Organometallics **2000,** *19,* 3569−3578

Cleavage of H−C(sp^2) and C(sp^2)−X Bonds (X = Alkyl, Aryl, OR, NR$_2$): Facile Decarbonylation, Isonitrile Abstraction, or Dehydrogenation of Aldehydes, Esters, Amides, Amines, and Imines by [RuHCl(P^{i}Pr$_3$)$_2$]$_2$

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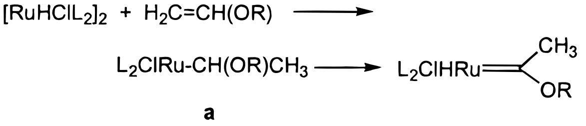
The $RuHClL_2$ fragment ($L = P^iPr_3$) reacts at 25 °C with a dozen different $G{=}CHE$ compounds ($G = O$, $E = R$, OR, NR_2; $G = NR$, $E = R$) to give π-acid abstraction products, $RuHCl(CG)L_2$, and $E{-}H$. For $E{-}H = C_2H_5OH$, alcohol is decarbonylated in a second step to give an additional CO ligand and CH_4. For $E{-}H = HNR(CR'_2H)$, amine can be dehydrogenated by $RuHClL_2$ to give $RuH(H_2)ClL_2$ and $CR'_2{=}NR$. X-ray crystallographic studies are presented for the DMF decarbonylation intermediate $Ru(H)_2Cl(\eta^2\text{-}C(O)NMe_2)L_2$, where the strong reducing potential of $RuHClL_2$ is manifested in the formally Ru(IV) species obtained from oxidative addition of $H{-}C(O)NMe_2$. The structure of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)L_2$, the product from aryl C−H activation of benzylidenemethylamine, $PhHC{=}NMe$, is also presented. This ability to abstract CO, isonitrile, or H_2 is traced to the considerable π-basicity of $RuHCl(P^iPr_3)_2$.

Introduction

The fragment $RuHClL_2$ ($L = P^iPr_3$), derived from the dimer $[RuHClL_2]_2$,[1] has been shown to react with vinyl ethers by addition of Ru−H across the C=C bond, followed by α-H migration from the primary product **a** to give a heteroatom-stabilized carbene complex.[2] We evaluate here the chemistry of this same electron-rich Ru fragment with analogous double bonds $G{=}CHE$, where $G = O$, NR′ and the group E is an electron donor (OR, NR_2) or even hydrocarbyl R. Reactivity analogous to that in eq 1 would lead to or proceed through $L_2ClRu{-}CHE(GH)$ or $L_2ClRu{-}GCH_2E$ species. However, the results reported here reveal that the ultimate products are not derived from the Ru−H addition across the G=C bond but, instead, from reactivity at the keto or imino C(sp^2)−H bond.



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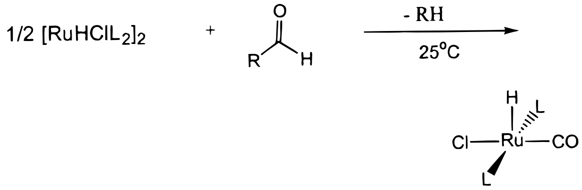
Results and Discussion

Decarbonylation of Aldehydes. Dimeric $[RuHClL_2]_2$ reacts with aldehydes (HC(O)R, R = alkyl) under mild conditions in benzene or cyclohexane to liberate $RuHCl(CO)(P^iPr_3)_2$ and RH (eq 2). For propionaldehyde (R = Et) as the carbonyl source, the reaction is complete and quantitative within 30 min, and ethane is observed by ^{1}H NMR when the reaction is monitored *in situ*. No intermediates or liberated ethylene were observed during this reaction, and it is presumed to proceed via a classical, least-motion mechanism initiated by oxidative addition of aldehydic C−H following initial coordination. Deinsertion of R from the resulting (H_2) or $(H)_2$ acyl intermediate and subsequent reductive elimination of alkane completes the process (Scheme 1). A C−H oxidative process was previously shown to operate for incorporation of electron-rich enones and enals into the $RuHCl(P^iPr_3)_2$ fragment,[3] though an alternate initial path involving addition of Ru−H across C=O cannot be immediately discounted and has the benefit of maintaining the preferred (+2) oxidation state of Ru (vs +4) throughout. Indeed, it may be said that there is some reluctance to propose oxidative addition to Ru(II), since this d^6 configuration may not be a competent reducing agent; however, results reported later here will prove this idea false. From transient Ru−C*H*R(OH), α-H



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[1] Coalter, J. N., III; Huffman, J. C.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.*, in press.

[2] Coalter, J. N., III; Bollinger, J. C.; Huffman, J. C.; Werner-Zwanziger, U.; Caulton, K, G.; Davidson, E. R.; Gérard, H.; Clot, E.; Eisenstein, O. *New J. Chem.* **2000**, *24*, 9.

[3] Coalter, J. N., III; Gérard, H.; Huffman, J. C.; Bollinger, J. C.; Davidson, E. R.; Eisenstein, O.; Caulton, K. G. *Inorg. Chem.*, in press.

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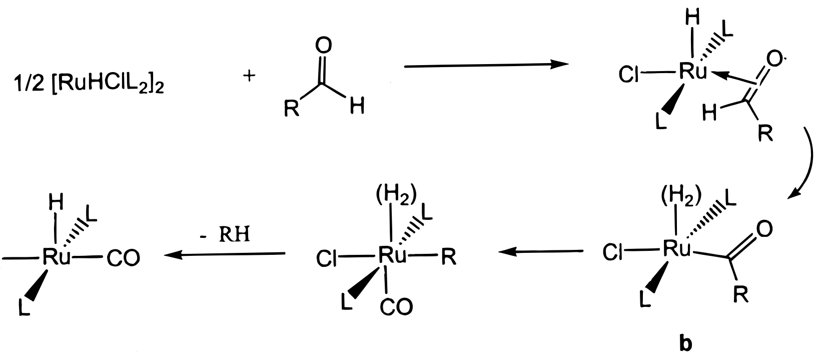
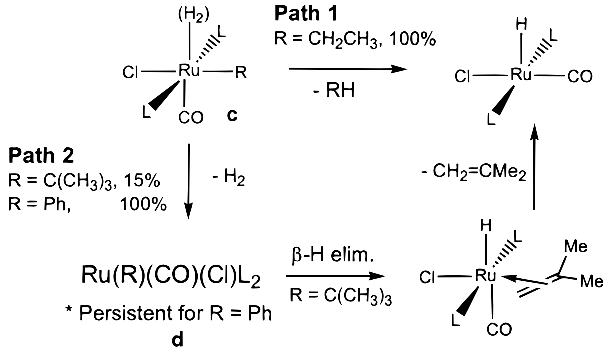
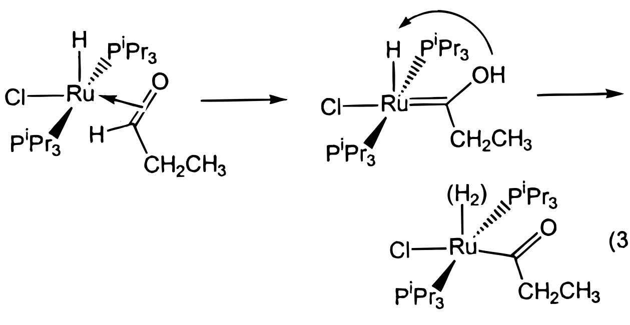
Scheme 1



Scheme 2



migration forms a hydroxycarbene, where subsequent tautomeric H transfer yields the acyl intermediate **b** (eq 3). The first step in this pathway was found to operate in reactions of vinyl ethers and amides with $[RuHCl(P^iPr_3)_2]_2$ to generate alkoxy and amido carbenes and is therefore feasible for the fleeting formation of transient hydroxycarbenes.



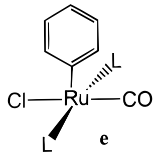
(3)

Reaction with the bulky pivaldehyde ($R = {}^tBu$) forms $RuHCl(CO)L_2$ as the primary product (70%), but at a much slower rate ($t_{1/2} \approx 15$ h). This kinetic sluggishness increases the occurrence of H_2 loss to available $RuHClL_2$ (to rapidly form $RuH(H_2)ClL_2$; 15% is observed) from proposed intermediate **c** (Scheme 2) to yield unsaturated $Ru({}^tBu)(CO)ClL_2$, which will be prone to β-H elimination. Evidence for such a (H_2) or $(H)_2$ alkyl intermediate (**c**) was observed after 30 min at room temperature (C_6D_6) in the form of a high-field ^1H NMR signal (δ −9.50, t, $^2J_{P-H} = 15$ Hz, 2H) for the Ru H's and an upfield-shifted ^tBu signal (δ 0.72, s, 9H). A corresponding $^{31}P\{^1H\}$ singlet was also observed (~50% of total P intensity), and these signals disappear in concert with $RuHCl(CO)L_2$ formation. β-H elimination after loss of H_2 to form **d** would generate the observed product $RuHCl(CO)L_2$ and isobutylene, a potentially reactive species (toward $RuHClL_2$), yielding a plausible origin for the balance (15%) of uncharacterized products (Scheme 2) from contact with unreacted $[RuHClL_2]_2$.

Reaction with 3,3-dimethylbutyraldehyde ($R = CH_2{}^tBu$) offers the opportunity to evaluate the potential for a β-H elimination of alkene to generate $RuHCl(CO)L_2$, because here intermediates **c** and **d** offer no β-hydrogens. In comparison to R = Et, if the added bulk of $R = CH_2{}^tBu$ (over propionaldehyde) slows the net relative rate of RH production as with pivaldehyde (vs H_2 loss and β-H elimination), intermediate **c** (Scheme 2) (or its H_2-loss product, **d**) should show longer life (vs $R = {}^tBu$), enabling more complete characterization. However, after 20 min at room temperature, quantitative conversion of $RuHClL_2$ and $HC(O)CH_2{}^tBu$ to $RuHCl(CO)L_2$ and neopentane ($CH_3{}^tBu$, observed) is complete. Thus, we speculate that the dominant factor in favoring one path over the other in Scheme 2 (i.e., hydrocarbon vs H_2 elimination) originates from electronic factors (e.g., 1° vs 3° alkyl) rather than sterics.

In support of this, analogous reaction with benzaldehyde (R = Ph) in C_6D_6 results in immediate consumption of starting $RuHClL_2$ and 75% conversion to an intermediate, but no formation of $RuHCl(CO)L_2$ after 30 min at room temperature; free H_2 (and 25% $RuH(H_2)ClL_2$) is also produced. After 48 h at room temperature (in a sealed tube), only 30% conversion to $RuHCl(CO)L_2$ and benzene (^1H NMR evidence) is achieved, but heating mildly (60 °C, 12 h) drives the reaction to completion. The sole kinetic product seen by NMR can be isolated cleanly by dropwise addition of a $[RuHClL_2]_2$ solution to a 5-fold excess (Ru:C=O) of stirred benzaldehyde in toluene. The molecule is characterized by ^1H NMR (C_6D_6, 25 °C) by the lack of a high-field (<0 ppm) signal(s), diastereotopic P^iPr_3 methyl groups, and three distinct resonances in the aromatic region centered at δ 6.73 (t, $^3J_{H-H} = 8$ Hz, 1H), δ 6.83 (t, $^3J_{H-H} = 8$ Hz, 2H), and δ 7.8 (broad s, $w_{1/2\,h} = 90$ Hz, 2H) for the para, meta, and ortho protons of a $Ru-C_6H_5$ moiety; $^{31}P\{^1H\}$ NMR shows only a singlet (δ 36.0). Cooling the sample to −20 °C (CD_2Cl_2) results in decoalescence of the o-C_6H_5 protons to two broad signals centered at δ 7.2 and δ 7.7 by ^1H NMR; two distinct resonances for the o-C_6H_5 carbons at 136.9 and 141.4 ppm and a broad signal (δ 125.9, $w_{1/2\,h} = 116$ Hz) for the m-C_6H_5 carbons are seen by $^{13}C\{^1H\}$ NMR. The ^{13}C NMR also shows a low-field signal (δ 205.6, t, $^2J_{P-C} = 14$ Hz) for the *ipso*-C_6H_5

carbon and ν_{CO} = 1905 cm^{-1}, consistent with the formulation Ru(Ph)Cl(CO)L$_2$ (**e**), where a trans ∠Cl−Ru−CO benefits from Cl pπ→CO π^* push−pull stabilization. These data correspond to a structure of C_s symmetry with transoid phosphines and C$_6$H$_5$ coplanar with a mirror plane in the ground state, and such a conformation was seen for the related molecule where L = P^{t}Bu$_2$Me, whose spectroscopic data resemble those reported here. However, with L = P^{t}Bu$_2$Me, sharp signals for the *o*-C$_6$H$_5$ protons were observed at room temperature showing slower rotation about Ru−C$_{ipso}$, and consistent with more C$_{ipso}$ pπ→Ru dπ donation (i.e., double-bond character) in these unsaturated molecules when the less electron donating P^{t}Bu$_2$Me is employed.[4] Treatment of this aryl complex with 1 atm of H$_2$ in C$_6$D$_6$ results in complete conversion to RuHCl(CO)L$_2$ and benzene within 12 h at room temperature.



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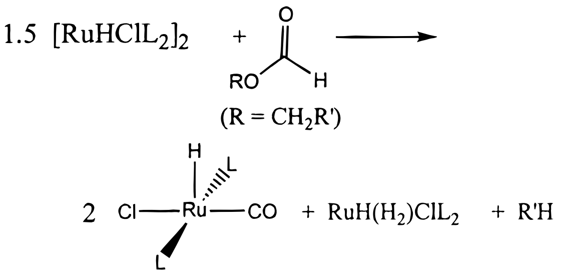
The isolation of such a complex shows that although decarbonylation of aryl aldehydes is effected under mild conditions, the general trend of slower aryl migrations and/or reductive eliminations (vs alkyl) results in complete loss of H$_2$ along path 2 in Scheme 2 to yield Ru(Ph)Cl(CO)L$_2$. Now, however, Ru−R has no low-energy mechanism for formation of RuHCl(CO)L$_2$ and alkene, and any liberation of benzene to form RuHCl(CO)L$_2$ from hydrogenolysis of Ru−C$_6$H$_5$ by free H$_2$ is inhibited by the binding site for H$_2$ in Ru(Ph)Cl(CO)L$_2$ being *trans* to the phenyl ligand with which it must react. An example of aryl substituent modification controlling insertion/deinsertion of C$_6$H$_4$X (incorporated as M(η^2-aroyl) or as M(C$_6$H$_4$X)(CO)) has been recently demonstrated and shows how a subtle change in electronics (compared to aryl vs alkyl) can shift the product outcome dramatically.[5]

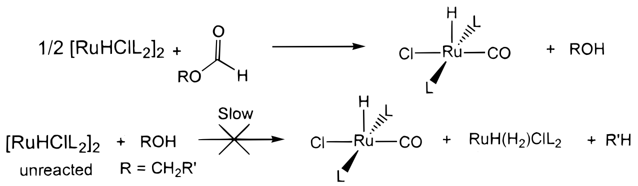
We turned next to substrates with less electrophilic carbonyl carbons.

Decarbonylation of Formates. The decarbonylation rate of ethyl formate (R = CH$_2$R′; R′ = Me) is comparable to that of propionaldehyde; within 30 min no trace of starting [RuHClL$_2$]$_2$ was observed by NMR. However, the presence of two potential CO units (i.e., formyl *and* OR) in the parent ester results in *double* decarbonylation of the ester (for primary alkyls) to *two* coordinated CO's, H$_2$ (scavenged as RuH(H$_2$)ClL$_2$), and R′H (methane observed for R = CH$_2$Me) as shown in eq 4. When [RuHClL$_2$]$_2$ and ethyl formate were combined (1:1 Ru:HCO$_2$R) in C$_6$D$_6$, the complex RuH(H$_2$)ClL$_2$ was detected in addition to anticipated RuHCl(CO)L$_2$ in a 1:2 ratio (^{31}P NMR). Approximately half the starting ethyl formate remained unreacted, and *no* free ethanol was seen.

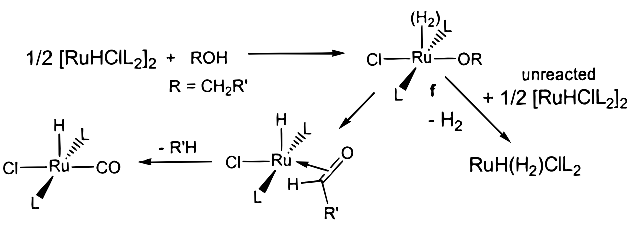


(4)

Scheme 3



Scheme 4



One explanation for this involves the liberation of *free* ethanol (ROH) after the first carbonyl extraction, which is then *rapidly* decarbonylated by unreacted [RuHClL$_2$]$_2$ to yield coordinated CO, H$_2$ (scavenged as RuH(H$_2$)ClL$_2$), and R′H (Scheme 3). We observe, however, that [RuHClL$_2$]$_2$ reacts only *slowly* with ethanol ($t_{1/2} \approx$ 12 h) under identical conditions to liberate equimolar RuHCl(CO)L$_2$ and RuH(H$_2$)ClL$_2$. Presumably this proceeds through alkoxy and η^2-aldehydic intermediates, which have strong precedent in similar decarbonylations,[6] though none were detected (Scheme 4). In light of this slow rate, a more plausible explanation can be formulated where the ethoxy group (R = CH$_2$Me) generated from deinsertion of Ru(H$_2$)ClL$_2$(−C(O)OEt) (**g**) never leaves Ru as ethanol but is more rapidly converted to *acetaldehyde* (R′ = Me) after release of H$_2$ (scavenged as RuH(H$_2$)ClL$_2$) and β-H elimination to generate the product RuHCl(CO)L. The liberated acetaldehyde is then decarbonylated *rapidly* to complete the process. This is illustrated in Scheme 5 (path 1), where the labilizing effect of a trans CO (in **h**) would facilitate H$_2$ loss. One may also reason that the slower reaction of [RuHClL$_2$]$_2$ with alcohol is due to the lack of this CO in intermediate **f** (Scheme 4), in addition to the weaker bridge-splitting power offered to the dimeric starting material (vs ester).

For further proof of this proposed mechanism, CO extraction from phenyl formate and *tert*-butyl formate (R = Ph, ^{t}Bu) were pursued where β-H elimination from RuOR is precluded, resulting in quantitative formation of RuHCl(CO)L$_2$ and ROH (observed) over 30 min at room temperature. Here, path 1 (Scheme 5) is eliminated and formation of Ru(CO) occurs exclusively from reductive elimination of ROH through path 2 (Scheme 5). Direct reaction of [RuHClL$_2$]$_2$ with free HOPh and

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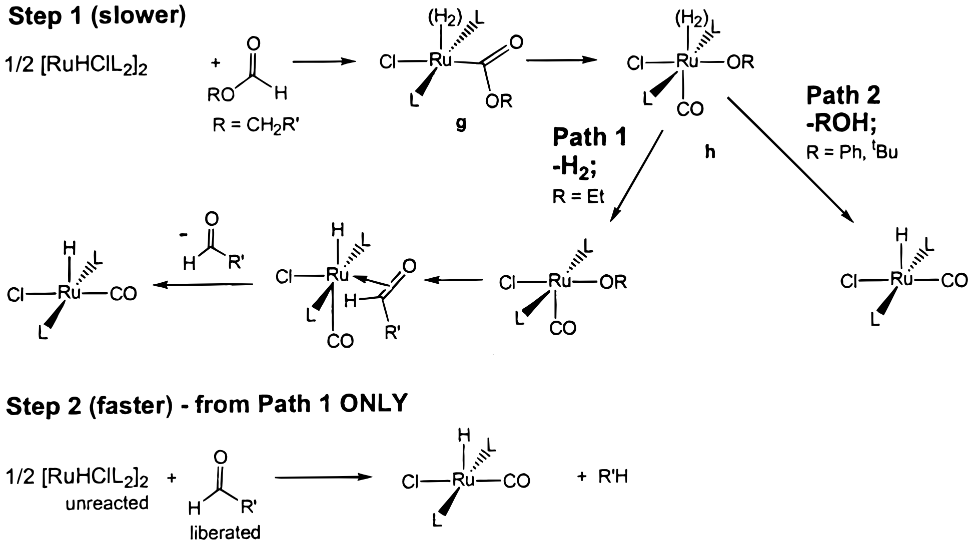
[4] Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087.

[5] Clark, G. R.; Roper, W. R.; Wright, J.; Yap, P. D. *Organometallics* **1997**, *16*, 5135.

[6] Chen, Y.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L. *Organometallics* **1997**, *16*, 1241−1246 and references within.

Scheme 5



HO^{t}Bu resulted in no formation of identifiable intermediates proposed in Schemes 4 and 5 after 12 h at room temperature but, instead, loss of one phosphine and subsequent metalation of ^{i}Pr to form $Ru_2H_3Cl_2L_2$-(η^2-$P(C_3H_6)^iPr_2$).[7]

Decarbonylation of Formamides. The decarbonylation of dimethylformamide (DMF, $HC(O)NR_2$; R = CHR'_2; R′ = H) by $[RuHClL_2]_2$ is significantly slower than that of aldehydes or esters at room temperature ($t_{1/2} \approx 2$ days) but can be effected in 3 h at 80 °C. Again, substantial (ca. 20%) formation of $RuH(H_2)ClL_2$ is observed in the product mixture (at 30 h, room temperature), suggesting H_2 loss to unreacted $[RuHClL_2]_2$ from a dihydrogen or dihydride intermediate. Indeed, when this reaction is monitored in C_6D_{12} by ^1H and ^{31}P NMR at room temperature, such an intermediate species is observed (~50% of total ^{31}P intensity at 30 h) concurrently with starting $[RuHClL_2]_2$ and the end product $RuHCl(CO)L_2$. This intermediate can be prepared in quantitative yield after 30 min in neat DMF and can be isolated in 45% yield from a pentane solution obtained by liquid−liquid extraction of the reaction products from the DMF solution.

Diagnostic features of the intermediate include $\nu_{CO} = 1591$ cm^{-1} and a $^{13}C\{^1H\}$ signal at 205.1 ppm (t, $J_{C-P} = 8.2$ Hz), consistent with the CO moiety incorporated as an η^2-carbamoyl ligand,[8] and a broad high-field ^1H NMR singlet at −10.4 ppm integrated for 2H (25 °C, C_6D_6). The methyl groups of the NMe_2 unit are inequivalent, resonating at 2.70 and 2.74 ppm; ^1H and $^{13}C\{^1H\}$ NMR spectra show diastereotopic P^iPr_3 methyl groups, and $^{31}P\{^1H\}$ NMR reveals a singlet at 49.5 ppm. The inequivalent NMe_2 methyl groups exclude N coordination in a structure having transoid phosphines. Variable-temperature ^1H NMR measurements from +20 to −60 °C (C_7D_8) show the decoalescence of the $Ru(H)_2$ unit to two equal-intensity doublets (broad) centered at −8.9 and −12.0 ppm (T_1(−60 °C, 400 MHz) = 110 and 125 ms, respectively) with a mutual coupling of 42 Hz ($^2J_{P-H}$ not resolved), identifying them as two *hydrides* and not coordinated H_2 (Figure 1). The somewhat short T_1 times originate from the geometric constraints of a pentagonal-bipyramidal geometry (72° is the ideal angle between equatorial sites) favoring a small ∠H−Ru−H, though $^2J_{H-H}$ is rather large, and is consistent with quantum exchange coupling. Confirmation of the structure proposed from IR and NMR data was sought through X-ray crystallography.

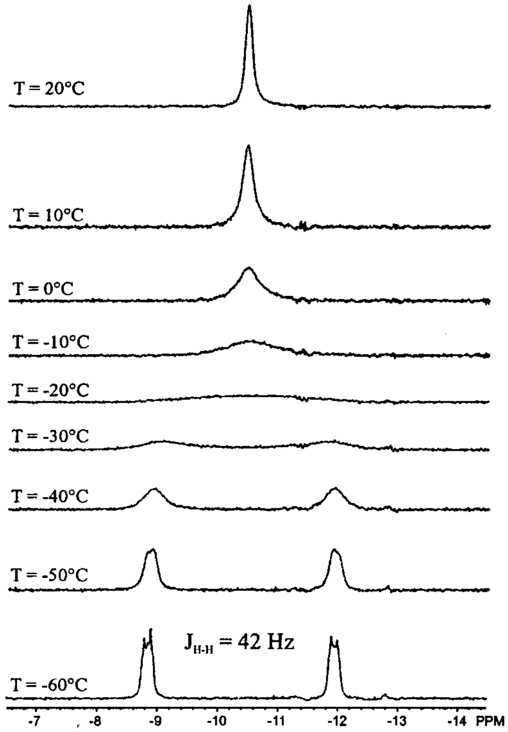


Figure 1. Variable-temperature ^1H NMR spectra (400 MHz) of the hydride region for $Ru(H)_2Cl(\eta^2$-$C(O)NMe_2)$-$(P^iPr_3)_2$ in toluene-d_8.

The structure determination (Figures 2 and 3) shows a molecule with a crystallographic mirror plane containing Ru, Cl, the $OCNMe_2$ groups (thus, the NMe_2 group is planar, with inequivalent methyl groups), and the hydride(s) (only one hydride was located in the X-ray data). The *trans* influence of hydride H1 and of the

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(7) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. Manuscript in preparation.

(8) Anderson, S.; Hill, A. F.; Ng, Y. T. *Organometallics* **2000**, *19*, 15.

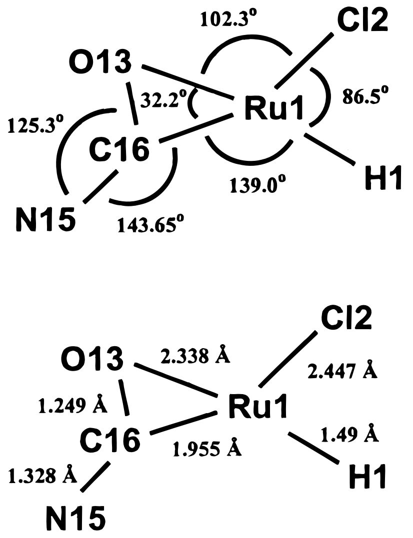


Figure 2. Illustration of the core bond distances and angles for $Ru(H)_2Cl(\eta^2\text{-}C(O)NMe_2)(P^iPr_3)_2$.

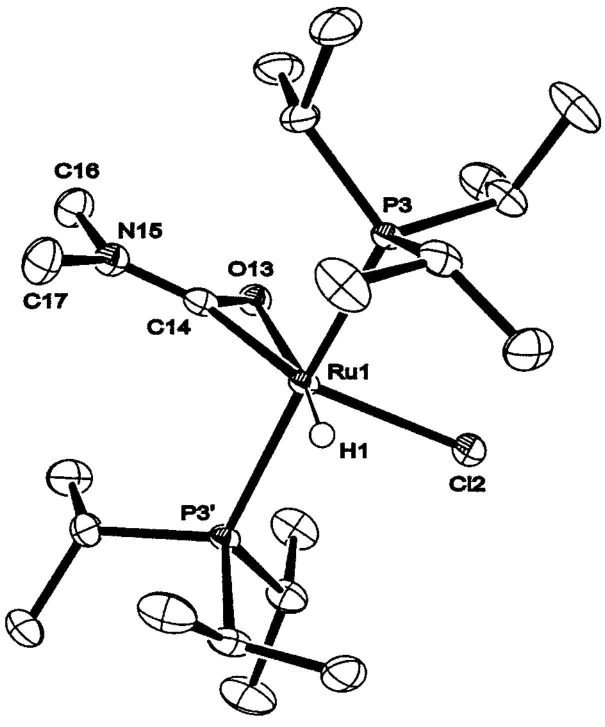


Figure 3. ORTEP view of $Ru(H)_2Cl(\eta^2\text{-}C(O)NMe_2)(P^iPr_3)_2$. The second hydride was not detected in the X-ray study.

hetero carbon C14 is apparently responsible for the long Ru−Cl2 (2.447 Å) and Ru−O13 (2.338 Å) bonds, but the carbamoyl group is definitely η^2: the N15−C14−Ru angle is very large (143.65°), to bring the keto oxygen closer to Ru. The keto carbon has a short (1.955 Å) bond length to Ru. The one hydride undetected in the X-ray study is presumably located in the large angle (139°) between keto C14 and H1. The P−Ru−P (168.5°) approaches 180°, in contrast to the smaller angles in truly five-coordinate $RuXYZ(PR_3)_2$ square pyramids. The angles to P from the ligands in the equatorial plane range from 95.5 to 84.3° (for the small hydride H1). From the IR, NMR, and X-ray data collected, the best assignment of this complex places it at a point along the continuum for the resonance forms shown in Figure 4.

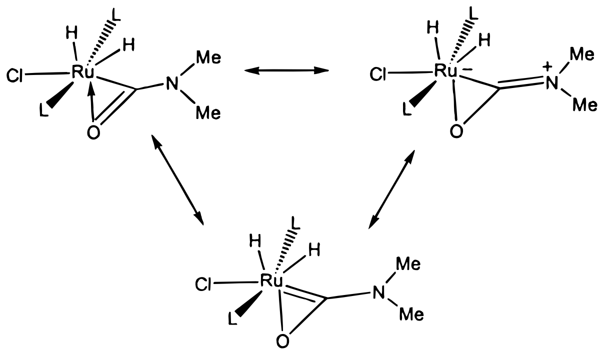
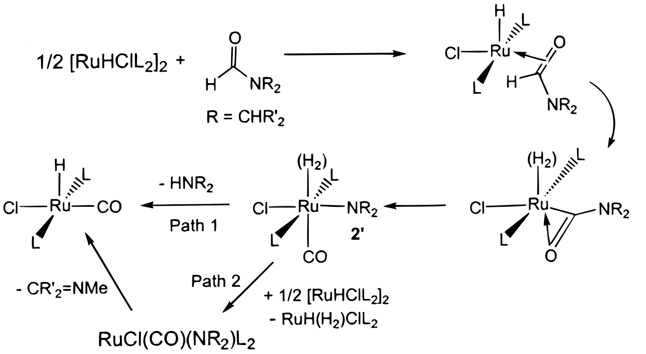


Figure 4. Bonding representations for $Ru(H)_2Cl(\eta^2\text{-}C(O)NMe_2)(P^iPr_3)_2$.

Scheme 6



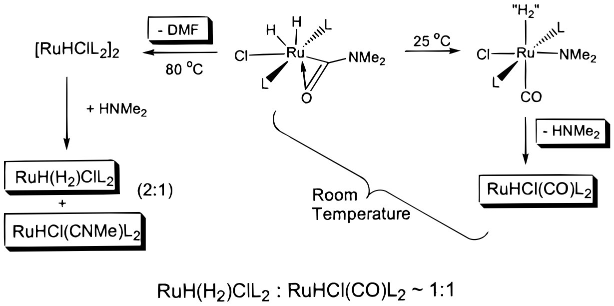
As with the formate reactions, formation of $RuHCl(CO)L_2$ can be accomplished from this species by (1) deinsertion of the NMe_2 group and reductive elimination of HNR_2 (Path 1, Scheme 6) or (2) deinsertion to form an intermediate Ru“H_2” amido complex (**2′**), which can then lose H_2 to starting $[RuHClL_2]_2$ (to form $RuH(H_2)ClL_2$) and then β-H eliminate $CH_2{=}NMe$ (R′ = H; path 2, Scheme 6). Monitoring a sample of $[RuHClL_2]_2$ and DMF in C_6D_6 at 25 °C by NMR showed, in addition to the only ^{31}P-containing products $RuH(H_2)ClL_2$ and $RuHCl(CO)L_2$, the production of free $HNMe_2$; no $CH_2{=}NMe$ was observed. This suggests that, at room temperature, the decarbonylation occurs along path 1 and that path 2 (Scheme 6) is inoperative here, in contrast to the reactions of formyl esters presented above.

A sample of $Ru(H)_2Cl(\eta^2\text{-}OCNMe_2)L_2$ heated at 80 °C for 3 h in C_6D_6 shows complete conversion to $RuHCl(CO)L_2$, $RuH(H_2)ClL_2$, and $RuHCl(CNMe)L_2$ (2:2:1 mole ratio), with expulsion of free DMF and $HNMe_2$ (both observed). These observations suggest that at elevated temperatures the initial oxidative addition step in DMF activation is reversible and that back-reaction yields free DMF and starting $[RuHClL_2]_2$, which can then react with liberated $HNMe_2$ to form the observed isonitrile complex. Although reaction along path 2 (Scheme 6) would liberate $CH_2{=}NMe$, which could potentially lead to formation of $RuHCl(CNMe)L_2$, the observation of free DMF requires the loss of it directly from $Ru(H)_2Cl(\eta^2\text{-}OCNMe_2)L_2$ as can be illustrated in Scheme 7.

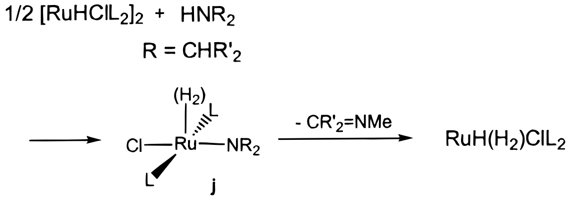
The control reaction of $[RuHClL_2]_2$ with $HNMe_2$, and more detailed spectroscopic characterization of isonitrile complexes $RuHCl(CNR)L_2$ follows.

Dehydrogenation of Amines. Reaction of $[RuHClL_2]_2$ with equimolar (N:Ru) $HNMe_2$ in cyclohexane gives no immediate reaction but after 30 h at at room

Scheme 7



temperature results in complete consumption of the Ru reagent and 75% production of $RuH(H_2)ClL_2$, consistent with β-H elimination from the proposed amido intermediate **j** (H$-$N oxidative addition product) to liberate $CH_2{=}NMe$. No methyl imine was observed in the reaction mixture, though the isonitrile complex RuHCl(CNMe)L_2 was found to be the other major ^{31}P-containing product, which is presumed to be formed from action of the liberated imine on unreacted $[RuHClL_2]_2$. Alternatively, it could be formed by analogy to ester double decarbonylation (see Scheme 4) where the dehydrogenated amine (coordinated imine) never dissociates and is dehydrogenated further to isonitrile concurrent with a net loss of 2 equiv of H_2 (which could be captured by available $RuHClL_2$). Prominent features of this isonitrile complex include a high-field hydride (δ -26.0 ppm, t, ^{1}H J_{P-H} = 19 Hz), a CN*Me* group (δ 2.6 ppm, s, 3H), and a $^{31}P\{^1H\}$ NMR singlet (δ 58.6 ppm). The identification of this isonitrile complex was confirmed by comparison to an authentic sample generated directly from $[RuHClL_2]_2$ and free CNMe. More thoroughly characterized examples of such complexes derived from $[RuHClL_2]_2$ and free imine follow.

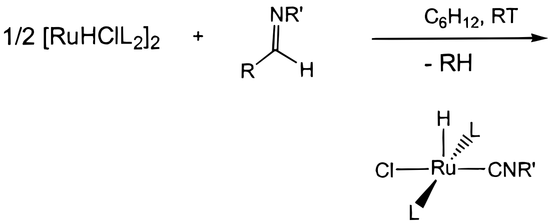


(5)

From these observations, it is clear that β-H elimination of Ru$-$NR(CH$_2$R$'$) to form imine (eq 5) operates in the dehydrogenation of free secondary amines, though the liberated imine is more reactive toward $RuHClL_2$ than $HNMe_2$ and, hence, never accumulates to an observable concentration. This parallels the previously established trend of aldehydes donating their π-acid functionality more readily than alcohols. To our knowledge, this is a rare example of secondary amine dehydrogenation to imine under mild conditions *without* evoking transfer hydrogenation.[9,10]

Reaction of $[RuHClL_2]_2$ with more sterically encumbered amines such as HN^{i}Pr$_2$, whose resulting imine should be restricted toward further reaction, shows no formation of free $Me_2C{=}N^iPr$ over 24 h at 80 °C. Likewise, reaction with the bulky $HN(SiMe_3)_2$ results in no direct observation of the intermediates proposed in eq 5. In all cases, decomposition of $RuHClL_2$ to a complex mixture of unidentified products was seen.

Isonitrile Abstraction from Imines. Unlike decarbonylation of the organic carbonyl, which is well known for aldehydes and has precedent for formyl esters and amides, the extraction of an isonitrile from a coordinated imine is unknown.[11,12] $[RuHClL_2]_2$ reacts with MeHC=NEt in less than 48 h at room temperature in cyclohexane to generate the new isonitrile complex RuHCl(CNEt)L_2 and methane in high yield. This complex is characterized by a high-field hydride at -26.4 ppm (1H, t, J_{P-H} = 20 Hz), diastereotopic P^{i}Pr$_3$ methyl groups, and an intact ethyl group by ^{1}H NMR (25 °C, C_6D_6) and by a $^{31}P\{^1H\}$ singlet at 59.0 ppm. The low-field resonance seen by $^{13}C\{^1H\}$ NMR at 182.0 ppm (t, J_{C-P} = 12 Hz) and ν_{CN} = 1996 cm^{-1} are consistent with this assignment. The bulkier imine MeHC=N^{t}Bu, however, failed to yield any appreciable amount of isonitrile complex after 5 days at room temperature or after 3 h at 60 °C. Since the ^{t}Bu substituent is somewhat remote from the C(sp^2)$-$H bond, this observation suggests the mechanistic necessity of either an η^1-N bound species or an η^2-imine species, rather than "direct" attack of Ru on the C$-$H bond. Recent work by Bianchini et al. has shown a base-catalyzed (H_2O) path for degradation of secondary amino carbenes (generated from vinylidene and primary amine) to coordinated isonitrile and alkane,[13] and such intermediates could be generated here by simple addition of Ru$-$H across MeHC=NEt followed by α-H migration to Ru (see eq 6). However, we propose a mechanism analogous to that of aldehyde decarbonylation above (eq 2 and Scheme 1), substituting the isolobal fragment =NR$'$ for =O for its simplicity, because of the use here of rigorously anhydrous conditions and because of strong precedent for oxidative addition reactions of H$-$C(sp^2) in the related molecules HC(=O)R.



(6)

To evaluate the effects of a phenyl substituent, the corresponding imine, PhHC=NMe, was prepared from H_2NMe and HC(O)Ph. Surprisingly, we find that the kinetic product from the reaction of $[RuHClL_2]_2$ with PhHC=NMe in toluene is not the anticipated aryl complex, RuCl(Ph)(CNMe)L_2, but retains an H_2 unit instead. This product is characterized in CD_2Cl_2 by a

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[9] Morales-Morales, D.; Chen, W.; Jensen, C. M. Presented at the 218th National Meeting of the American Chemical Society, New Orleans, LA, 1999. Jensen, C. M. Personal communication.

[10] Catalytic dehydrogenative silylation of amines has recently been reported: Takaki, K.; Kamata, T.; Miura, Y.; Shishido, T.; Takehira, K. *J. Org. Chem.* **1999**, *64*, 3891.

[11] The insertion of isocyanide into Fe$-$CH$_3$ (reverse reaction of that reported here) has been recently documented: Bellachiona, G.; Cardaci, G.; Macchioni, A.; Zuccaccia, C. *J. Organomet. Chem.*, **2000**, *594*, 119.

[12] Jones, N. D.; MacFarlane, K. S.; Smith, M. B.; Schutte, R. P.; Rettig, S. J.; James, B. R. *Inorg. Chem.* **1999**, *38*, 3956.

[13] Bianchini, C.; Masi, D.; Romerosa, A.; Zanobini, F.; Peruzzini, M. *Organometallics* **1999**, *18*, 2376.

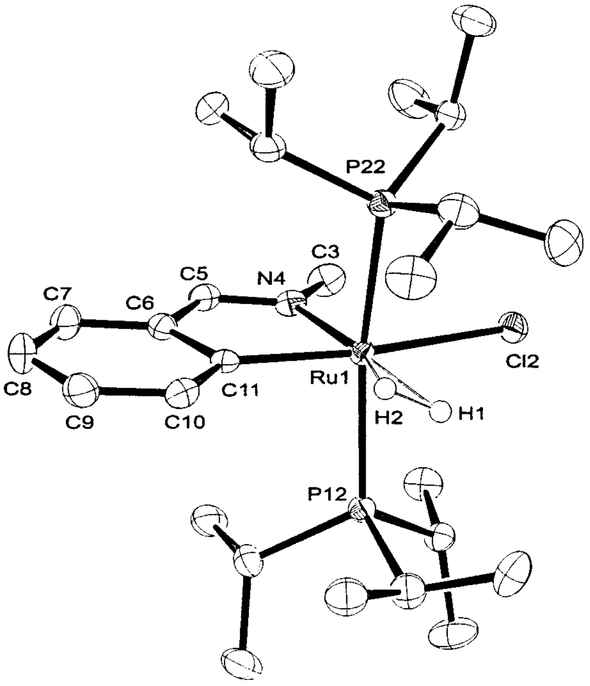

Figure 5. ORTEP view of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$.

room-temperature high-field ^1H NMR signal (δ −9.1, br t, $^2J_{P-H} = 11$ Hz, 2H) whose T_1(min) (300 MHz) of 10 ms at −70 °C indicates a dihydrogen ligand. A singlet (δ 4.13, s, 3H) for N*Me* and diastereotopic P^iPr_3 methyls are seen, and a $^{31}P\{^1H\}$ NMR singlet is present at δ 38.3. At room temperature, ^1H NMR shows four distinct aryl C−H units and $^{13}C\{^1H\}$ NMR shows six aromatic carbons (*ipso*-C_6H_4 at δ 172.3, t, $^2J_{C-P} = 3$ Hz); a singlet integrated to one proton and consistent with an imine X*H*C═NMe group is also seen by ^1H NMR at 8.37 ppm. The C═N carbon resonates at δ 190.8 (t, $^2J_{C-P} = 9$ Hz) and is also consistent with this proposed XH*C*═NMe functionality. No strong ν_{CN} bands in the region of 2000 cm^{-1} are found, though the presence of an aryl ring prohibits concrete assignment of the C═N band. The observed data indicate the formation of a kinetic product derived from aryl C−H oxidative addition (rather than reactivity at H−C(Ph)═NMe) that can be represented as $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)L_2$. Confirmation of this proposed identity was sought by X-ray crystallography.

The structure determination (Figure 5), carried out using an area detector, shows a molecule with idealized C_s symmetry containing a planar $C_6H_4CH{=}NMe$ moiety. The angle ∠P12−Ru1−P22 is 164.7°, and the P's are bent away from N4. Cl2 is *trans* to the *ipso* carbon C11 (170.7°), and the Ru1−Cl2 distance of 2.53 Å is substantially lengthened by the strong *trans* influence of the coordinated aryl ring. The distances C11−Ru1 and C6−C5 are normal for C(sp²)−Ru and C(sp²)−C(sp²) bonds at 2.04 and 1.43 Å, respectively, and the C5−N4 distance of 1.29 Å is consistent with a double bond. The angle ∠C11−Ru1−N4 is a small 78.3(1)° to accommodate the five-membered ring and the angles ∠Ru1−N4−C5 (114.4(2)°) and ∠Ru1−N4−C3 (128.7(2)°) reinforce sp² hybridization about N4. The two H atoms of the coordinated H_2 unit were included in the refinement and found to be approximately *trans* to N4 at 162 and 168° for ∠N4−Ru1−H2 and ∠N4−Ru1−H1 with an H1−H2 distance of 0.86(5) Å, although these "light atom" values should be taken as *approximate* only.

To test the reliability of modern X-ray crystallography for the location of poorly visible H ligands, this structure was determined twice, on two different crystals. All distances and angles involving Ru, C, and N within the coordination sphere were identical within 1.2 esd's between the two determinations. Remarkably, the structural parameters of the Ru, H1, H2 triangle were also equal within 1 esd and suggest that both the Ru−H asymmetry (1.76(3) and 1.47(3) Å to H1 and H2, respectively) is real and the H1/H2 distance of 0.85(4) Å from this second determination is real and establishes this as a compound containing rather unstretched H_2. The minimal lengthening of the H−H distance from that (0.71 Å) in free H_2 can be attributed to the minimal π-donation from the trans imine nitrogen and the long Ru−Cl bond (which diminishes the π-donor ability of chloride). The longer Ru−H1 distance can be attributed to this H being nearly trans to the imine nitrogen (∠N−Ru−H1 = 171.2(10)°), while the other H is less so (∠N−Ru−H2 = 159.4(12)°).

The H_2 ligand of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)L_2$ is lost at elevated temperatures to form unsaturated $RuCl(\eta^2\text{-}C_6H_4CH{=}NMe)L_2$. When a sample of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)L_2$ is subjected to 80 °C for 12 h in C_6D_6, the H_2 loss product is formed in 50% yield, as evidenced by new ^1H and ^{31}P NMR signals similar to those of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMR)L_2$, but *no* corresponding high-field ^1H resonance (<0 ppm). Also observed is 15% $RuH(H_2)ClL_2$ and free PhHC═NMe from the hydrogenation of the starting complex's Ru−C(sp²) bond by the liberated H_2.

Conclusions

The reactions reported here illustrate the following characteristics of $[RuHClL_2]_2$.

(1) This dimer is unsaturated and thus has the potential to bind even weak donors (although alcohols themselves, in the absence of base, push the limit on binding to Ru). The preference to bind π-acidic ligands is exemplified here, as it was reported that $[RuHClL_2]_2$ forms an immediate adduct with the very weakly σ-donating (but mildly π-accepting) N_2 ligand,[2] usually taken to be a much poorer ligand than ROH. The C═G (G = O, NR) groups reported here are other examples of weakly π-acidic ligands.

(2) Halide bridge splitting of the dimeric $[RuHClL_2]_2$, or its adduct with substrates, generates still more unsaturation, in preparation for "deeper" substrate transformation.

(3) $[RuHClL_2]_2$ and its monomer unit lack any strong π-acid ligands and, thus, have considerable reducing power within their d^6 configurations. This is most fully evident in the structure of $Ru(H)_2Cl[C(O)NMe_2]L_2$, where the dihydr*ide* character indicates the formal metal oxidation state IV. In the absence of π-acid ligands, Ru(II) should be seriously considered as a reducing agent.

(4) This reducing power permits oxidative addition of a broad variety of H−C(sp²)═G bonds, as well as a phenyl C−H. "Deinsertion" of the resulting Ru[C(G)R] group is the C−C scission event. In concert with the

elimination of H_2 or RH, a Ru(II) center is regenerated, thereby enhancing the Ru(CG) bond.

(5) When OR or NR_2 is part of the keto substrate, and when R is a primary or secondary alkyl, β-hydrogen migration to Ru of such a hydrogen dehydrogenates the C$-$heteroatom single bonds, creating more H_2 and a C$-$heteroatom double bond. When the heteroatom is oxygen, the resulting aldehyde can consume a second mole of ruthenium reagent.

(6) (Dihydride)ruthenium(IV) and (dihydrogen)ruthenium(II) complexes mediate these reactions, the hydrides can be fluxional, and one example of quantum exchange coupling between inequivalent but fluxional hydrides has been observed.

(7) The contrast of dihydride for the carbamoyl vs dihydrogen for the ortho-metalated phenylimine ligand may be due in significant part to the larger steric demand of the metalated phenylimine, which thus favors the more compact H_2 alternative.

Thus, while formation of $RuRCl(CO)L_2$ or $RuRCl(CNR')L_2$ (R = H, Ph) may be a strong thermodynamic driving force for these reactions, the kinetic facility rests on the several features of $[RuHClL_2]_2$.

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, Na/benzophenone, P_2O_5, or CaH_2, degassed prior to use, and stored over 4 Å molecular sieves in airtight vessels. Alumina (neutral, activity I, 60$-$325 mesh) was dried by heating (250 °C) at 0.003 Torr (48 h). $[RuHCl(P^iPr_3)_2]_2$[14] and imines[15] (EtN=CHR′) were prepared as previously reported, and all other reagents were used as received from commercial vendors after drying and degassing when necessary. In situ NMR identification of $RuHCl(CO)(P^iPr_3)_2$,[16,17] $RuH(H_2)Cl(P^iPr_3)_2$,[18,19] and organic products were made by comparison to literature data and/or authentic samples. ^1H NMR chemical shifts are reported in ppm relative to protio impurities in the deuterio solvents. ^{31}P NMR 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). Infrared spectra were recorded using a Nicolet 510P FT-IR spectrometer.

$RuHCl(CO)(P^iPr_3)_2$. From HC(O)Et. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 2.4 μL (0.032 mmol) of propionaldehyde was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR taken after 30 min at room temperature showed quantitative conversion to $RuHCl(CO)(P^iPr_3)_2$ and ethane.

From HC(O)^{t}Bu. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 3.5 μL (0.032 mmol) of pivaldehyde was added and the tube shaken. The sample was monitored periodically by ^1H and $^{31}P\{^1H\}$ NMR, and after 24 h at room temperature, the mixture was found to contain 70% $RuHCl(CO)(P^iPr_3)_2$ and 15% $RuH(H_2)Cl(P^iPr_3)_2$.

From HC(O)CH_2^{t}Bu. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 2.4 μL (0.032 mmol) of 3,3-dimethylbutyraldehyde was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR taken after 30 min at room temperature showed quantitative conversion to $RuHCl(CO)(P^iPr_3)_2$ and neopentane.

$Ru(Ph)Cl(CO)(P^iPr_3)_2$. A 200 mg (0.218 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ in 5 mL of toluene was added dropwise via syringe to a stirred solution of 225 μL (2.21 mmol) of benzaldehyde in 5 mL of toluene at ambient temperature. The reaction mixture was stirred for 12 h under argon, and the solvent was removed to yield a red solid. Washing with pentane (2 × 2 mL) to remove any residual benzaldehyde and drying *in vacuo* yielded 160 mg (65%) of the title compound as a red powder. The yield is quantitative when monitored in situ by ^{31}P NMR. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ 1.08 (dvt; $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, $P(CHMe_2)_3$), 1.13 (dvt, $J_{P-H} = {}^3J_{H-H} = 7$ Hz, 18H, $P(CHMe_2)_3$), 2.59 (m, 6H, $P(CHMe_2)_3$), 6.73 (t, $J_{H-H} = 8$ Hz, 1H, p-C_6H_5), 6.82 (apparent t, $J_{H-H} = 8$ Hz, 2H, m-C_6H_5), 7.8 (vbr s, 2H, o-C_6H_5). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 36.0 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_7D_8, -20 °C): δ 19.5 (s, $P(CHMe_2)_3$), 19.7 (s, $P(CHMe_2)_3$), 24.2 (vt, $J_{P-C} = 9.1$ Hz, $P(CHMe_2)_3$), 120.6 (s, p-C_6H_5), 125.9 (br s, $w_{1/2\,h} = 116$ Hz, m-C_6H_5), 136.9 (br s, $w_{1/2\,h} = 90$ Hz, o-C_6H_5), 141.4 (br s, $w_{1/2\,h} = 93$ Hz, o-C_6H_5), 155.8 (t, $J_{P-C} = 9.7$ Hz, i-C_6H_5), 205.6 (t, $J_{P-C} = 14.0$ Hz, Ru(CO)). IR (Nujol): $\nu_{CO} = 1905$ cm^{-1}.

$RuHCl(CO)(P^iPr_3)_2$. From HC(O)OEt. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 2.6 μL (0.032 mmol) of ethyl formate was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR taken after 30 min at room temperature showed clean conversion to $RuHCl(CO)(P^iPr_3)_2$ and $RuH(H_2)Cl(P^iPr_3)_2$ (2:1), in addition to half the starting formate and liberated methane.

From HC(O)OPh. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 3.6 μL (0.032 mmol) of phenyl formate was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR taken after 30 min at room temperature showed quantitative conversion to $RuHCl(CO)(P^iPr_3)_2$ and phenol.

From HC(O)O^{t}Bu. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 3.8 μL (0.032 mmol) of *tert*-butyl formate was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR taken after 30 min at room temperature showed quantitative conversion to $RuHCl(CO)(P^iPr_3)_2$ and *tert*-butyl alcohol.

$[RuHCl(P^iPr_3)_2]_2$ plus EtOH. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Via syringe, 1.9 μL (0.032 mmol) of ethanol was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR spectra taken periodically as the sample was allowed to stand at room temperature showed quantitative conversion to $RuHCl(CO)(P^iPr_3)_2$ and $RuH(H_2)Cl(P^iPr_3)_2$ (1:1) after 3 days (methane was also observed).

$RuHCl(CO)(P^iPr_3)_2$. From HC(O)NMe_2. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_{12} in an NMR tube. Via syringe, 2.5 μL (0.032 mmol) of DMF was added and the tube shaken. ^1H and $^{31}P\{^1H\}$ NMR taken after 3 h at 80 °C showed conversion to 80% $RuHCl(CO)(P^iPr_3)_2$ and 15% $RuH(H_2)Cl(P^iPr_3)_2$, with the balance consisting of $RuHCl(CNMe)(P^iPr_3)_2$.

$Ru(H)_2Cl(P^iPr_3)_2(\eta^2\text{-}OCNMe_2)$. A 200 mg (0.218 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was stirred in 3 mL of dry DMF for 45 min to yield a homogeneous dark orange solution. ^{31}P NMR assay at this time showed a single resonance (s, 49.8 ppm). In a glovebox, pentane was added (10 × 7 mL), the mixture was stirred until the pentane layer darkened, and

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[14] $[RuHCl(P^iPr_3)_2]_2$ was prepared by dropwise addition (over 2 h) of a toluene solution of lithium tetramethylpiperidide to a stirred suspension of $RuH_2Cl_2(P^iPr_3)_2$ in toluene.[1−3]

[15] Imines were prepared by Schiff base condensation of the appropriate aldehyde and amine using the method of: Cambell, K. N.; Sommers, A. H.; Campell, B. K. *J. Am. Chem. Soc.* **1944**, *66*, 82−84. This procedure was modified as detailed in this work for the preparation of benzylidenemethylamine, PhHC=NMe.

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Table 1. Crystallographic Data[a] for $Ru(H)_2Cl(OCNMe_2)(P^iPr_3)_2$

formula	$C_{21}H_{50}NOP_2Ru$	space group	$Cmc2_1$
a, Å	21.472(1)	T, °C	−158
b, Å	8.816(0)	λ, Å	0.710 69
c, Å	14.015(1)	ρ_{calcd}, g/cm^{-3}	1.330
V, Å^3	2653.08 Å^3	μ(Mo Kα), cm^{-1}	8.237
Z	4	R^b	0.0193
fw	531.10	$R_w{}^c$	0.0184

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

Table 2. Crystallographic Data[a] for $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$

formula	$C_{26}H_{52}ClNP_2Ru$	space group	$C2/c$
a, Å	39.331(1)	T, °C	−158
b, Å	9.075(0)	λ, Å	0.710 69
c, Å	16.513(1)	ρ_{calcd}, g/cm^{-3}	1.319
β, deg	99.62(0)	μ(Mo Kα), cm^{-1}	7.557
V, Å^3	5811.48 Å^3	R^b	0.0242
Z	8	$R_w{}^c$	0.0223
fw	577.18		

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

each pentane layer was removed using a disposable pipet. The combined pentane extracts (~70 mL) were reduced to 3 mL in vacuo with precipitation of a yellow solid and a few microliters of DMF. After the mixture was cooled overnight at −20 °C to complete precipitation, the light brown supernatant was decanted via cannula, and the yellow solid was washed with ether (1 × 2 mL) to remove any trace DMF. Drying *in vacuo* yielded 105 mg (45%) of the title compound as a bright yellow powder. ^1H NMR (400 MHz, C_7D_8, −60 °C): δ −12.0 (br d, $^2J_{H-H}$ = 42 Hz, 1H, Ru *H*; T_1 = 125 ms), −8.87 (br d, $^2J_{H-H}$ = 42 Hz, 1H, Ru *H*; T_1 = 110 ms), 1.07 (br dvt; $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), 1.13 (br dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), 2.10 (m, 6H, $P(CHMe_2)_3$), 2.48 (s, 3H, NMe_2), δ 2.61 (s, 3H, NMe_2). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 49.5 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_7D_8, 0 °C): δ 19.5 (s, $P(CHMe_2)_3$), 19.8 (s, $P(CHMe_2)_3$), 25.0 (vt, J_{P-C} = 9.9 Hz, $P(CHMe_2)_3$), 37.0 (s, NMe_2), 39.2 (s, NMe_2), 205.1 (t, J_{P-C} = 8.2 Hz, $Ru(\eta^2\text{-}OCNMe_2)$). Variable-temperature ^1H NMR measurements (400 MHz, C_7D_8) add the following data. (1) The two hydrides coalesce at −20 °C to yield a broad singlet at room temperature (δ −10.5, 2H). (2) When the temperature is increased over the temperature range −60 to 20 °C, $\Delta\delta$ for the diastereotopic NMe_2 groups decreases from 53 to 8 Hz. IR (Nujol): ν_{CO} = 1591 cm^{-1}.

X-ray Structure of $Ru(H)_2Cl(P^iPr_3)_2(\eta^2\text{-}OCNMe_2)$. The crystal was affixed to a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to −168 °C using a gas-flow cooling system of local design. Standard inert-atmosphere techniques were used during the handling and mounting process. The data were collected on a Bruker SMART 6000 CCD diffractometer using 5 s frames with an ω scan of 0.30°. 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. An absorption correction was performed using the SADABS program supplied by Bruker AXS. The structure was solved using SHELXTL and Fourier techniques. A difference Fourier phased on the non-hydrogen atoms clearly located all of the non-hydride hydrogen atoms. After several successive least squares in which hydrogen atoms were allowed to vary isotropically, it was possible to locate one of the two metal hydrides, but not the other. Several additional attempts failed as well, even though it seems apparent that there is a satisfactory coordination site available. A final difference Fourier was essentially featureless. The results are shown in Tables 1 and 2.

Thermolysis of $Ru(H)_2Cl(P^iPr_3)_2(\eta^2\text{-}OCNMe_2)$. A 10.0 mg (0.019 mmol) amount of $Ru(H)_2Cl(P^iPr_3)_2(\eta^2\text{-}OCNMe_2)$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. ^1H and $^{31}P\{^1H\}$ NMR taken periodically show conversion to $RuHCl(CO)(P^iPr_3)_2$ (40%), $RuH(H_2)ClL_2$ (40%), and $RuHCl(CNMe)L_2$ (20%), with the liberation of DMF and $HNMe_2$ after 3 h at 80 °C.

$[RuHCl(P^iPr_3)_2]_2$ plus $HNMe_2$. A 15.0 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube. Using a calibrated bulb, 0.032 mmol of anhydrous $HNMe_2$ was condensed into the sample after freezing it with liquid N_2, and the tube was tumbled while being warmed to room temperature. After 30 h at room temperature, the volatiles were removed *in vacuo* and the residue was redissolved in C_6D_6 to show 75% formation of $RuHCl(H_2)(P^iPr_3)_2$ and 20% production of $RuHCl(CNMe)(P^iPr_3)$ by ^1H and $^{31}P\{^1H\}$ NMR.

$RuHCl(CNEt)(P^iPr_3)_2$. A 400 mg (0.44 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 15 mL of cyclohexane, and 128 μL (1.31 mmol) of ethylideneethylamine (EtN=CHMe) was added via syringe. After the mixture was stirred at room temperature for 48 h, the solvent was removed to a liquid N_2 trap to yield a viscous red-brown oil. NMR assay at this time showed >90% conversion to the title compound. The residue was dissolved in 5 mL of hexane and cooled at −60 °C to precipitate a small amount of dark solid. The supernatant was separated via cannula (the precipitate was discarded), and the filtrate was evaporated to dryness to yield a dark oil. The oil was taken up in a small amount of hexane and this solution eluted through a 1.5 in. column of alumina in an argon-filled glovebox with hexane/EtOAc (50:1). The orange-brown band was collected, and the solvent was removed *in vacuo* to yield the isonitrile complex as an orange-brown, pasty solid (350 mg, 78%). ^1H NMR (400 MHz, C_6D_6, 20 °C): δ −26.4 (t, $^2J_{P-H}$ = 20.0 Hz, Ru *H*), 0.85 (t, $^3J_{H-H}$ = 6.8 Hz, 3H, $Ru(CNCH_2CH_3)$), 1.31 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 6.4 Hz, 18H, $P(CHMe_2)_3$), 1.33 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 6.4 Hz, 18H, $P(CHMe_2)_3$), 2.61 (m, 6H, $P(CHMe_2)_3$), 3.04 (q, $^3J_{H-H}$ = 6.8 Hz, 2H, $Ru(CNCH_2CH_3)$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): 59.0 (s). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 20 °C): δ 16.3 (s, $Ru(CNCH_2CH_3)$), 20.1 (s, $P(CHMe_2)_3$), 20.8 (s, $P(CHMe_2)_3$), 24.9 (vt, J_{P-C} = 9.9 Hz, $P(CHMe_2)_3$), 39.6 (s, $Ru(CNCH_2CH_3)$), 182.0 (t, J_{P-C} = 12.0 Hz, $Ru(CNCH_2CH_3)$). IR (Nujol): ν_{CN} = 1996 cm^{-1}. Anal. Calcd for $C_{21}H_{48}ClNP_2Ru$: C, 49.16; H, 9.43. Found: C, 48.16; H, 9.00.

$RuHCl(CNMe)(P^iPr_3)_2$. A 15 mg (0.016 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ was dissolved in 0.5 mL of C_6D_6, and 1.8 μL (0.33 mmol) of methyl isocyanide was added via syringe. After 3 h at 80 °C, ^1H and $^{31}P\{^1H\}$ NMR showed quantitative conversion to the title compound. ^1H NMR (300 MHz, C_6D_6, 20 °C): δ −26.0 (t, $^2J_{P-H}$ = 19 Hz, Ru *H*), 1.30 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), 1.33 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), 2.59 (m, 6H, $P(CHMe_2)_3$), 2.64 (s, 3H, $Ru(CNCH_3)$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 58.6. Immediately after the addition of CNMe at room temperature, the product mixture was found to be 50% unreacted $[RuHCl(P^iPr_3)_2]_2$ and 50% of the bis(isonitrile) complex $RuHCl(CNMe)_2(P^iPr_3)_2$. ^1H NMR (400 MHz, C_6D_6, 20 °C): δ −6.90 (t, $^2J_{P-H}$ = 22 Hz, Ru *H*), 1.42 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), 1.47 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, $P(CHMe_2)_3$), 2.40 (s, 3H, $Ru(CNCH_3)$), 2.42 (s, 3H, $Ru(CNCH_3)$), 2.68 (m, 6H, $P(CHMe_2)_3$). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 62.8 (s).

PhHC=NMe. Approximately 15 mL (0.34 mol) of anhydrous methylamine was condensed under argon at −40 °C in a thick-walled flask equipped with Solv-Seal joints and a Teflon stopcock. At this temperature, 20.0 mL (0.20 mol) of benzaldehyde was added *dropwise* to the stirred amine so that no reflux occurred. The vessel was sealed, warmed to room temperature, and stirred overnight. After recooling to −40 °C, 10 g of crushed KOH was added in portions under a slow argon purge. The flask was resealed and stirred with warming to room temperature, resulting in the formation of organic and aqueous layers. After 1 h, the flask was vented to the air and the organic layer was washed through Celite with 100 mL of ether. The solvent was removed on a rotary evaporator, and the resulting yellow oil was distilled through a Vigreux column under reduced pressure. After a 1.5 mL forerun, 16.8 g (72%) of the target imine was collected as a colorless liquid (37−39 °C, 0.3 Torr). ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 3.27 (s, 3H, N*Me*), 7.12 (m, 3H, *m*,*p*-C_6H_5), 7.73 (d, $^3J_{H-H}$ = 8 Hz, 2H, *o*-C_6H_5), 7.90 (s, 1H, Ph*H*C═NMe). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 20 °C): δ 48.1 (s, N*Me*), 128.3 (s, C_6H_5), 128.7 (s, C_6H_5), 130.4 (s, C_6H_5), 137.2 (s, *i*-C_6H_5), 161.7 (s, Ph*HC*═NMe).

$Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$. A 100 mg (0.108 mmol) amount of $[RuHCl(P^iPr_3)_2]_2$ in 4 mL of cyclohexane was added dropwise via syringe to a stirred solution of 30 μL (0.243 mmol) of benzylidenemethylamine (PhHC═NMe) in 3 mL of cyclohexane at ambient temperature. The reaction mixture was stirred for 4 h under argon (connected to a bubbler), and the solvent was removed to yield an orange solid. Washing with cold pentane (2 × 10 mL, −78 °C) to remove any residual imine and drying in vacuo yielded 95 mg (75%) of the title compound as a bright orange powder. Product prepared in this manner contained 10% $RuCl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$ as a byproduct from H_2 loss. This side reaction can be eliminated by conducting the reaction in a sealed vessel, decreasing the stirring time to 60 min, and drying *in vacuo* for a maximum of 1 h. The yield is quantitative when monitored in situ by ^{31}P NMR in a *sealed* NMR tube. ^{1}H NMR (400 MHz, CD_2Cl_2, 20 °C): δ −9.13 (br t; J_{P-H} = 10.8 Hz, 2H, $Ru(H_2)$; T_1(20 °C) = 44 ms), 1.01 (dvt; $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.07 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.14 (m, 6H, P(C*H*Me$_2$)$_3$), 4.13 (s, 3H, N*Me*), 6.77 (m, 2H, C_6H_4), 7.32 (dd t, J = 3 Hz, 8 Hz, 1H, C_6H_4), 7.69 (d, J = 6 Hz, 1H, C_6H_4), 8.37 (s, 1H, C_6H_4C*H*═NMe). $^{31}P\{^1H\}$ NMR (162 MHz, CD_2Cl_2, 20 °C): δ 38.3 (s). $^{13}C\{^1H\}$ NMR (101 MHz, CD_2Cl_2, 20 °C): δ 19.5 (s, P(CH*Me*$_2$)$_3$), 19.6 (s, P(CH*Me*$_2$)$_3$), 24.5 (vt, J_{P-C} = 9.1 Hz, P(*C*HMe$_2$)$_3$), 47.3 (s, N*Me*), 119.2, 128.3, 128.4, 144.9, 146.2 (s, C_6H_4), 172.3 (t, J_{P-C} = 2.8 Hz, *ipso*-C_6H_4), 190.8 (t, J_{P-C} = 9.1 Hz, Ru-*C*). $\nu_{C=N}$ was not identified due to overlap with $\nu_{C=C}$ of C_6H_5 (Nujol).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Ru(H)_2Cl(OCNMe_2)(P^iPr_3)_2$

Ru(1)−Cl(2)	2.4474(11)	N(15)−C(14)	1.327(5)
Ru(1)−P(3)	2.3676(6)	N(15)−C(16)	1.464(5)
Ru(1)−O(13)	2.3384(22)	N(15)−C(17)	1.447(6)
Ru(1)−C(14)	1.955(4)	Ru(1)−H(1)	1.49(4)
O(13)−C(14)	1.249(6)		
Cl(2)−Ru(1)−P(3)	90.46(3)	Ru(1)−C(14)−O(13)	91.04(28)
Cl(2)−Ru(1)−O(13)	102.29(14)	Ru(1)−C(14)−N(15)	143.7(3)
Cl(2)−Ru(1)−C(14)	134.56(12)	O(13)−C(14)−N(15)	125.3(4)
P(3)−Ru(1)−P(3)′	168.51(3)	Cl(2)−Ru(1)−H(1)	86.5(22)
P(3)−Ru(1)−O(13)	95.500(14)	P(3)−Ru(1)−H(1)	84.31(4)
P(3)−Ru(1)−C(14)	93.762(24)	O(13)−Ru(1)−H(1)	171.2(22)
Ru(1)−O(13)−C(14)	56.70(21)	C(14)−Ru(1)−H(1)	138.9(22)

Table 4. Selected Bond Distances (Å) and Angles (deg) for $Ru(H)_2Cl(OCNMe_2)(P^iPr_3)_2$

Ru(1)−P(12)	2.3799(7)	N(4)−C(5)	1.289(3)
Ru(1)−P(22)	2.4071(7)	Ru(1)−H(1)	1.81(4)
Ru(1)−N(4)	2.1412(21)	Ru(1)−H(2)	1.48(4)
Ru(1)−C(11)	2.0403(25)	H(1)−H(2)	0.86(5)
N(4)−C(3)	1.470(4)		
P(12)−Ru(1)−P(22)	164.656(26)	P(12)−Ru(1)−H(1)	73.0(12)
P(12)−Ru(1)−N(4)	98.40(6)	P(12)−Ru(1)−H(2)	83.8(14)
P(12)−Ru(1)−C(11)	91.40(7)	P(22)−Ru(1)−H(1)	92.0(12)
P(22)−Ru(1)−N(4)	96.91(6)	P(22)−Ru(1)−H(2)	81.3(14)
P(22)−Ru(1)−C(11)	90.69(7)	N(4)−Ru(1)−H(1)	167.8(13)
N(4)−Ru(1)−C(11)	78.34(9)	N(4)−Ru(1)−H(2)	162.2(14)
Ru(1)−N(4)−C(3)	128.74(19)	C(11)−Ru(1)−H(1)	110.0(12)
Ru(1)−N(4)−C(5)	114.37(19)	C(11)−Ru(1)−H(2)	83.9(14)
Ru(1)−C(11)−C(6)	114.32(19)	H(1)−Ru(1)−H(2)	28.3(17)
Ru(1)−C(11)−C(10)	130.89(20)		

X-ray Structure of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$. A nearly equidimensional sample was affixed to a glass fiber using silicone grease and transferred to the goniostat, where it was cooled to −158 °C using a gas-flow cooling system of local design. Standard inert-atmosphere handling techniques were used. An initial data set was collected using 5 s frames. The crystal was then realigned, and the data were collected using 15 s frames. Data collection and processing followed the methods cited above. The structure was solved using SHELXTL and Fourier techniques. As shown in the figures, the molecule has near-*m* symmetry with the Ru atom, H_2, and C_8H_8N ligand lying approximately on the mirror plane. The H_2 is slightly skewed as shown in the figures. The data for the 15 s frames were significantly better, allowing integration to 2θ = 65°, as opposed to 55° for the 5 s frames. A final difference Fourier was essentially featureless. The results are shown in Tables 3 and 4.

$RuCl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$. A 15.0 mg (0.026 mmol) amount of $Ru(H_2)Cl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$ was dissolved in 0.5 mL of C_6D_6 in an NMR tube equipped with a Teflon seal and heated at 80 °C for 12 h. ^{1}H and $^{31}P\{^1H\}$ NMR showed 50% conversion to $RuCl(\eta^2\text{-}C_6H_4CH{=}NMe)(P^iPr_3)_2$ in addition to 15% production of $RuH(H_2)Cl(P^iPr_3)_2$ and PhCH═NMe. ^{1}H NMR (400 MHz, C_6D_6, 20 °C): δ 1.11 (dvt; $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), 1.14 (dvt, $J_{P-H} = {}^3J_{H-H}$ = 7 Hz, 18H, P(CH*Me*$_2$)$_3$), 2.44 (m, 6H, P(C*H*Me$_2$)$_3$), 3.49 (s, 3H, N*Me*), 6.87 (m, 2H, C_6H_4), 7.29 (t, J = 3 Hz, 1H, C_6H_4), 8.93 (d, J = 8 Hz, 1H, C_6H_4), δ 7.84 (s, 1H, C_6H_4C*H*═NMe). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 20 °C): δ 33.0 (s).

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Supporting Information Available: Tables giving full crystallographic details for $Ru(H)_2Cl(OCNMe_2)(P^iPr_3)_2$ and $Ru(H_2)Cl(C_6H_4CHNMe)(P^iPr_3)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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