure 3. NMR spectra (in benzene) showing deuterium flow in labeling study with *trans*-(EtO)CH═CDC(O)CD_3. X = residual solvent.

(b) With D = NMe_2, compound **L** (P^iPr_3 ligands out of this plane are omitted for clarity) is generated in quantitative yield in the time of mixing in benzene with no detectable intermediates by ^{1}H or ^{31}P{^{1}H} NMR. A very broad resonance observed

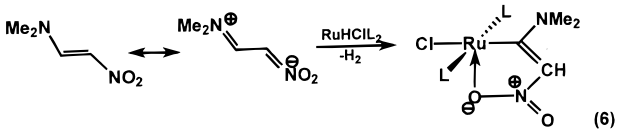


by ^{1}H NMR at −9.6 ppm shows no coupling to the phosphorus atoms at room temperature. The two metal-bound hydrogens decoalesce below 0 °C, which suggests a rearrangement barrier too high for an H_2 complex, and each signal becomes an apparent quartet at −50 °C. The $T_{1(min)}$ values both occur near −60 °C (400 MHz), and they are 99 and 111 ms, which is more consistent with a classical dihydride structure. Selective decoupling of the ^{31}P nuclei and each hydride signal sequentially at −50 °C permits accurate determination of the H/H and P/H coupling constants. Each hydride is a doublet ($J_{HH'}$) of triplets (J_{H-P}) with mutual coupling of 18.8 Hz. This hydride/hydride coupling is relatively large, which might favor structure **M** (phosphines perpendicular to the $Ru(H)_2$ plane are omitted for simplicity in **L**−**N**), except that **L** and **N** are preferred because their intrinsically shorter H/H distance of *cis* hydrides better accounts for the fairly short $T_{1(min)}$ values.

Decoalescence of the Me_2N resonance ^{1}H NMR into two signals at −70 °C shows that the molecular structure has the Me_2N group in the conformation which allows N lone pair interaction with the C(sp^2) π system.

(c) When D = phenyl, the reaction gives a metallacycle as in **I**, but H_2 is eliminated to produce a five-coordinate product. Although product isolation involves drying in vacuo for several days, H_2 is observed to be lost after 24 h in solution at room temperature when the reaction progress is monitored spectroscopically *in situ*. Five resonances are observed for the phenyl protons and nonquaternary carbons by ^{1}H and ^{13}C{^{1}H} NMR, indicating that the phenyl group lies in the plane perpendicular to the phosphines and is not rotating rapidly on the NMR time scale. The π system of the aromatic ring is thus in the correct orientation to allow for conjugation with the π system of the metallacycle. During this reaction, an intermediate believed to be a dihydrogen adduct is observed by ^{1}H and ^{31}P{^{1}H} NMR. Although no $T_{1(min)}$ measurement has been performed on the upfield signal, the fact that dihydrogen is readily lost offers some evidence for a nonclassical structure.

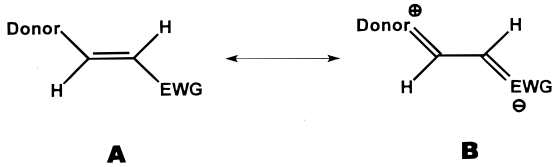
(d) The Nitroolefin *trans*-$Me_2N(H)C{=}C(H)NO_2$. This reagent represents a class of compounds similar in structure to π-rich, α,β-unsaturated aldehydes and ketones, but containing the highly electron withdrawing nitro group in place of a carbonyl (eq 6, Scheme 2). When these reagents are combined



in benzene, an immediate color change to purple is observed. The major species present by ^{1}H and ^{31}P{^{1}H} NMR assay after 15 min are $RuH(H_2)ClL_2$, unreacted olefin, an H_2 adduct of the final product, and the final product itself. Apparently unreacted $RuHClL_2$ serves as an effective H_2 scavenger. The H_2 of $L_2Cl(H_2)Ru(\eta^2\text{-}C(NMe_2){=}C(H)NO_2)$ is eventually lost completely to generate the five-coordinate species shown in eq 6. Twenty hours after a 2:1 mixture (dehydrogenated species:H_2 adduct) is placed in C_6D_6, the ratio of compounds was found to be 20:1 by ^{31}P integration, illustrating this loss of H_2. Once the H_2 is lost, recoordination is unfavored since, when a sample of the above 2:1 mixture is treated with 1 atm of H_2 in toluene-d_8, the ratio of compound shifts only to 1:1 after 24 h. The $T_{1(min)}$ value for this adduct was found to be 27 ms (−40 °C, 400 MHz), proving the adduct to be a dihydrogen complex.

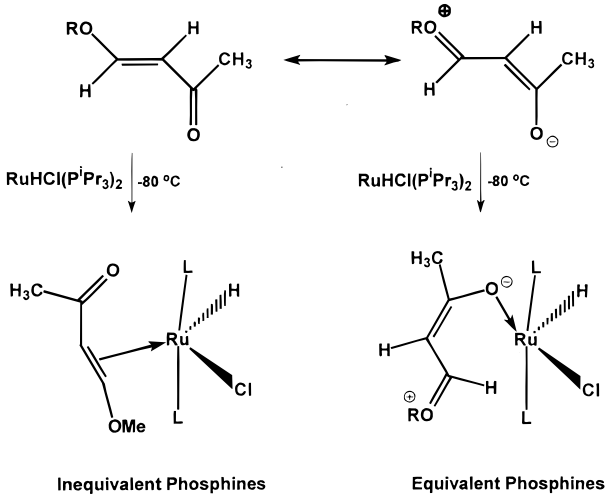
Discussion

Reaction Mechanism. With the mechanism of the electron-rich enone and enal addition now established as differing fundamentally from those involving vinyl ethers, an understanding as to the origin of this difference was sought. The push/pull resonance contributor involving these carbonyl and nitro substituents offers a starting point (**A**−**B**). This resonance effect



can be clearly seen in NMR spectra of the free olefins $(Me_2N)HC{=}C(Me)C(O)H$ and $(Me_2N)HC{=}C(H)NO_2$. At room tem-

Scheme 4



perature in C_6D_6, the dimethylamino enal shows a single but very broad resonance for the amino methyl groups by $^{13}C\{^1H\}$ NMR, indicative of hindered rotation about the Me_2N-C bond. In the nitro-containing species, the effect is even more pronounced, with *trans*-$(Me_2N)HC{=}C(H)NO_2$ showing two sharp signals for the dimethylamino group by ^1H NMR at 25 °C. In this extreme case, rotation around the Me_2N-C bond is frozen on the NMR time scale, illustrating that considerable C/N double bond character is present and all the non-hydrogen atoms lie in a plane in the ground state. From these observations, it is clear that zwitterionic character is present in these "push−pull" stabilized olefins which should certainly have the effect of *increasing* the nucleophilicity of the EWG with a corresponding nucleophilicity *decrease* for the *olefinic* portion of the molecule.

These differences suggest that the mechanistic divergence begins with initial coordination of the olefin to ruthenium. The vinyl ethers were shown[9] to bind through the C=C bond, as evidenced by the AB pattern in the low-temperature $^{31}P\{^1H\}$ NMR spectrum, but alkenes with electron-withdrawing substituents may bind through the nucleophilic EWG instead. Binding through the π system of electron-rich alkenes would yield inequivalent phosphines in an observable adduct, while binding through the carbonyl or nitro oxygens of the EWG would yield an adduct where the phosphines are symmetry-related (Scheme 4). Unfortunately, attempts to determine which binding mode dominates by low-temperature ^1H and $^{31}P\{^1H\}$ NMR have failed. When $RuHCl(P^iPr_3)_2$ and *trans*-4-ethoxy-3-buten-2-one are combined at −80 °C in toluene-d_8 and placed in a precooled NMR probe at this temperature, the only species observed by ^1H and $^{31}P\{^1H\}$ NMR are the two starting materials and, remarkably, a significant amount of final product. As the temperature is raised, the reaction proceeds smoothly to completion with no detectable intermediates. Although this fails to identify an adduct, *product* formation at such low temperatures is consistent with binding via the EWG, since the less-hindered ethyl vinyl ether does not yield carbene until 0 °C.

Carbene or Vinyl? As reported with reactions of $[RhCl(P^iPr_3)_2]_n$,[13] the metallacyclic products of $RuHClL_2$ with α,β-unsaturated ketones and aldehydes illustrate a continuum between two resonance structures. Spectroscopically, the two extremes differ in that carbene complexes of ruthenium and osmium give (M=*C*) chemical shifts around 300 ppm, while metal vinyl compounds show the α carbon closer to 200 ppm.

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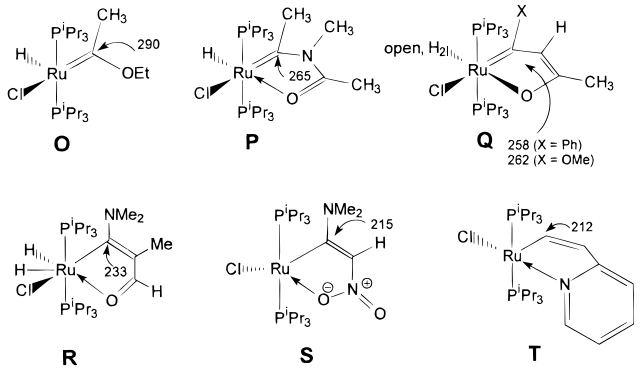
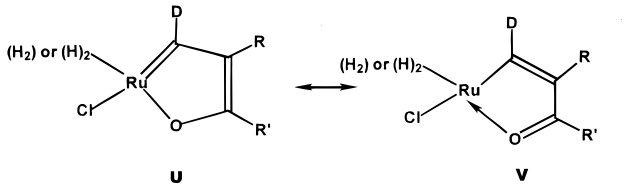
Scheme 5

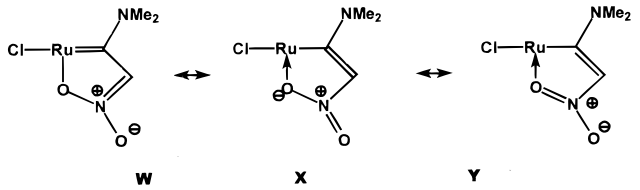


Examples of this can be seen in the reference compounds **O** and **T**, whose bond lengths (by X-ray diffraction) are consistent with a metal carbene and a metal vinyl, respectively (Scheme 5).

From the low barrier to dimethylamino rotation for E = NMe_2 and upfield ^{13}C chemical shift relative to E = OMe or Ph, one may conclude that the amino-substituted species **R** is closer to **V**. The similar ^{13}C shift of E = OMe, Ph to that of the product of $RuHClL_2$ with vinyl amides (Ru=C of 265 ppm by ^{13}C NMR), coupled with the fact that $RuHClL_2(=C(Me)NC(O)CH_2CH_2CH_2)$ (an analogue of **P**) was shown by X-ray analysis to have an Ru−C distance compatible with a double bond,[9] lends considerable evidence to the assignment as more like **U**.

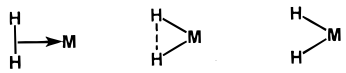


A continuum of resonance contributors exist to explain the bonding in the nitro species in eq 5, but species **X** is perhaps a major one. The $^{13}C\{^1H\}$ chemical shift of the carbon atom α

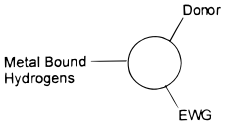


to Ru (215 ppm) argues against the carbene structure (**W**) and is much more consistent with a σ-vinyl group (**X** and **Y**). Additionally, the facile loss of H_2 from this molecule can be interpreted as stemming from the *trans* influence of the Ru-bound alkoxide oxygen of the nitro group in structure **X**. At room temperature, this molecule exhibits inequivalent methyl groups of the NMe_2 unit by ^1H NMR which can be attributed to slow rotation about the C(α)−N bond. Although this is consistent with a Fischer carbenic structure, the large separation of the methyl signals (1.3 ppm, 400 MHz) highly exaggerates the true rotational barrier magnitude. In the molecule $Ru(H)_2ClL_2(\eta^2\text{-}C(NMe_2)Me{=}C(O)H)$, **R**, where the methyl groups decoalesce at −70 °C (400 MHz), the amino methyl groups differ in chemical shift by only 0.1 ppm. From these observations, it is appropriate to assign structures to these molecules that are more vinylic than carbenic.

Scheme 6



Scheme 7



Donor	EWG	H atoms
Ph	MeC=O	not bound
OMe	MeC=O	H_2 complex
NMe_2	HC=O	dihydride complex
NMe_2	NO_2	not bound

H_2 as a Probe of Electronic Structure. The structures in Scheme 6 reveal a range of behavior along a continuum of bonding possibilities. Starting with only the H−H σ bond density donating to an empty metal orbital, increasing electron density from a filled d orbital is back-donated into the σ^* orbital of dihydrogen, first stretching and finally splitting the H−H bond to form two hydrides. The more reducing a metal center is, the more likely hydride formation will occur (oxidative addition of H_2). In cases where the metal is not very reducing (less electron-rich), back-donation is reduced, with the result being a η^2 dihydrogen complex. In general, however, at least a little back-donation is necessary to bind H_2 since the σ bond of H_2 is not very nucleophilic. For example, very few H_2 adducts of even extremely electrophilic high-valent early transition metal complexes are known, presumably due to the lack of d electrons for back-donation.

With the bonding nature of dihydrogen in mind, the results obtained from reaction of $RuHCl(P^iPr_3)_2$ with heteroatom-substituted enones and enals illustrate how effectively H_2 can serve as a gauge of metal reducing character.[14−18] This is best represented (Scheme 7) with the metallacycle (the circle) viewed as a conduit through which electron-donating and -withdrawing substituents express their influence. An alternative view is to consider metallacycle resonance structures **U** and **V**. Form **U** has a metal oxidation state two units higher than **V**, if a carbene is taken as dianionic. Whatever favors this carbene form (e.g., less electron-donating D or more electron-withdrawing EWG) will work against the ligand-reduced dihydride form. As a better π donor is placed on the metallacycle with the electron-withdrawing group held constant, the mode of H_2 binding changes distinctly. With the weakly donating phenyl group present, H_2 does not even remain bound upon product formation, while with the strongly donating NMe_2 substituent, ruthenium becomes electron-rich enough that it not only keeps H_2 bound but reduces it to a classical dihydride. When the donor is OMe, a middle ground is reached and H_2 does indeed remain bound, but as a dihydrogen complex. The nitro group is so electron-withdrawing that not even the NMe_2 group can compensate sufficiently: hydrides are oxidized, and the resulting H_2 is lost from the coordination sphere.

Experimental Section

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 airtight vessels. $[RuHCl(P^iPr_3)_2]_2$ was prepared according to published procedures.[1,9] All other reagents were obtained from standard suppliers (unless otherwise indicated) and used after drying and degassing. ^1H NMR chemical shifts are reported in parts per million relative to protio impurities in the deutero solvents, and ^{31}P spectra are referenced to an external standard of 85% H_3PO_4 (0 ppm). NMR spectra were recorded with either a Varian Gemini 2000 (300 MHz ^1H; 121 MHz ^{31}P; 75 MHz ^{13}C) or a Varian Unity INOVA instrument (400 MHz ^1H; 162 MHz ^{31}P; 101 MHz ^{13}C).

$RuCl(P^iPr_3)_2(CH{=}CH{-}C_5H_4N)$. Under Ar, 150 mg (0.328 mmol) of $RuHCl(P^iPr_3)_2$ was dissolved in 15 mL of benzene in a Schlenk flask. Via syringe, 35.3 μL (0.328 mmol) of 2-vinylpyridine was added, and the reaction mixture was stirred overnight at room temperature. The mixture was then heated for 2 h at 50 °C before removal of solvent to a N_2 trap. The dark red residue was then dissolved in 20 mL of pentane and placed in a −80 °C bath. The bright red precipitate was washed with cold pentane and dried *in vacuo* to yield 65 mg of product (75% by $^{31}P\{^1H\}$ integration before workup). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ 1.04 (dvt, $J_{P-H} = {}^3J_{H-H} = 7.6$ Hz, 18H, $P(CHMe_2)_3$), 1.16 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.4$ Hz, 18H, $P(CHMe_2)_3$), 2.22−2.32 (m, 6H, $P(CHMe_2)_3$), 6.25 (dt, $^3J_{H-H} = 5.6$ Hz, $^3J_{P-H} = 4.0$ Hz, 1H, Ru−C*H*=CH−py), 6.72 (dt, $^3J_{H-H} = 5.6$ Hz, $^4J_{P-H} = 1.6$ Hz, 1H, Ru−CH=C*H*−py), 6.86−6.89 (m, 2H, py-H), 8.89 (d, $^3J_{H-H} = 6.0$ Hz, 1H, py-H), 12.05 (d, $^3J_{H-H} = 5.2$ Hz, 1H, py-H). $^{31}P\{^1H\}$ NMR (121 MHz, C_6D_6, 20 °C): δ 37.8 (s). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6, 20 °C): δ 19.8 (s, $P(CHMe_2)_3$), 20.5 (s, $P(CHMe_2)_3$), 24.4 (vt, $J_{P-C} = 8.5$ Hz, $P(CHMe_2)_3$), 114.1, 118.4, 125.6, 131.7, 171.0 (s, C_5H_4N), 153.5 (s, Ru−CH=*C*H−py), 211.8 (t, $J_{P-C} = 8.8$ Hz, Ru−*C*H=CH−py). Anal. Calcd for $C_{25}H_{48}ClNP_2Ru$: C, 53.51; H, 8.62. Found: C, 53.25; H, 8.96.

Table 1. Crystallographic Data for $RuCl(P^iPr_3)_2(\eta^2\text{-}CH{=}CHC_5H_4N)$

formula	$C_{25}H_{48}ClNP_2Ru$
a, Å	36.815(3)
b, Å	8.810(1)
c, Å	18.997(1)
β, deg	115.51(1)
V, Å^3	5560
Z	8
fw	561.13
space group	$C2/c$
T, °C	−164
λ, Å	0.71069
ρ_{calcd}, g/cm^{-3}	1.340
μ(Mo Kα), cm^{-1}	7.9
R^a	.0324
$R_w{}^b$	.0393

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

Structure Determination of $RuCl(P^iPr_3)_2(CH{=}CHC_5H_4N)$. A crystal of suitable size was obtained by cleaving a large rod-shaped piece of the air-sensitive sample in a nitrogen atmosphere glovebag. The crystal was mounted using silicone grease, and it was then transferred to a goniostat, where it was cooled to −164 °C for characterization and data collection ($6° < 2\theta < 55°$) (Tables 1 and 2). A preliminary search for peaks followed by analysis using the programs DIRAX and TRACER revealed a C-centered monoclinic cell. After intensity data collection, the condition $1 = 2n$ for $h0l$ limited the space group to Cc or $C2/c$. An initial choice of $C2/c$ was later proven correct by the successful solution of the structure. The data were corrected for absorption. The structure was solved using a combination of direct methods (MULTAN78) and Fourier techniques. The position of the ruthenium atom was obtained from an initial E-map. The positions of the remaining non-hydrogen atoms were obtained from iterations of a least-squares refinement, followed by a difference Fourier calculation. Hydrogens were included in fixed, calculated positions with thermal parameters fixed at one plus the isotropic thermal parameter of the parent carbon atom. In the final cycles of refinement, the non-hydrogen atoms were varied with anisotropic thermal parameters to give a total of 272 variables. The final difference map was featureless, the largest peak being 0.33 and the deepest hole being −0.35 e/Å^3.

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Table 2. Selected Bond Distances (Å) and Angles (deg) for $RuCl(P^iPr_3)_2(\eta^2\text{-}CH{=}CHC_5H_4N)$

Ru(1)−Cl(2)	2.4134(8)	C(4)−C(5)	1.374(5)
Ru(1)−P(11)	2.3874(8)	C(5)−C(6)	1.393(6)
Ru(1)−P(21)	2.3860(8)	C(6)−C(7)	1.374(6)
Ru(1)−N(3)	2.0576(27)	C(7)−C(8)	1.413(5)
Ru(1)−C(10)	1.943(3)	C(8)−C(9)	1.425(5)
N(3)−C(4)	1.355(4)	C(9)−C(10)	1.356(5)
N(3)−C(8)	1.376(4)		

Cl(2)−Ru(1)−P(11)	84.759(27)	N(3)−Ru(1)−C(10)	77.91(13)
Cl(2)−Ru(1)−P(21)	86.659(27)	Ru(1)−N(3)−C(4)	126.96(23)
Cl(2)−Ru(1)−N(3)	176.63(8)	Ru(1)−N(3)−C(8)	115.67(22)
Cl(2)−Ru(1)−C(10)	105.34(11)	C(4)−N(3)−C(8)	117.4(3)
P(11)−Ru(1)−P(21)	168.22(3)	N(3)−C(8)−C(7)	120.6(3)
P(11)−Ru(1)−N(3)	95.97(7)	N(3)−C(8)−C(9)	112.4(3)
P(11)−Ru(1)−C(10)	94.22(9)	C(7)−C(8)−C(9)	127.0(3)
P(21)−Ru(1)−N(3)	92.14(7)	C(8)−C(9)−C(10)	114.7(3)
P(21)−Ru(1)−C(10)	95.83(9)	Ru(1)−C(10)−C(9)	119.24(26)

$Ru(H_2)Cl(P^iPr_3)_2(-CH{=}CH-C_5H_4N)$. Treatment of a sample (10 mg) of $RuCl(P^iPr_3)_2(-CH{=}CH-C_5H_4N)$ with 1 atm of H_2 in C_6D_6 yields complete conversion in the time of mixing to a dihydrogen adduct. This species represents a readily detectable intermediate (1 h after combination of $RuHClL_2$ and 2-vinylpyridine) in the formation of the dehydrogenated species immediately above. Facile loss of H_2 then occurs with continued stirring/workup under vacuum. NMR data follows. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −8.76 (broad s, 2H Ru(*H*$_2$)); $T_{1(min)}$ = 15 ms (−50 °C, 400 MHz), δ 0.94 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.7 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.09 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.7 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.19−2.24 (m, 6H, P(C*H*Me$_2$)$_3$), 6.49 (td, $^3J_{H-H}$ = 6.0 Hz, $^3J_{P-H}$ = 1.5 Hz, 1H, Ru−C*H*=C−py), 6.90 (d, $^3J_{H-H}$ = 6.0 Hz, 1H, Ru−CH=C−py), 6.99−7.05 (m, 2H, py-H), 9.82 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, py-H), 10.49 (d, $^3J_{H-H}$ = 4.8 Hz, 1H, py-H). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 41.2 (s).

$Ru(H_2)Cl(P^iPr_3)_2(\eta^2\text{-}C(OMe)CHC(O)Me)$. Under Ar, 100 mg (0.218 mmol) of $RuHCl(P^iPr_3)_2$ was dissolved in 10 mL of toluene in a Schlenk flask. Via syringe, 25.0 μL (0.240 mmol) of *trans*-4-methoxy-3-buten-2-one was added and the reaction mixture stirred for 1 h at room temperature. Attempts to precipitate at low temperature from toluene failed, but solvent removal and washing with pentane followed by drying *in vacuo* yielded 55 mg of pale orange powder (95% by ^{31}P{^{1}H} integration before workup). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −11.38 (broad triplet, $^2J_{P-H}$ = 8.7 Hz, 2H, Ru−(*H*$_2$), 1.13 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.4 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.29 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.4 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.14 (t, J_{P-H} = 1.4 Hz, 3H, Ru=C(OMe)−CH=C(O)*Me*), 2.26−2.38 (m, 6H, P(C*H*Me$_2$)$_3$), 3.25 (s, 3H, Ru=C(O*Me*)−CH=C(O)Me), 5.61 (s, 1H, Ru=C(OMe)−C*H*=C(O)Me). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 44.2 (s). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, −20 °C): δ 19.4 (s, P(CH*Me*$_2$)$_3$), 20.4 (s, P(CH*Me*$_2$)$_3$), 23.7 (vt, J_{P-C} = 9.5 Hz, P(*C*HMe$_2$)$_3$), 24.4 (s, Ru=C(OMe)−CH=C(O)*Me*), 56.8 (s, Ru=C(O*Me*)−CH=C(O)Me), 107.3 (s, Ru=C(OMe)−*C*H=C(Me)O), 198.3 (s, Ru=C(OMe)−CH=*C*(O)-Me), 261.5 (t, J_{P-C} = 8.5 Hz Ru=C). $T_{1(min)}$(Ru−(*H*$_2$)) = 16.6 ms (400 MHz, −50 °C). Anal. Calcd for $C_{23}H_{51}ClO_2P_2Ru$: C, 49.50; H, 9.21. Found: C, 49.51; H, 8.95.

***trans*-$CD_3C(O)C(D){=}C(H)OEt$.** A combination of literature preparations for methoxy methylene ketones[19,20] was modified as follows. To a stirred slurry of 4.7 g (0.20 mol) of finely chopped Na in 40 mL of ether at 0 °C was added a solution of 15.0 mL (0.20 mol) of acetone-d_6 and 19.8 mL (0.25 mol) of ethyl formate in 40 mL of ether via dropping funnel over a period of 2 h. The mixture was then allowed to warm to room temperature and stirred overnight. The supernatant was then removed via cannula, and the yellow precipitate was washed with 50 mL of ether and dried in vacuo. The isolated yield of the sodium salt, $CD_3C(O)C(D){=}C(H)ONa$, was 18.5 g (84%). Under Ar, 10.0 g (0.09 mol) of the sodium salt in 80 mL of DMF was then treated with 13.0 mL (0.18 mol) of ethyl bromide at 0 °C. The reaction mixture was then stirred for 4 h at room temperature after slowly warming, and the organic products were extracted with pentane (4 × 75 mL). The pentane extracts were combined, the solvent was removed on a rotary evaporator, and the oily product was fractionally distilled under reduced pressure, the fraction boiling at 37−39 °C (0.1 Torr) being collected (literature specifies 91−93 °C at 20 Torr for the protio analogue). Yield: approximately 2.0 g (20%). The product was confirmed to contain 99+ atom % D at the CD_3 group and 93 atom % D at the vinylic site by ^{1}H NMR. ^{2}H NMR (61.4 MHz, C_6H_6, 20 °C): δ 1.78 (s, 3D, C*D*$_3$), 5.43 (d, $^3J_{H-D}$ = 1.6 Hz, 1D, $CD_3C(O)C(D){=}$C(H)OEt). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 0.88 (t, $^3J_{H-H}$ = 7.1 Hz, 3H, OCH$_2$C*H*$_3$), 3.30 (q, $^3J_{H-H}$ = 7.1 Hz, 2H, OC*H*$_2$CH$_3$), 7.31 (broad s, 1H, $CD_3C(O)C(D){=}C(H)$OEt). In addition, a small doublet ($^3J_{H-H}$ = 13.0 Hz) was observed at δ 5.43 (and corresponding satellites at δ 7.31) in ^{1}H NMR with a relative intensity of 7%, corresponding to 93% deuterium incorporation at $CD_3C(O)C(D){=}$C(H)OEt.

$Ru(H_2)Cl(P^iPr_3)_2(\eta^2\text{-}C(OEt)CDC(O)CD_3)$. Under Ar, 200 mg (0.44 mmol) of $RuHCl(P^iPr_3)_2$ was dissolved in 20 mL of benzene in a Schlenk flask. Via syringe, 51 μL (0.44 mmol) of $CD_3C(O)C(D){=}$C(H)OEt was added, and the reaction mixture was stirred for 3 h at room temperature. The solvent was removed to a liquid N_2 trap and the product washed with pentane (4 × 10 mL) and dried *in vacuo*. Isolated yield: 75 mg, (30%). Note that the lowered yield from heavy washing was preferred at the gain of extremely pure material for accurate integrations. ^{2}H NMR (61.4 MHz, C_6H_6, 20 °C): δ 2.07 (s, 3D, C*D*$_3$), 5.61 (s, 1D, Ru=C(OEt)−C*D*=C(O)CD$_3$). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −11.39 (broad triplet, $^2J_{P-H}$ = 10.8 Hz, 2H, Ru−(*H*$_2$), 1.08 (t, J_{P-H} = $^3J_{H-H}$ = 9.4 Hz, 3H, OCH$_2$C*H*$_3$), 1.14 (dvt, J_{P-H} = $^3J_{H-H}$ = 7.6 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.30 (dvt, J_{P-H} = $^3J_{H-H}$ = 7.6 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.27−2.39 (m, 6H, P(C*H*Me$_2$)$_3$), 3.51 (q, J_{P-H} = $^3J_{H-H}$ = 9.4 Hz, 2H, OC*H*$_2$CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 45.7 (s). Further, a small singlet was observed at δ 5.59 in ^{1}H NMR with a relative intensity of 7%, arising from the protio impurity in the labeled reagent. No signals were observed in the region of −11.4 ppm by ^{2}H NMR.

$Ru(H)_2Cl(P^iPr_3)_2(\eta^2\text{-}C(NMe_2)C(Me)CHO)$. Under Ar, 200 mg (0.44 mmol) of $RuHCl(P^iPr_3)_2$ was dissolved in 20 mL of toluene in a Schlenk flask and cooled to −78 °C. A solution of 50 mg of 3-(dimethylamino)-2-methylpropen-2-al in 3 mL of toluene (0.44 mmol) was slowly added via syringe and the mixture allowed to warm to room temperature. After stirring for 3 h at room temperature, the solvent was removed to a liquid N_2 trap and the residue was washed with small portions of pentane. Drying *in vacuo* yielded 80 mg of light yellow powder (90% by ^{31}P{^{1}H} integration before workup). ^{1}H NMR (400 MHz, CD_2Cl_2, −50 °C): δ −8.22 (apparent quartet, selective decoupling reveals $^2J_{P-H}$ = 16.8 Hz, $^2J_{H-H}$ = 18.8 Hz, 1H, $T_{1(min)}$ = 110.9 ms at −57 °C, Ru−*H*), −11.19 (apparent quartet, $^2J_{P-H}$ = 16.2 Hz, $^2J_{H-H}$ = 18.8 Hz, 1H, $T_{1(min)}$ = 98.5 ms at −66 °C, Ru−*H*), 1.04 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.4 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.17 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.4 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.04 (s, 3H, Ru−C(NMe$_2$)=C(*Me*)−CHO), 2.11 (broad s, 6H, P(C*H*Me$_2$)$_3$), 3.10 (s, 6H, Ru−C(N*Me*$_2$)=C(Me)−CHO), δ 7.36 (s, 1H, Ru−C(NMe$_2$)=C(Me)−C*H*O). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2, −20 °C): δ 49.7 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, −20 °C): δ 13.6 (s, Ru−C(NMe$_2$)=C(*Me*)−CHO), 19.0 (s, P(CH*Me*$_2$)$_3$), 19.3 (s, P(CH*Me*$_2$)$_3$), 24.4 (vt, J_{P-C} = 9.6 Hz, P(*C*HMe$_2$)$_3$), 43.3 (broad s, Ru−C(N*Me*$_2$)=C(Me)−CHO), 98.6 (s, Ru−C(NMe$_2$)=*C*(Me)−CHO), 161.3 (s, Ru−C(NMe$_2$)=C(Me)−*C*HO), 233.4 (t, J_{P-C} = 7.2 Hz, Ru−C). In addition to resolving the hydride peaks that are seen as a broad singlet at −9.6 ppm at room temperature, variable-temperature ^{1}H NMR shows decoalescence of the amino methyl groups from slowed rotation about the C−NMe$_2$ bond. At −90 °C, the sharp singlet at 3.10 ppm has evolved into two equal-intensity singlets at 3.14 and 3.04 ppm. Anal. Calcd for $C_{24}H_{54}ClNOP_2Ru$: C, 50.47; H, 9.53. Found: C, 49.94; H, 9.38.

$RuCl(P^iPr_3)_2(C(Ph)-CHC(O)Me)$. Under Ar, 200 mg (0.44 mmol) of $RuHCl(P^iPr_3)_2$ was dissolved in 20 mL of toluene in a Schlenk flask. Via syringe, 70 mg (0.44 mmol) of *trans*-4-phenyl-3-buten-2-one was added and the reaction mixture stirred overnight at room temperature. The solvent was removed and the product dried *in vacuo* for 1 week to yield 175 mg of a dark red solid; 66%. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 1.13 (dvt, J_{P-H} = $^3J_{H-H}$ = 6.4 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.20

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(dvt, $J_{P-H} = {}^3J_{H-H} = 6.4$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.09 (t, $J_{P-H} = 1.4$ Hz, 3H, Ru=C(Ph)−CH=C(O)*Me*, 2.26−2.36 (m, 6H, P(C*H*Me$_2$)$_3$), 7.04 (s, 1H, Ru=C(OMe)−C*H*=C(O)Me, 6.98−7.30 (m, 4H, Ru=C(*Ph*)−CH=C(O)Me, 8.69 (d, $J_{H-H} = 7.2$ Hz, 1H, Ru=C(*Ph*)−CH=C(O)Me. ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 38.9 (s). ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2, 20 °C): δ 19.3 (s, P(CH*Me*$_2$)$_3$), 19.8 (s, P(CH*Me*$_2$)$_3$), 22.8 (vt, $J_{P-C} = 9.6$ Hz, P(*C*HMe$_2$)$_3$), 22.5 (s, Ru=C(Ph)−CH=C(O)*Me*, 125.0 (s, Ru=C(Ph)−*C*H=C(O)Me, 127.5, 128.2, 128.6, 128.7, 129.1, 129.5 (s, Ru=C(*Ph*)−CH=C(O)Me, 199.0 (s, Ru=C(OMe)−CH=*C*(O)Me, 257.7 (t, $J_{P-C} = 8.6$ Hz Ru=*C*).

RuCl(P^{i}Pr$_3$)$_2$(η^2-C(NMe$_2$)C(H)NO$_2$). Under Ar, 100 mg (0.22 mmol) RuHCl(P^{i}Pr$_3$)$_2$ and 25.4 mg (0.22 mmol) of 1-(dimethylamino)-2-nitroethylene were charged in a Schlenk flask. Benzene was then added (15 mL), and the reaction mixture was stirred for 2 h at room temperature. The solvent was removed to a liquid N_2 trap, and the crude product was washed with pentane (3 × 10 mL) and dried *in vacuo* to yield 65 mg of a deep purple powder found to be a mixture of dehydrogenated species and H_2 adduct (2:1 ratio) (52%). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 1.11 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.4$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.25 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.4$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.35 (s, 3H, N*Me*$_2$), 2.35−2.50 (m, 6H, P(C*H*Me$_2$)$_3$), 3.63 (s, 3H, N*Me*$_2$), 6.74 (s, 1H, C(NMe$_2$)=C(*H*)NO$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 41.2 (s). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6, 20 °C): δ 19.7 (s, P(CH*Me*$_2$)$_3$), 19.8 (s, P(CH*Me*$_2$)$_3$), 23.4 (vt, $J_{P-C} = 8.5$ Hz, P(*C*HMe$_2$)$_3$), 39.1 (s, N*Me*$_2$), 50.9 (s, N*Me*$_2$), 114.7 (s, C(NMe$_2$)=*C*(H)NO$_2$), 214.7 (t, $J_{P-C} = 9.7$ Hz Ru−*C*).

Ru(H$_2$)Cl(P^{i}Pr$_3$)$_2$(η^2-C(NMe$_2$)C(H)NO$_2$). During the formation of the dehydrogenated species immediately above, an H_2 adduct was observed. It can be partially regenerated by addition of 1 atm of H_2 to an NMR tube containing the above (2:1) mixture. After 24 h under excess H_2, the ratio was 1:1 (dehydrogenated:adduct). In addition, a sample of the above mixture (2:1) placed in benzene-d_6 with *no* H_2 added was found in a 20:1 ratio (no other ^{31}P-containing products) after 20 h by ^{31}P NMR, illustrating facile loss of coordinated H_2. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ −11.08 (s, 2H Ru−(H2)), 1.04 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.6$ Hz, 18H, P(CH*Me*$_2$)$_3$), 1.21 (dvt, $J_{P-H} = {}^3J_{H-H} = 6.6$ Hz, 18H, P(CH*Me*$_2$)$_3$), 2.24 (s, 3H, N*Me*$_2$), 2.32−2.48 (m, 6H, P(C*H*Me$_2$)$_3$), 2.73 (s, 3H, N*Me*$_2$), 7.03 (s, 1H, C(NMe$_2$)=C(*H*)NO$_2$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6, 20 °C): δ 43.7 (s). $T_{1(min)}$ of Ru−(*H*$_2$) = 27 ms at −40 °C (400 MHz).

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Supporting Information Available: An X-ray crystallographic file in CIF format for the structure of RuCl(P^{i}Pr$_3$)$_2$(CHCHC$_5$H$_4$N). This material is available free of charge via the Internet at http://pubs.acs.org.

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