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Ligand-Promoted Carbene Insertion into the Aryl Substituent of an *N*-Heterocyclic Carbene Ligand in Ruthenium-Based Metathesis Catalysts

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Abstract: Addition of L = carbon monoxide or aryl isocyanides to the Grubbs second-generation carbene complexes $Ru(H_2IMes)(CHR)(PCy_3)Cl_2$ (H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene; R = Ph, Me, H, $CH{=}CMe_2$) triggers carbene insertion into an aromatic ring of the *N*-heterocyclic carbene supporting ligand, forming Ru{1-mesityl-3-(-7′-*R*-2′,4′,6′-trimethylcycloheptatrienyl)-4,5-dihydroimidazol-2-ylidene}-$L_2(PCy_3)Cl_2$. Insertions are also promoted for other PR_3 substituted complexes by carbon monoxide and aryl isocyanides, and for the phosphine-free Hoveyda−Blechert complex $Ru(H_2IMes)(CH(i\text{-}PrOC_6H_4))Cl_2$ by aryl isocyanides and small phosphites but only after initial displacement of the coordinated ether. Heteroatom substituted carbenes do not undergo CO-promoted insertion unless poorer electron donor phosphine (PPh_3) and carbene ($CH(OC_6H_4\text{-}p\text{-}NO_2)$ ligands are both present. Insertion depends on the added ligand, the carbene substituent, and to a lesser degree on the PR_3 ligand trans to the *N*-heterocyclic carbene.

Introduction

The development of functional group tolerant ruthenium-based alkene metathesis catalysts (Figure 1) has led to numerous applications in organic and materials synthesis.[1] A major milestone was reached in 1999 when the Grubbs group reported the 'second-generation' ruthenium carbene complex **3**, bearing an *N*-heterocyclic carbene (NHC) ligand, 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (H_2IMes).[2] Use of this complex in organic synthesis applications led to expanded scope of both the alkene and enyne metathesis reactions. Moreover, the increased reactivity compared to the first-generation Grubbs' carbene complex **1** has proven complementary in many applications, thereby giving the chemist versatility in choice of catalyst. Recently, phosphine-free catalysts **4**,[3,4] **5**,[5] and **6**[6] have been developed, which has provided a wider repertoire of reactive alkenes in cross-metathesis applications.

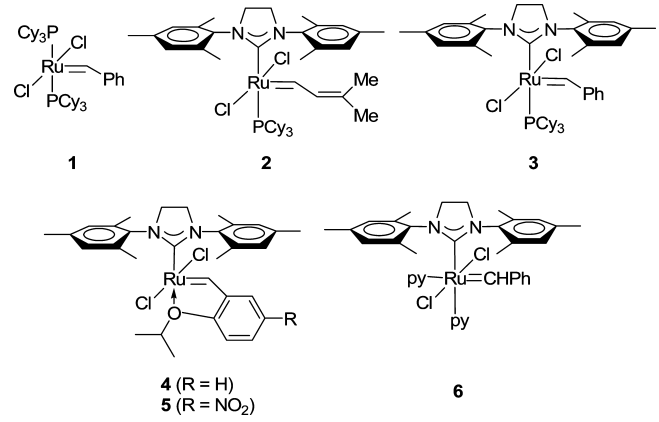

Figure 1. Carbene complexes **1**−**6**.

Generally, the *N*-heterocyclic carbene ligand of the catalysts **2**−**6** plays an important role as noninterfering supporting ligand in metathesis reactions.[7] The strong σ-donating properties of the *N*-heterocyclic carbene contribute electron density to the metal, which serves to stabilize the reactive intermediates in

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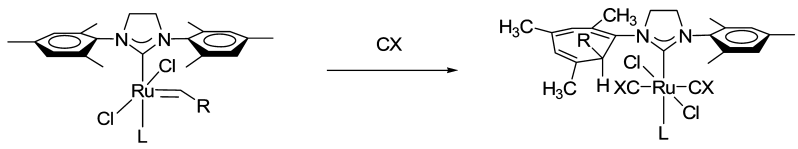
Scheme 1. Carbene Insertion Promoted by Carbon Monoxide or 4-Chlorophenyl Isocyanide



carbene reactant	alkylidene R	ligand L	promoting ligand CX	insertion product
3	Ph	Cy_3P	CO	**7**
8	H	Cy_3P	CO	**9**
10	Me	Cy_3P	CO	**11**
12	$CH{=}CHMe_2$	Cy_3P	CO	**13**
3	Ph	Cy_3P	*p*-ClC_6H_4NC	**14**
8	H	Cy_3P	*p*-ClC_6H_4NC	**15**
10	Me	Cy_3P	*p*-ClC_6H_4NC	**16**
22	4-$NO_2C_6H_4O$	Ph_3P	CO	**23**
24	Ph	Me_3P	CO	**28**
25	Ph	Bu_3P	CO	**29**
26	Ph	Ph_3P	CO	**30**
27	Ph	$(i\text{-}PrO)_3P$	CO	**31**
25	Ph	Bu_3P	*p*-ClC_6H_4NC	**32**
26	Ph	Ph_3P	*p*-ClC_6H_4NC	**33**
24	Ph	Me_3P	*p*-ClC_6H_4NC	**34**
27	Ph	$(i\text{-}PrO)_3P$	*p*-ClC_6H_4NC	**35**
36	2-(*i*PrO)-C_6H_4	Cy_3P		
37	2-(*i*PrO)-C_6H_4	Ph_3P	*p*-ClC_6H_4NC	**38**

alkene metathesis. In the crystal structure of the H_2IMes-liganded ruthenium carbene, one mesityl group drapes over the carbene. The close proximity of the aromatic ring and the activated benzylic position to an electrophilic carbene could lead to unwanted reactions between propagating metal alkylidenes and the aromatic ligand. For instance, the Grubbs group has identified a benzylic CH insertion product as a minor byproduct in the synthesis of complex **3**.[8]

In 2005 we reported, in a preliminary communication, a novel carbene insertion reaction involving the Grubbs' second-generation complex, and the carbene insertion was found to be initiated by added carbon monoxide or an added isocyanide ligand (Scheme 1).[9] This is an example of a ligand-promoted Buchner reaction, followed by rearrangement of the norcaradiene to the corresponding cycloheptatriene. This reaction provides a method to quench metathesis activity and to remove ruthenium from the product mixture when the promoting ligand is potassium isocyanoacetate.[10] The reaction is also important because it may provide a decomposition route for ruthenium carbenes during alkene metathesis. Ethylene is frequently used to promote difficult enyne metatheses using **3** and other carbenes.[11] Ethylene has donor−acceptor properties similar to CO, and it might be expected to induce the Buchner insertion. For this reason, it is important to determine how the reaction is affected by the ligand environment of the metal and by the steric and electronic properties of the added ligand. In this contribution we provide complete characterizations of the insertion products, and we evaluate the scope of ligands which cause this insertion, the carbenes which will undergo this reaction, and the effects of other phosphorus donor ligands in the coordination sphere.

Results

Our discovery of the ligand-induced Buchner reaction began as part of a kinetic study[12] of the enyne metathesis catalyzed by the Grubbs second-generation complex **3**. To monitor the kinetics we wanted an efficient, rapid, and clean method of quenching metathesis. We rationalized that carbon monoxide could be used to block all available coordination sites on the metal carbene, thereby preventing further metathesis. The quenching reaction proved to be very efficient and rapidly stopped an enyne metathesis reaction. However, upon investigating the fate of the carbene complex upon treatment with CO, we were very surprised to find that CO coordination resulted in carbene insertion into the C−C bond of the mesityl substituent of the heterocyclic carbene. Subsequently, we found that isocyanides would also cause insertions from **3**. Preliminary results concerning complexes **7**, **9**, and **14** including crystal structures, have appeared previously.[9,10]

Grubbs' Carbene Insertions Promoted by CO. Our initial experiments examined the scope of carbene substituents. Since we were focused upon quenching enyne metatheses, we wanted to determine if the primary chain-carrying carbenes in enyne metathesis−alkylidenes, benzylidene, methylidene, and allylidene−would all undergo this insertion reaction. Four ruthenium carbenes were investigated: (1) benzylidene, (2) methylidene, (3) ethylidene, and (4) 3-methyl-2-butenylidene. In each case, the ruthenium carbene furnished the cycloheptatrienyl Buchner insertion product when exposed to one atmosphere of carbon monoxide, as illustrated in Scheme 1.

Benzylidene. Treatment of a purple solution of complex **3** with one atmosphere of carbon monoxide resulted in a rapid color change to canary yellow. Concentration followed by trituration with anhydrous ethanol deposited complex **7** as a

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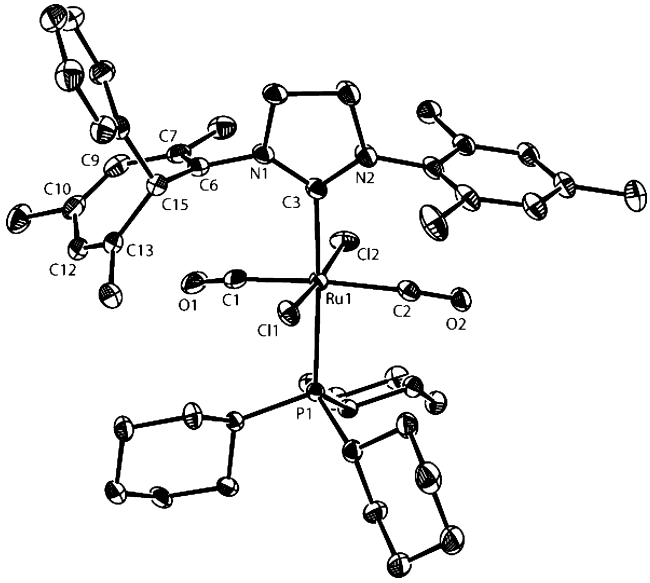

Figure 2. Molecular structure of complex **7**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at 50% probability.

bright yellow solid in 90% yield. The structure of **7** was determined by an X-ray crystal structure analysis.

Crystal structure determination of the complex revealed a slightly distorted octahedral geometry with a single PCy_3 trans to the *N*-heterocyclic carbene, two *trans*-carbonyl ligands, and two *trans*-chloride ligands, Figure 2. The benzylidene fragment is inserted into the 1,2-carbon−carbon bond of one of the mesityl moieties, to form a 2,4,6-trimethyl-7-phenylcycloheptatrienyl substituent. The alternating short and long bonds of the seven-membered ring clearly indicate the cycloheptatrienyl substructure. The phenyl substituent of the cycloheptatrienyl substructure, derived from the ruthenium benzylidene, is oriented anti to the ruthenium center in an axial position.

An important structural feature of this complex, and indeed all structurally characterized examples in this work, is the orientation of the *N*-heterocyclic carbene plane relative to the ligand−metal−ligand axes. The plane of the *N*-heterocyclic carbene is oriented along the OC−Ru−CO (or RNC−Ru−CNR in other structures) axis rather than parallel to the Cl−Ru−Cl axis or bisecting the OC−Ru−Cl bond angle, which might be assumed to be favored on steric grounds. Taking the OC−Ru−CO axis as the *x* axis and the P−Ru−C (*N*-heterocyclic carbene carbon) axis as the *z* axis, the d_{xz} and d_{xy} orbitals have the appropriate symmetry to bond with the π^* orbitals of the carbon monoxide ligands whereas the d_{yz} orbital will interact with the carbene p orbital. In this orientation, the carbene p orbital does not compete with the CO ligands for π-back-bonding from ruthenium. In a number of complexes we see inequivalent NMR resonances for the *trans*-CO (or isocyanide) ligands, which suggests a significant barrier to rotation about the Ru−NHC bond. Hindered rotation about the Ru−NHC bond has been previously reported for 5-coordinate, 16-electron complexes such as **3**.[13,14] Typically the most stable coordination geometry of ruthenium complexes of the general formula $Ru(CO)_2X_2L_2$, where X is a halide and L is a phosphine ligand donor, is Ru(*cis*-$CO)_2$(*cis*-$X)_2$(*trans*-$L)_2$.[15] The trans orientation of the carbonyl ligands suggest that the observed complex is kinetically determined.

The spectroscopic data are consistent with the same structure present in solution. The ^{1}H NMR spectrum of the complex in chloroform-d_1 displayed three characteristic resonances at δ 5.90, 5.75, and 4.57 ppm 1:1:1 ratio, assigned to the vinylic protons and a benzylic proton. The carbonyl ligands are observable in the ^{13}C NMR as an unresolved broad resonance at 198.1 ppm. DEPT analysis provided the existence of three new methine groups within the molecule with chemical shifts of 126.7, 126.3, and 54.6 ppm, respectively. A HMQC spectrum of the complex correlated the vinylic protons at δ 5.90 and 5.75 ppm with sp^2 hybridized carbons observed at 126.7 and 126.3 ppm, while the benzylic resonance correlated with a ^{13}C resonance at δ 54.6 ppm. The ^{31}P NMR spectrum gave a single peak at δ 16.0 ppm for the PCy_3 ligand. A single, intense absorption in the IR spectrum is found at 1982 cm^{-1} for the CO stretch, consistent with *trans*-carbonyl ligands.

Methylidene. Complex **8** was synthesized according to literature procedures[16] and reacted under identical conditions as complex **3** to give the analogous cycloheptatrienyl insertion product, complex **9**. The ^{1}H NMR spectrum of the resulting yellow solid in benzene-d_6 showed four new proton resonances in a 1:1:1:1 ratio: two singlets at 6.31 ppm and 5.77 ppm assigned to the 3,5-cycloheptatrienyl protons and a pair of doublets at 4.05 ppm and 2.90 ppm (J = 13.2 Hz) assigned to the methylene. The chemical shift of the alkylidene proton of substituted cycloheptatrienes is diagnostic for axial vs equatorial orientations.[17] The chemical shift for the equatorial proton is deshielded by 1.3−1.5 ppm relative to the axial proton. The ^{31}P NMR spectrum shows the resonance for the PCy_3 ligand at 13.45 ppm. The IR spectrum contains a single absorption at 1981 cm^{-1} which is expected for a *trans*-CO complex. The carbonyls in the ^{13}C NMR spectrum appear as an unresolved broad resonance centered at 200.0 ppm. DEPT and HSQC NMR spectroscopy was used in making assignments. The DEPT experiment provided the existence of two new methine groups and a methylene within the molecule with chemical shifts of 129.9, 126.0, and 42.3 ppm, respectively. The HSQC experiment correlated the ^{13}C chemical shifts of the methine carbons with the two new ^{1}H resonances at 6.31 and 5.77 ppm, and the AB quartet corresponded to a single methylene carbon at 42.3 ppm.

X-ray quality crystals of **9** were obtained by slow evaporation of a saturated acetone solution at −20 °C and the crystal structure is shown in Figure 3. The cycloheptatrienyl moiety is evident in the methylidene insertion product. Like the structure of the benzylidene insertion product the carbon monoxide and chloride ligands are in *trans*−*trans* configurations. The orientation of the *N*-heterocyclic carbene is also similar to that in the benzylidene insertion product **7**. However, the methylene adopts a conformation bent toward the ruthenium atom rather than away from it as in **7**.

Ethylidene. Similarly, treatment of the ethylidene complex **10**[18] with CO *in situ* in an NMR tube gives the analogous

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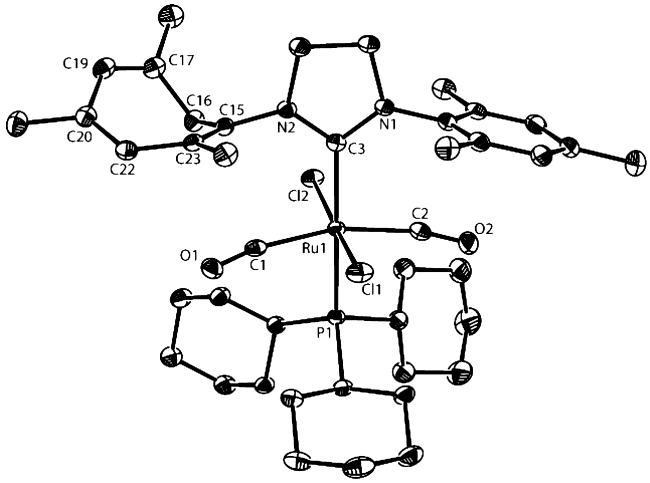

Figure 3. Molecular structure of complex **9**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

cycloheptatrienyl insertion product **11**. The ^{1}H NMR spectrum of the yellow solution in chloroform-d_1 showed three new proton resonances in a 1:1:1 ratio: two singlets at 6.10 and 5.77 corresponding to the 3,5-cycloheptatrienyl protons and a quartet 3.27 ppm (J = 6.8 Hz) for the methine proton. A single ^{31}P resonance at 15.9 ppm was assigned to the PCy_3 ligand and an IR absorption at 1982 cm^{-1} was assigned to the *trans*-carbon monoxide ligands.

However, upon standing, the initial product is transformed into a mixture containing an additional isomer. Three new resonances were observed in the ^{1}H NMR spectrum of the product mixture. Two new singlets at 5.99 and 5.85 ppm as well as a new quartet resonance at 3.02 ppm (J = 6.8 Hz) were present in a roughly 1.5:1 ratio with the initial insertion product. The ^{31}P NMR spectrum displays a second resonance at 19.1 ppm, in addition to that of the initial product. IR analysis of the resulting mixture shows two new absorptions at 1978 (overlapped with the absorption due to the initial product) and 1935 cm^{-1} in dichloromethane, suggesting isomerization to the *cis*-dicarbonyl complex. Under one atmosphere of carbon monoxide in $CDCl_3$, isomerization was complete in 5 days to yield a 2.2:1 ratio of the new carbonyl complex to the initially formed complex. No further isomerization occurred over the next week. A freshly prepared *trans*-carbonyl complex underwent rapid isomerization to an equilibrium mixture in approximately 15 min when heated to 55 °C in the NMR probe. Prolonged heating or heating above 60 °C caused significant decomposition. The mechanism of isomerization is currently unknown; however, isomerization is inhibited under elevated pressures of carbon monoxide. This suggests that the isomerization involves CO dissociation. A freshly prepared sample of the *trans* isomer sample kept under 60 psi of carbon monoxide in $CDCl_3$ appears to be indefinitely stable at room temperature, allowing for full characterization. The ethylidene complex is currently the only complex for which we observed isomerization. Attempts to isomerize the *trans*-dicarbonyl benzylidene insertion complex **7** by heating or by UV irradiation were unsuccessful.

Mawby[15] and Jacobson[19] have reported that ruthenium(II) complexes $RuCl_2(CO)_2(PR_3)_2$ undergo reversible light- and thermal-initiated isomerizations. The all-*trans* isomer of $RuCl_2(CO)_2(PR_3)_2$, *ttt*, thermally isomerizes in solution to form the all-*cis* isomer, *ccc*-$RuCl_2(CO)_2(PR_3)_2$. This process was inhibited by added carbon monoxide which suggests CO loss is the initial step in the isomerization process. The all-*cis* isomer proceeds to isomerize further to the thermodynamically stable *cct* isomer in which only the phosphines are trans. Our ligand system is significantly different as the NHC is present, and isomerizations of similar complexes to the best of our knowledge have not been studied, but the mechanism presumably is analogous.

3-Methyl-2-butenylidene. The 3-methyl-2-butenylidene complex **12** was reacted with carbon monoxide to yield the corresponding insertion product **13** (Scheme 1). The NMR spectra for **13** differed from the previous examples in that there are at least three isomers present in solution, and a fluxional process exchanging two of these makes the ^{1}H and ^{31}P NMR spectra difficult to interpret. The resonances assigned to the 3,5-cycloheptatrienyl protons, and the protons of the vinylcarbene were significantly broadened in the ^{1}H NMR spectrum at room temperature. The ^{31}P NMR spectrum was more informative as two major resonances were observed: a sharp singlet at 16.1 ppm and a very broad resonance at 13.8 ppm. As the sample was cooled to −40 °C, the singlet at 16.1 remained sharp but gradually shifted to 19.8 ppm. The broad resonance at 13.8 began to sharpen, eventually resolving into two resonances located at 17.4 (major) and 13.2 (minor) ppm in roughly an 8:1 ratio. The ratio of the two major isomers is 1.4:1.

The ^{1}H NMR spectrum at −40 °C was difficult to interpret due to overlapping signals. However, the two major isomers both appear to contain cycloheptatrienyl moieties. The cycloheptatrienyl proton resonances occur at 5.87 and 5.77 ppm for one isomer and 6.10 and 5.90 ppm for the other isomer in roughly a 1.2:1 ratio. Three doublets are also observed at 6.06 (J = 10.8 Hz), 5.37 (J = 12.4 Hz), and 3.26 (J = 10.8 Hz) ppm, assigned to the methine protons of the 3-methyl-2-butenylidene moiety, while the fourth is not observed, most likely due to overlapping resonances.

The NMR spectra are indicative of three isomers, two of which are exchanging in a dynamic process on the NMR time scale. The NMR data for the two major, nonexchanging isomers indicate that both contain cycloheptatrienyl moieties. The chemical shifts for the protons in the 7-positions of the two major isomers are quite different, with one doublet at 3.26 ppm and the other obscured by other resonances at 3.6−4.0 ppm. This suggests that the 3.26 ppm signal is due to an axially oriented proton, while the obscured resonance is due to an equatorial proton. The crystallographic data obtained for **38** and **39** (*vide infra*) also suggest that the isomers are due to conformational and rotational isomers involving the cycloheptatrienyl moiety (Scheme 2). Hindered rotation about the *N*-mesityl bonds of **3** and other phosphine-substituted derivatives have been previously reported, with activation barriers of about 20 kcal/mol.[13,14] All of the 7-substituted cycloheptatrienyl products can exhibit rotational isomerism due to the orientation of the substituent relative to the face of the ring, syn or anti to the metal atom, and conformational isomerism due to the substituent occupying an axial or equatorial site. Like the isopropoxybenzylidene, the 3-methyl-2-butenylidene substituent also introduces rotational isomerism due to the orientation of the substituent relative to the cycloheptatrienyl group. The two major isomers are proposed to be analogues of the two isomers of **38** (*vide infra*), which differ in the syn vs anti orientation of the alkenyl substituent relative to the ruthenium atom, with the

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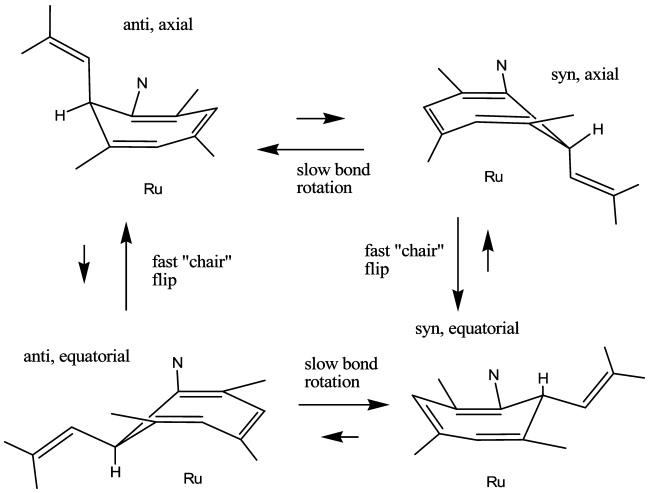
Scheme 2. Conformational and Rotational Isomers for **13**



syn (equatorial) isomer and the anti (axial) isomer both having the alkenyl group oriented away from the cycloheptatrienyl ring face. The third, minor isomer exchanges with one of these two. We hypothesize that the anti, axial isomer is exchanging with the anti, equatorial isomer via a low-energy flipping of the C7 carbon, analogous to the different conformations observed in the crystal structures of **7** and **9**. Ring inversions in sterically unhindered cycloheptatrienes are rapid, requiring very low temperatures to obtain the static NMR spectra. However, a relatively slow ring inversion for isomeric axial−equatorial 7-*tert*-butyl conformers was proposed for the NMR behavior of 1,3,5,7-tetra-*tert*-butylcyclohepta-1,3,5-triene above 55 °C.[20] Another possibility is that the minor isomer is due to a norcaradiene valence tautomer.

Grubbs' Carbene Insertions Promoted by Aryl Isocyanides. Isocyanides are isolobal with carbon monoxide and have very similar ligand characteristics; however, compared to carbon monoxide, isocyanides have greater σ-donor/π-acceptor ratios.[21−24] Nonetheless, isocyanides are capable π-acceptors[25] and we were gratified to observe that isocyanides promote the insertion of the carbene moiety into the mesityl group of the *N*-heterocyclic carbene. For all the reactions reported here, *p*-chlorophenyl isocyanide was utilized due to the ease of handling and purification, but it should be noted that aliphatic isocyanides and other aryl isocyanides such as *p*-methoxyphenyl isocyanide also promote the Buchner insertion.

Treatment of a solution of complex **3** with 2.2 equiv of *p*-chlorophenyl isocyanide resulted in a rapid color change to light orange-yellow. Precipitation of the product with pentane deposited complex **14** as a bright yellow solid in 79% yield. The ^{1}H NMR spectrum of the product displayed three resonances at 5.61, 5.41, and 5.04 ppm in a 1:1:1 ratio corresponding to the two cycloheptatrienyl protons and the benzylic proton, consistent of the presence of a cycloheptatrienyl moiety. The

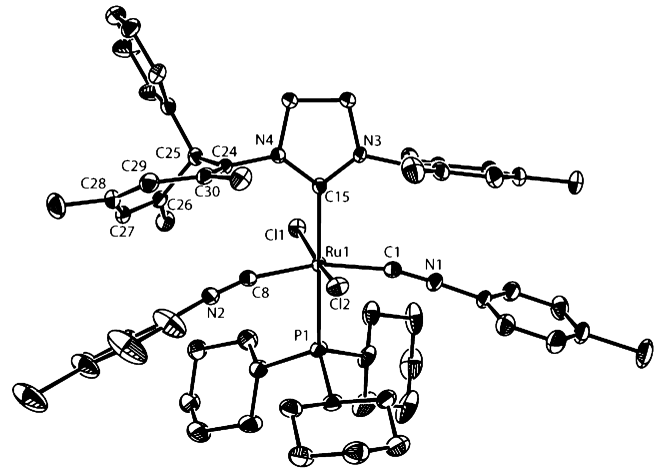


Figure 4. Molecular structure of complex **14**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level.

^{13}C NMR spectrum clearly shows the resonances for the isocyanide ligands as two separate doublets at 173.9 and 172.2 ppm with cis coupling constants to the PCy_3 ligand ($^2J_{CP}$ 18 and 16 Hz, respectively). The ^{31}P NMR spectrum gave a single peak at δ 16.9 ppm which was assigned to the PCy_3 ligand, and the IR spectrum (in dichloromethane) revealed an intense absorption at 2057 cm^{-1} with smaller shoulders at 2161, 2100, and 2012 cm^{-1}. The IR spectrum of free *p*-chlorophenyl isocyanide showed a single intense absorption at 2129 cm^{-1} in CH_2Cl_2. The significant decrease in the CN stretching frequency indicates a significant degree of back-donation into the π* orbitals of the isocyanide.

Dark-yellow X-ray quality crystals were grown from a saturated CH_2Cl_2 solution at −20 °C. The crystal structure is presented in Figure 4. Compound **14** shares analogous structural features with the carbon monoxide-promoted insertion products. A trans relationship is observed for both the chloride and isocyanide ligands. The phenyl substituent on the cycloheptatrienyl group is oriented anti to the metal atom and in an axial position, as for **7**.

Similarly, reactions of **8** and **10** with *p*-chlorophenyl isocyanide gave **15** (96% by NMR, 63% isolated yield), and **16** (83% isolated yield), respectively (Scheme 1). Both products were characterized by spectroscopic methods (Supporting Information).

Fischer Carbene Complexes: Effect of π Donor Carbene Substituents. Fischer carbenes were also investigated in the ligand-promoted Buchner insertion. In a recent paper by Louie and Grubbs,[26] Fischer carbenes of the general formula $(L)(PCy_3)Cl_2RuCH(ER)$ where L = PCy_3 or H_2IMes and E = O, S, or N were synthesized and were found to be thermally more robust than the parent benzylidene. Carbene complexes **17**−**19** (Figure 5) were synthesized and reacted with carbon monoxide or *p*-chlorophenyl isocyanide.

Reacting compound **17** with 1 atm of carbon monoxide or with 2.2 equiv of *p*-chlorophenyl isocyanide did not result in carbene insertion as determined by ^{1}H NMR spectroscopy. Only the initial starting material was observed. Increasing the pressure to 60 psi of carbon monoxide for 12 h resulted in decomposition of the starting material. A small amount of a ruthenium hydride was detected in the ^{1}H NMR spectrum at −25.0 ppm, J_{H-P} =

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(21) Csonka, I. P.; Szepes, L.; Modelli, A. *J. Mass Spectrom.* **2004**, *39*, 1456–1466.
(22) Knorr, M.; Jourdain, I.; Lentz, D.; Willemsen, S.; Strohmann, C. *J. Organomet. Chem.* **2003**, *684*, 216–229.
(23) Malatesta, L.; Bonati, F. *Isocyanide Complexes of Metals*; Interscience: New York, 1969.
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(25) Cotton, F. A.; Zingales, F. *J. Am. Chem. Soc.* **1961**, *83*, 351–355.
(26) Louie, J.; Grubbs, R. H. *Organometallics* **2002**, *21*, 2153–2164.

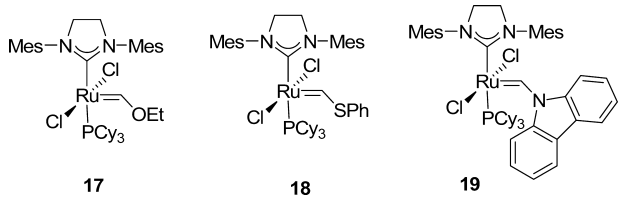
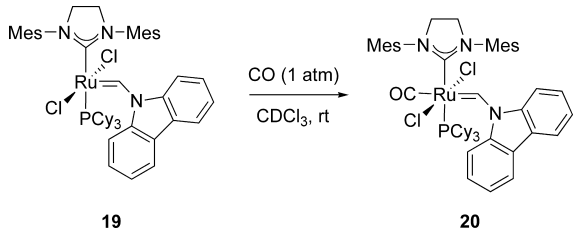


Figure 5. Fischer carbenes **17**−**19**.

Scheme 3. Reaction of **19** with CO



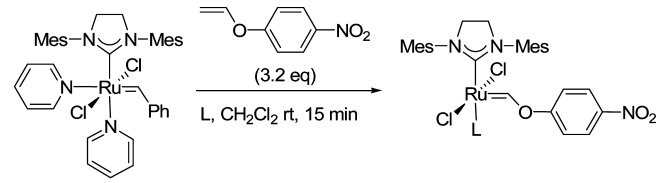
21 Hz. This hydride resonance has a chemical shift similar to that of the thermal decomposition product $RuH(PCy_3)(CO)Cl(H_2IMes)$ observed by Grubbs[26] and others.[27,28]

Treatment of the thiophenyl carbene **18** with carbon monoxide or *p*-chlorophenyl isocyanide did result in decomposition of the ruthenium carbene, but multiple products were observed by both ^{1}H and ^{31}P NMR spectroscopy, and the characteristic NMR resonances of the cycloheptatrienyl moiety were not observed. The products could not be identified by standard spectroscopy, and attempts to crystallize products from the crude reaction mixtures were unsuccessful.

Complex **19** reacts differently with carbon monoxide but does not appear to react with *p*-chlorophenyl isocyanide. Treatment of a solution of **19** with carbon monoxide resulted in a rapid color change from purple to red. The ^{1}H NMR spectrum indicated that no insertion had taken place as a carbene proton resonance was still present, but shifted upfield to 14.2 ppm from 16.8 ppm. The ^{31}P NMR spectrum showed a single resonance at 13.5 ppm, corresponding to a coordinated PCy_3 ligand, and the IR spectrum showed a single absorption at 1982 cm^{-1}. Using ^{13}CO (99% isotopic enrichment) as the reagent, a ^{13}C NMR spectrum was obtained to determine the number of coordinated carbonyl ligands. The ^{13}C NMR spectrum of the resulting solution reveals a single ^{13}CO resonance at 206.4 ppm (d, J_{C-P} = 14.3 Hz), suggesting a single carbonyl ligand coordinated cis to the PCy_3 ligand. The spectroscopic data support the formulation of the product as the 18-electron complex **20** shown in Scheme 3. The product, however, is unstable in solution and readily decomposes at room temperature within 30 min, preventing further characterization. The new complex can be isolated as a bright-red solid from a saturated acetone solution at −20 °C but rapidly decomposes upon isolation. The decomposition products have not been identified, but the characteristic ^{1}H NMR resonances of Buchner insertion product were not detected in the product mixture.

The failure of oxygen-substituted Fischer carbenes to undergo insertion or decomposition suggested that π donating heteroatom substituents made the carbene insufficiently electrophilic to undergo the ligand-promoted Buchner reaction. We rationalized

Scheme 4. Synthesis of Fischer Carbenes **21** and **22**



that electron withdrawing substituents on the carbene would increase the electrophilicity and facilitate insertion. Synthesis of complex **21** was achieved in 76% yield by reacting the Grubbs pyridine solvate[6] with 3.2 equiv of *p*-nitrophenyl vinyl ether, followed by quenching with PCy_3 (Scheme 4). Reaction of this complex with carbon monoxide failed to give insertion as only the starting material was observed by ^{1}H NMR spectroscopy.

Rationalizing that the carbene carbon was still insufficiently electron-deficient we sought to prepare a less electron-rich complex by replacing the PCy_3 ligand with the less basic triphenylphosphine. Reaction of complex **22** with carbon monoxide generated the insertion product **23** in 77% yield by ^{1}H NMR spectroscopy (Scheme 1); however, the insertion product is not stable and begins to decompose upon formation. Reaction of complex **22** with *p*-chlorophenyl isocyanide did not result in Buchner insertion into the NHC ligand.

Results from these experiments suggest that the carbene must be rendered sufficiently electrophilic to undergo Buchner insertion. Heteroatom substituents on the carbene as well as strongly σ-donating ligands on the ruthenium center, such as PCy_3, provide suitable stabilization to inhibit insertion. Thus far, no Buchner insertion by a Fischer carbene has been observed using aryl isocyanides although decomposition of the thio-ether complex does occur. Although isocyanides are considered π-acceptors, carbon monoxide is much better in destabilizing the ruthenium carbene, thus promoting insertion. These observations suggest that ligand electronics play a key role in promoting the Buchner insertion.

Effect of Variation in PR_3 for Grubbs' Complexes. In order to determine whether the size of the phosphine ligand influences carbene insertion, phosphine derivatives of **3** were synthesized according to the procedure of Grubbs et al.[6] Using the Grubbs-pyridine solvate, **6**, the trimethyl- (complex **24**), tri-*n*-butyl- (complex **25**), and triphenylphosphine (complex **26**), and triisopropylphosphite (complex **27**) derivatives were synthesized. The cone angles of the phosphine ligands are 118° for PMe_3, 132° for $P(n\text{-}Bu)_3$, and 145° for PPh_3.[29] The triisopropylphosphite complex was stable enough to isolate and characterize; this ligand has a cone angle of 130°. Due to the increased solubility of the phosphine derivatives in noncoordinating solvents, some of the complexes were generated *in situ* and characterized by NMR spectroscopy. Proton NMR yields are reported where appropriate versus a 1,4-dinitrobenzene internal standard.

CO-promoted insertions were observed for complexes **24**−**27** (Scheme 1). Treatment with 1 atm of carbon monoxide resulted in a color change from brown to yellow, forming insertion products **28**−**31**. These products were characterized by ^{1}H NMR, ^{31}P NMR, and IR spectroscopy (see Supporting Informa-

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(28) Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F.; Thiel, O. R. *Chem.*−*Eur. J.* **2001**, *7*, 3236–3253.
(29) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313–348.

tion). NMR yields were determined for **28** (92%) and **29** (97%) by integration against an internal standard, while **30** (52%) and **31** (54%) were isolated as yellow to yellow-brown solids. On the basis of the spectroscopic data (Supporting Information), the structures are all assigned as *trans*-dichloride, *trans*-dicarbonyl complexes.

Reactions of the above phosphine and phosphite complexes with *p*-chlorophenyl isocyanide were analogous to the reactions with carbon monoxide. In some cases the decreased solubilities of the complexes allowed for isolation and further characterization. Yields and characterizations of **32**−**35** are given in the Supporting Information.

Phosphine-Free Carbene Complexes. "Phosphine-free" complexes such as the Hoveyda−Blechert[30] complex **4**[3,4] and the Grubbs pyridine solvate **6**[6,31] were also found to yield Buchner insertion products with varying results when reacted with *p*-chlorophenyl isocyanide or alkylphosphites. Reactions of **4** or **6** with carbon monoxide resulted in complex mixtures of insertion products which were not readily characterizable by ^{1}H NMR or IR spectroscopy. The likely explanation for the complex mixtures arises from the chelating isopropoxybenzylidene which may inhibit insertion and lead to decomposition via other pathways as well as the possibility for the complexes to form multiple conformational isomers due to orientations of the isopropoxy group.

Coordination of carbon monoxide trans to the carbene is likely to occur in complex **4** as in complex **3**, making the carbene electrophilic and apt to insert into the mesityl group. However, if the isopropoxy ether is coordinated to ruthenium upon CO binding, the carbene may be prevented from cyclopropanation due to constraints of the chelate. Dissociation of the ether is most likely needed prior to CO binding to facilitate the Buchner reaction.

Blechert has shown that, when **4** is treated with an excess of strong nucleophile such as PCy_3, the coordinated isopropoxy ether is easily displaced.[3] However, the phosphine adduct is unstable and reverts back to **4** in 2 h at room temperature in CH_2Cl_2.

The phosphine adducts of the Hoveyda−Blechert complex[3,4] were investigated to determine whether clean insertion would occur. Indeed, complexes **36** and **37** reacted with carbon monoxide and arylisocyanides to give the expected insertion complexes (Scheme 1). Due to the rapid conversion of these phosphine adducts back into the starting material **4** while in solution, only the isocyanide reaction proved feasible, as a solution of the isocyanide could be added directly to a solid sample of the ruthenium carbene. This reduced the amount of phosphine dissociation and minimized side reactions.

The tricyclohexylphosphine adduct **36** proved to be a very difficult system when reacted with *p*-chlorophenyl isocyanide as its solubility prevented isolation. Attempts to precipitate or crystallize material from a saturated solution failed. Repeated attempts only resulted in decomposition of the complex.

The triphenylphosphine insertion product **38** was much easier to isolate as layering the crude reaction mixture with pentane afforded X-ray quality crystals after 24 h. The ^{1}H NMR spectrum of the isolated product clearly indicates the presence of two isomers in solution as there are two sets of three resonances present in a 1:1:1 ratio and this also confirmed by

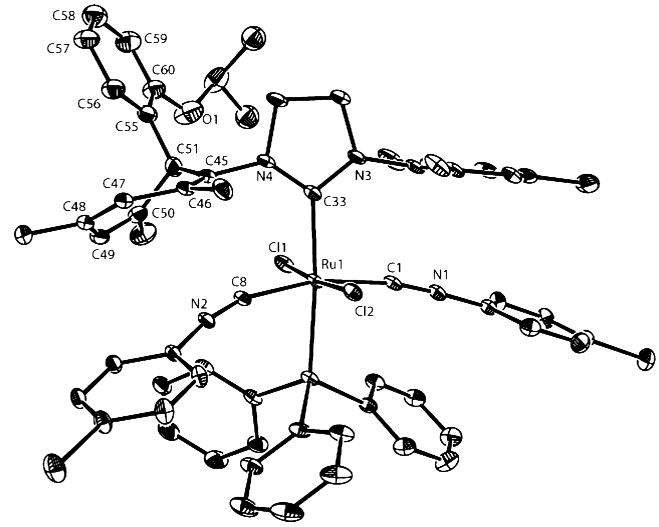


Figure 6. Molecular structure of complex **38a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

the presence of ^{31}P resonances at 33.8 and 32.6 ppm. The cycloheptatrienyl proton resonances occur at 5.92, 5.86, 5.59, 5.49, 5.39, and 4.20 ppm. Two methine resonances are clearly resolved as septets at 4.65 and 4.14 ppm both with coupling constants of $J = 5.6$ Hz. One-dimensional TOCSY and NOE were used to correlate the resonances at 5.92, 5.86, and 4.20 ppm to a single isomer, while the proton resonances at 5.59, 5.49, and 5.39 ppm correspond to the other isomer. The ^{13}C NMR spectrum was not very informative as the large number of aromatic carbons prevented clear resolution of isocyanide carbons. However, resonances corresponding to the NHC carbons were identified at 211.7 (d, $J_{C-P} = 103$ Hz) and 210.2 (d, $J_{C-P} = 103$ Hz). These resonances confirm the presence of two isomers and their relatively large coupling constants suggest a trans relationship with the PPh_3 ligand. The possibility of one isomer being the product of ligand substitution of PPh_3 by an arylisocyanide has been ruled out as no coupling to the NHC carbene would be observed. Variable temperature NMR experiments did not show interconversions of the two isomers at elevated temperatures and decomposition was observed at 35−45 °C in toluene-d_8.

The solid-state structure of **38** was determined by X-ray crystallography. The structure is severely disordered, due to the presence of solvent molecules, but more importantly, the crystal contains two isomeric molecules differing in the orientations of the isopropoxyphenyl group. One molecule, **38a**, at about 62% occupancy, presented above in Figure 6, adopts a conformation with the isopropoxybenzylidene fragment anti to the ruthenium atom and in an axial position with the isopropyl group pointing away from the 1,3,5-cycloheptatrienyl moiety. The other molecule, **38b**, Figure 7, adopts a conformation with the isopropoxybenzylidene fragment syn to the ruthenium atom in an equatorial position and with the isopropyl group pointing toward the 1,3,5-cycloheptatrienyl moiety. This is strong evidence that the two isomers observed in solution differ in the *syn*−*anti* orientation of the isopropoxyphenyl group. Interconversion between these isomers can be achieved by rotation about the *N*-cycloheptatrienyl bond (higher energy) and rotation about the cycloheptatrienyl−isopropoxyphenyl bond (lower energy). On the basis of the chemical shifts of the H(7) protons, the ^{1}H

(30) The Hoveyda−Blechert complex **4** is available commercially as the Hoveyda−Grubbs complex.
(31) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035–4037.

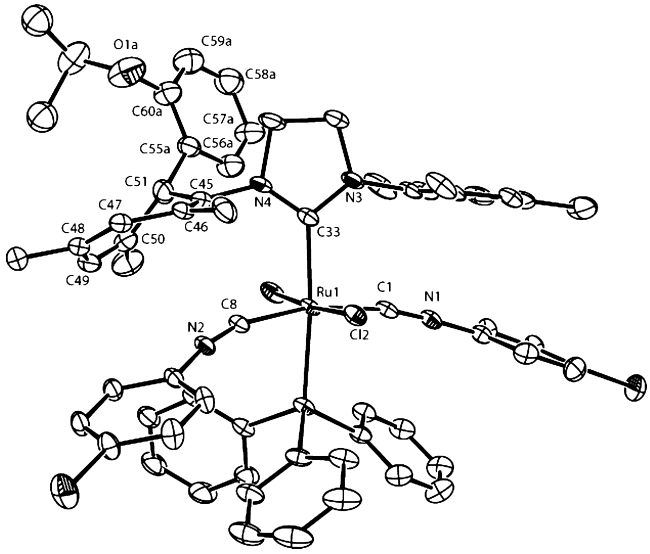
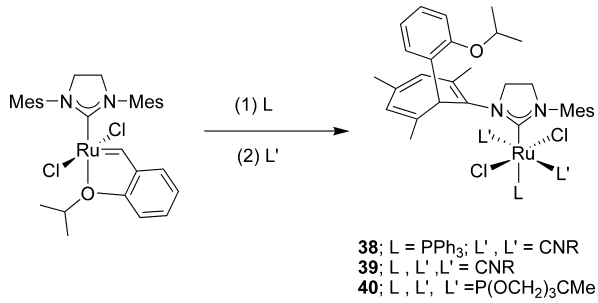


Figure 7. Molecular structure of complex **38b**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

Scheme 5. Buchner Insertions with the Hoveyda−Blechert Complex



NMR resonance at 4.20 ppm can be assigned to **38b** and the resonance at 5.39 ppm to the orientation as in **38a**.

Rotations about *N*-mesityl bonds in **3** and substituted analogues have been previously determined.[13] For **3**, rotations about *N*-mesityl bonds have barriers of ∼62 kJ/mol, observable as broadening of ^{1}H NMR resonances above −50 °C and coalescence by 60 °C. The higher coordination numbers for these insertion products are expected to raise the free energy barrier for rotation. We see no evidence of rotations about either the *N*-mesityl or *N*-cycloheptatrienyl bonds on the NMR time scale.

We rationalized that the aryl isocyanides would be sufficiently good nucleophiles to displace the isopropoxy group of complex **4** and allow for Buchner insertion once the second isocyanide coordinated trans to the carbene. Treatment of a solution of complex **4** with excess *p*-chlorophenyl isocyanide (4.2 equiv) resulted in a rapid color change from green to orange-yellow. Precipitation of the product **39** (Scheme 5) with pentane deposited a bright-yellow solid in 86% yield. NMR spectra reveal that the product is a mixture of two isomeric insertion products. The ^{1}H NMR spectrum of the major isomer (85%) displayed three resonances at 6.16 and 5.46 and 4.27 ppm corresponding to the two cycloheptatrienyl protons and the benzylic proton respectively. The methine proton resonance of the isopropoxy ether is a septet at 4.16 ppm (J_{H-H} = 6 Hz). The minor isomer (15%) also appears to contain the cycloheptatrienyl moiety as three resonances of equal intensities are observed at 5.70, 5.16, and 5.09 ppm, with the methine

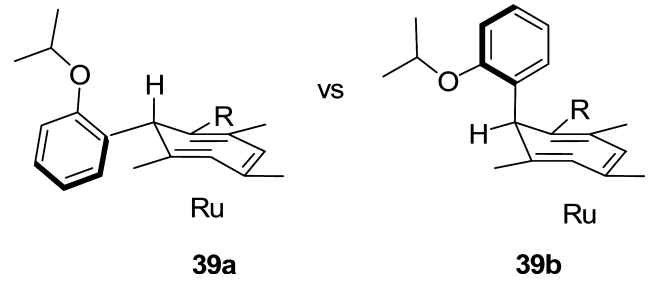


Figure 8. Rotamers of the isopropoxybenzylidene moiety.

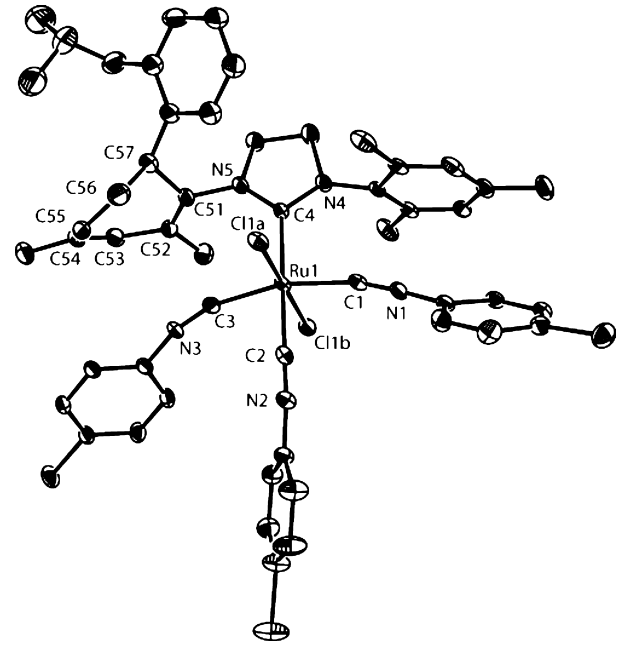


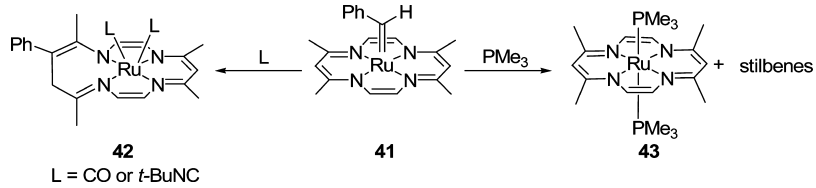
Figure 9. Molecular structure of complex **39a**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. C56 is eclipsed by a methyl group.

resonance of the isopropoxy group at 4.63 ppm (sept, J_{H-H} = 6.5 Hz). The ^{13}C NMR spectrum contains resonances for NHC carbenes at 211.8 (major) and 210.5 (minor) ppm. The elemental analysis of the product mixture was consistent with the proposed formula.

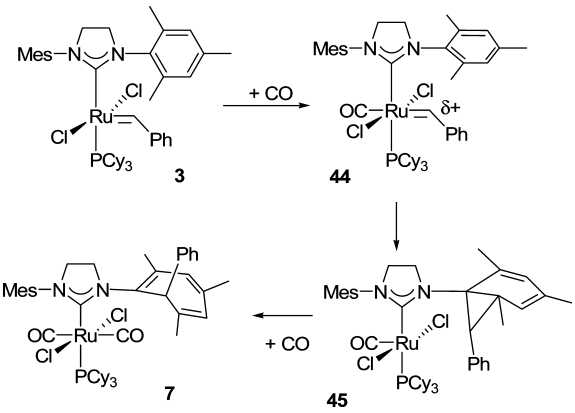
The two isomers most likely are due to different rotational orientations of the isopropoxyphenyl substituent relative to the cycloheptatrienyl ring, one in which the isopropoxyphenyl substituent is axially oriented and anti to the Ru atom and the other with the isopropoxyphenyl substituent equatorially oriented and syn to the Ru atom, in both cases the isopropoxy group adopts an orientation pointing toward H_b (Figure 8). The structure of the major isomer is assigned to isomer **39a**. The minor isomer is assigned as isomer **39b** in which the isopropoxyphenyl group is anti to the Ru atom in an axial position, and with the isopropoxy group oriented away from the cycloheptatrienyl moiety.

X-ray quality crystals of **39** were obtained by vapor diffusion of pentane into a saturated benzene solution at room temperature. The crystal structure (Figure 9) confirms the *mer*-configuration of the isocyanide ligands. The solid-state structure also reveals that isopropoxybenzylidene fragment is oriented syn to the Ru atom in an equatorial position and the isopropyl group is draped over the cycloheptatrienyl moiety of the *N*-heterocyclic carbene. Only one conformation was found in the crystal structure.

Scheme 6. Ligand-Promoted Ru Carbene Insertion into a Macrocyclic Ligand (Floriani et al., refs 34 and 35)



Scheme 7. Proposed Mechanism for CO Promoted Buchner Insertion



Grubbs' Carbene Insertions Promoted by Phosphorus Donor Ligands. Small tertiary alkylphosphites were also discovered to react with the Grubbs family of ruthenium carbenes to yield Buchner insertion products. However, unlike the reactions performed with carbon monoxide or aryl isocyanides, the products were difficult to characterize due to decomposition upon attempted isolation or competing decomposition during the reaction. As a result of the competing decomposition of the insertion complexes, their exact structures remain ill-defined.

Reactions using Grubbs' catalyst **3** were very slow and never reached full consumption of the ruthenium carbene. Based on the proposed mechanism (see following section) this is most likely due to steric reasons as the PCy_3 and NHC ligands inhibit phosphite coordination trans to the ruthenium carbene. To simplify the system, the Grubbs pyridine solvate **6** and Hoveyda−Blechert complex **4** were used as the lack of PCy_3 helped facilitate the reaction. In most cases, both complexes yielded similar results; however, for the former, the excess pyridine present in solution complicated the NMR results, and the Hoveyda−Blechert complex was used exclusively for the NMR experiments.

Addition of 4 equiv of $P(OCH_2)_3CCH_3$ to a solution of **4** resulted in an immediate color change from green to yellow-brown to bright yellow due to the Buchner insertion, forming **40** (Scheme 5). The ^{1}H NMR spectrum of the resulting solution indicated a single isomer with the formation of three new resonances at 5.80, 5.64, and 5.20 ppm which were assigned as the cycloheptatrienyl protons and the benzylic proton respectively. The methine resonance appeared as a septet, $J_{H-H} = 6.0$ Hz, at 4.61 ppm. The ^{31}P NMR spectrum contained a broadened resonance centered at 130 ppm. The broad ^{31}P resonance suggests a fluxional process. Low temperature ^{31}P NMR spectroscopy was unsuccessful in resolving the broadened resonance down to temperatures as low as −50 °C. At −30 °C the resonance nearly disappeared into the baseline but at −50 °C was still broad, indicating a low energy barrier for the fluxional process. The process appears to only involve coordinated phosphite as there is no broadening of the ^{31}P resonance of free phosphite. Integration of the benzylic proton of the cycloheptatrienyl moiety at 5.20 with the methylene and methyl protons of the phosphite ligands indicates that 3 phosphites are coordinated to the metal. Elemental analysis of the isolated complex was inconclusive and was most likely complicated by inclusion of solvent. Isolated yield of this complex was 98% on a preparative scale. This product was the only isolatable phosphite complex of the series of phosphites investigated.

Addition of 4 equiv of freshly distilled trimethylphosphite to complex **4** resulted in an immediate color change from green to yellow-brown. The ^{1}H NMR spectrum of the resulting solution indicate the formation of three new resonances located at 5.90, 5.66, and 5.17 ppm, assigned as the cycloheptatrienyl protons and benzylic proton respectively. The ^{31}P NMR spectrum contained a broadened resonance centered at 135 ppm. The broadening of the ^{31}P resonance also suggests a fluxional process. The yield of this complex was 61% by NMR. A ^{1}H NMR resonance (23%) was observed at 19.4 (s) ppm; this is assigned to the phosphite adduct of the Hoveyda−Blechert complex in which the phosphite had displaced the isopropoxy ether. A small amount (10%) of the carbene starting material is also observed at 16.6 ppm in the ^{1}H NMR spectrum. Monitoring the reaction over the course of one hour did not find more of the insertion complex as decomposition of the new phosphite carbene was observed.

Addition of 4 equiv of triisopropylphosphite to complex **4** resulted in an immediate color change from green to brown. The ^{1}H NMR spectrum of the resulting solution indicated that insertion did not occur and only substitution of the isopropoxy ether was observed. A new resonance was observed at 19.5 ppm in approximately 1:1 ratio with the starting material, 16.6 ppm. Over the course of an hour, the final observed ratio was 4:1.

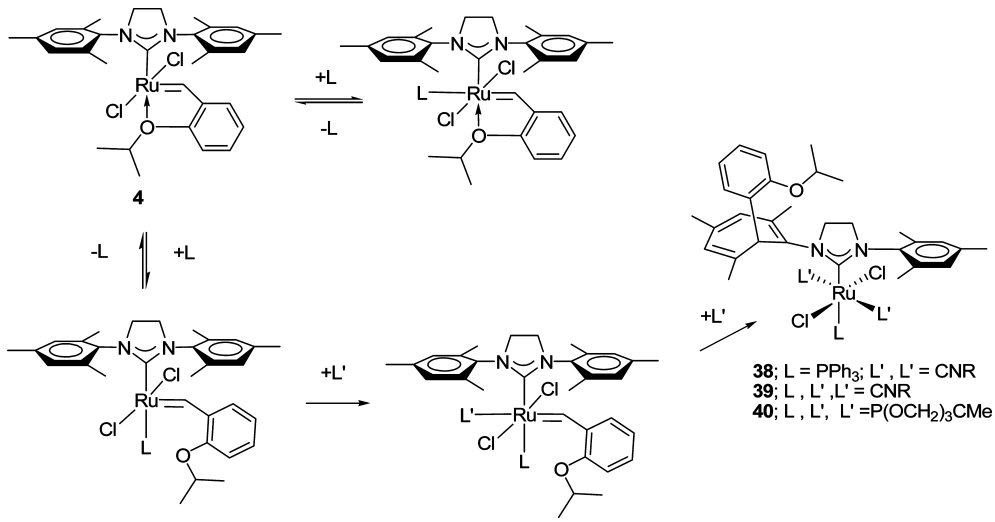
Addition of 4 equiv of triphenylphosphite to complex **4** did not result in any noticeable color change. The ^{1}H NMR spectrum of the resulting solution indicated that insertion did not occur and only starting material was observed.

Discussion

Mechanism of Ligand-Induced Buchner Insertion. In 1885 Buchner reported the cyclopropanation of aromatic rings by free carbenes to give norcaradienes, in equilibrium with the corresponding cycloheptatrienes. In recent years metal-catalyzed diazoalkane decompositions in the presence of arenes and alkenes have shown synthetic utility for the preparation of both cycloheptatrienes and cyclopropanes.[32,33] Metal carbenoid additions to carbon−carbon π bonds typically involve very electrophilic carbenes. Ruthenium carbenes used in alkene metathesis are much less electrophilic and typically do not form cyclopropanation products.

(32) Doyle, M. P.; McKervey, M. A.; Ye, T. In *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds: From Cyclopropanes to Ylides*; Wiley-Interscience: New York, 1998; pp 289−354.
(33) Anciaux, A. J.; Demonceau, A.; Noels, A. F.; Hubert, A. J.; Warin, R.; Teyssie, P. *J. Org. Chem.* **1981**, *46*, 873–876.

Scheme 8. Proposed Mechanism for Ligand-Promoted Buchner Insertion Involving the Hoveyda−Blechert Complex



A ligand-promoted insertion of a ruthenium carbene into a coordinated ligand was reported by Floriani et al. in 1998 (Scheme 6).[34,35] Macrocyclic ruthenium carbene **41** containing a dibenzotetramethyltetraaza[14] annulene dianion (tmtaa) ligand environment undergoes carbene migration in the presence of carbon monoxide or *tert*-butyl isocyanide. This migration results in an expansion of the macrocycle to give **42**. Reaction of **41** with PMe_3, however, results in complex **43** and a mixture of stilbenes. Hückel calculations of the macrocyclic complex reveal that strong π-acids (CO) and strong σ-donors (PMe_3) each decrease the energy of the metal carbene bond (i.e., labilization). Weaker σ-donors such as pyridine and THF do not facilitate the labilization of the carbene ligand, most likely because they exert a weaker trans influence than more basic σ-donors such as PMe_3.

The mechanism of the ligand-induced Buchner reaction observed in the Grubbs second-generation ligand environment is believed to follow a similar pathway. Using **3** as the carbene and carbon monoxide as the ligand, a proposed mechanism for the formation of **7** is presented in Scheme 7. In the presence of carbon monoxide, coordination of CO trans to the benzylidene occurs to form an 18-electron ruthenium carbene species **44**. Due to the strong π-back bonding to carbon monoxide, the ruthenium center no longer is able to stabilize the π-orbital of the carbenic carbon of the benzylidene. This lack of stabilization weakens the ruthenium−carbene bond, making the carbene more electrophilic.[35] Cyclopropanation of the proximal mesityl moiety of the *N*-heterocyclic carbene generates 16-electron norcaradiene intermediate **45**, which is followed by CO addition and electrocyclic ring-opening to provide the cycloheptatrienyl product **7**. The high isolated yield and absence of regioisomers (e.g., distal cyclopropanation of the C2−C3 or C3−C4 bonds) suggests that the insertion is intramolecular and does not involve a free carbene. Supporting this inference, analysis of the crude solution used to produce **7** did not show any stilbenes that could have been derived from dimerization of free benzylidene carbenes. The vacant coordination site thus generated is then occupied with another molecule of carbon monoxide, giving the *trans*-dicarbonyl product before rearrangement can occur. Although none of the intermediates of the proposed mechanism are observable by NMR spectroscopy, the 18-electron ruthenium complex **20**, characterized from the reaction of carbon monoxide with the *N*-carbazole derived carbene (Scheme 3), supports the intermediacy of species **44**.

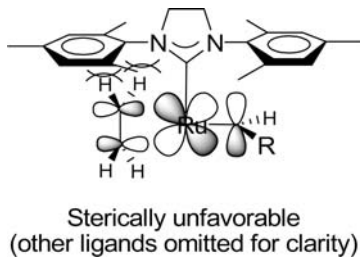


Figure 10. Competition of π-acceptor ethylene and carbene for metal d electrons which would increase the electrophilicity of the carbene.

Influence of Added Ligands, Carbene Substituents, and Ancillary Ligands on Insertion. The ligand-induced Buchner reaction exhibits restrictions on (1) the nature of the in-coming ligand, (2) the nature of the carbene ligand, and (3) the nature of the ligand coordinated trans to the NHC ligand.

The vacant coordination site of **3** and other phosphine-substituted analogues is sterically constrained. Therefore, only small ligands such as CO, isocyanides, or pyridine (i.e., complex **6**) can add to generate 18-electron, 6-coordinate complexes. For derivatives of **3** substituted with smaller PR_3 ligands, such as $P(OMe)_3$ or $P(OCH_2)_3CMe$, which are generated by adding excess phosphite to complex **4**, the sterically less hindered access allows coordination of a second phosphite ligand, inducing the Buchner insertion. However, since complex **6** does not undergo the Buchner insertion, there also are electronic restrictions: the incoming ligand must be a π acceptor to make the carbene sufficiently electrophilic to undergo the Buchner cyclopropanation. It should be noted that Grubbs et al.[36] reported that decomposition of the methylidene complex **8** in the presence of excess pyridine forms $MePCy_3^+$ and $Ru(H_2IMes)(py)_3Cl_2$.

The electrophilicity is also mediated by the carbene substituents and by the ligand trans to the NHC ligand. Fischer carbenes with π donating heteroatoms reduce the electrophilicity of the carbene such that CO does not induce the reaction.

(34) Klose, A.; Solari, E.; Floriani, C.; Geremia, S.; Randaccio, L. *Angew. Chem., Int. Ed.* **1998**, *37*, 148–150.
(35) Klose, A.; Solari, E.; Hesschenbrouck, J.; Floriani, C.; Re, N.; Geremia, S.; Randaccio, L. *Organometallics* **1999**, *18*, 360–372.
(36) Hong, S. H.; Wenzel, A. G.; Salguero, T. T.; Day, M. W.; Grubbs, R. H. *J. Am. Chem. Soc.* **2007**, *129*, 7961–7968.

However, the combination of PPh_3 replacement for PCy_3 and the *p*-nitrophenyl ether makes the carbene of **22** electrophilic enough to undergo insertion upon treatment with CO, but not with the poorer π acceptor isocyanide ligand. In the case of the Hoveyda−Blechert complexes, displacement of the isopropoxy ether is likely to occur before insertion (Scheme 8). This is evidenced by the appearance of the new carbenes observed in the ^{1}H NMR spectrum for the resulting trimethyl- and triisopropylphosphite complexes and is most likely true for the aryl isocyanide complexes as well.

An important question is thus raised: **Why does ethylene not induce the Buchner insertion?** Ethylene is frequently used to promote difficult enyne metatheses using **3** and other carbenes.[11] Grubbs et al. reported that decomposition of **3** under 1 atm ethylene occurs over 5 days at room temperature to give $MePCy_3^+$ (quantitative) and a dimetallic product (70%) derived by C−H activation of the methyl group of the mesityl of the H_2IMes ligand; no Buchner products were reported.[36] Ethylene has donor−acceptor properties similar to those of CO. The "cone angle" of ethylene is not available for comparison of the sizes of the ligands used in this study. Ethylene may be sufficiently larger than CO that it cannot occupy the vacant coordination site in sterically constrained environments such as **3**. There is also a possible electronic explanation. CO and isocyanides have two π* orbitals available to interact with the Ru t_{2g} orbitals, and one of these d orbitals is also interacting with the carbene p orbital, so there will be direct competition between the carbene and the incoming ligand for the d electron pair. However, for ethylene the only orientation which would give direct competition of the single π* orbital with the carbene p orbital is with the C=C bond parallel to the NHC−Ru−P axis, which would be sterically prohibitive (Figure 10). In the sterically favored orientation, parallel to the Cl−Ru−Cl axis, the ethylene π* orbital accepts d electrons from a different orbital than that which interacts with the carbene. Consequently, even if ethylene does coordinate, it may not make the carbene sufficiently electrophilic to induce the Buchner reaction. Nonetheless, it may be that, for complexes with less electron-donating PR_3 ligands or more electron-withdrawing carbene substituents, ethylene may cause ligand-induced Buchner decomposition of metathesis catalysts.

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Supporting Information Available: Full experimental data, including syntheses and characterizations of new complexes; X-ray crystallographic data in cif format for complexes **7**, **9**, **14**, **38**, and **39a.** This material is available free of charge via the Internet at http://pubs.acs.org.

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