Catalytic C–C Bond Formation via Ortho-Metalated Complexes

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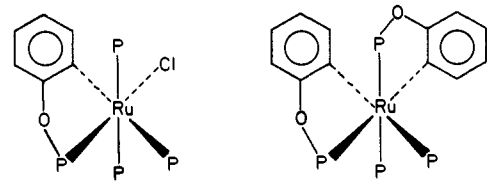
Abstract: The ortho-metalated ruthenium complexes I and II react with ethylene to give ortho-ethylated phosphite products.

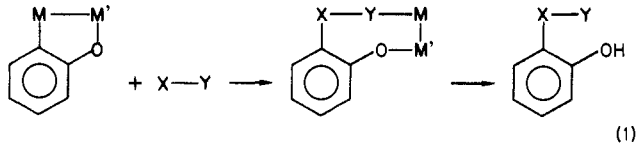


I II

Complex II reacts to give products with five and six ethyl groups/phosphorus $P(O(2,6\text{-}Et_2\text{-}C_6H_3))_2(O(2\text{-}Et\text{-}C_6H_4))$ (III_5) and $P(O(2,6\text{-}Et_3\text{-}C_6H_3))_3$ (III_6), while complex I reacts to mainly give the phosphite products $P(O(2,6\text{-}Et_2\text{-}C_6H_3))_2(OPh)$ (III_4) and $P(O(2,6\text{-}Et_2\text{-}C_6H_3))_2(O(2\text{-}Et\text{-}C_6H_4))$ (III_5). Complex II and KOPh are cocatalysts for the selective ortho ethylation of phenol with ethylene. The reaction of I with propylene results in a lower degree of alkylation, i.e., $P(O(2,6\text{-}(i\text{-}Pr)_2\text{-}C_6H_3))(OPh)_2$ (IV_2), than is obtained from ethylene. The product of the reaction of styrene with I gives low molecular weight polystyrene containing a triphenyl phosphite end group. A proposed mechanism for the insertion reaction involves phosphite substitution by ethylene, insertion (C–C bond formation) of ethylene into the Ru–C bond, ortho-metalation, and finally reductive elimination to give an ethyl group. The proposed intermediates of the reaction are generated by use of $acacRh(C_2H_4)_2$ (X), "phosphine sponge", and these intermediates are observed spectroscopically.

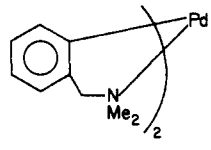
There is currently great interest in transition metal mediated C–H bond activation.[1-3] One goal of this endeavor is to uncover new routes to selective C–C bond formation.[2] Understanding the mechanism by which a selective C–C bond-forming process occurs is crucial for designing such a synthetic method.

Ortho-metalated complexes with the general structure shown below, eq 1, were first synthesized in the mid-1960's and are recognized as among the first examples of C–H bond activation.[4,5] There are several examples of stoichiometric C–C bond formation via insertion reactions of the type shown in eq 1, where X–Y is a small molecule capable of inserting into the M–C bond of ortho-metalatted complexes (X = carbon).[6,7] For example, the

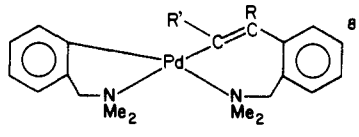


(1)

palladium complex

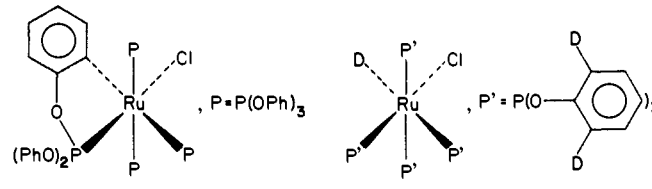


reacts with alkynes, RC≡CR′, to give the insertion product



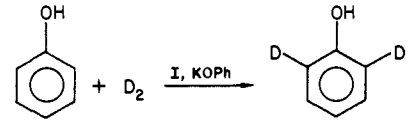
While there are a number of ortho-metalated complexes which participate in stoichiometric C–C bond formation, no catalytic reactions of this type have been previously reported. Work in this laboratory has focused on attempts to develop specific ortho-metalated complexes which can be used to carry out C–C bond-forming reactions. Recently, several groups have demonstrated that repetitive H–D exchange could occur between D_2 and the ortho position for a number of ortho-metalated systems.[9-11] For example, complex I reacts with D_2 to give complete deuteration of all 24 ortho positions in I, eq 2.[11] Recent work in this laboratory

$$\text{I} + \text{excess } D_2 \longrightarrow \text{I}' + \text{HD} + H_2 \qquad (2)$$



I I′

has demonstrated that I can be used as a selective catalyst for the ortho deuteration of phenols, eq 3.[12] the KOPh in eq 3 is



(3)

a cocatalyst for the transesterification step needed to replace the substituted phenoxide in I′ ($O(2,6\text{-}D_2\text{-}C_6H_3)$, eq 2) with protio phenoxide.

This report discusses the first example of selective, catalytic C–C bond formation employing ortho-metalated complexes. The reaction of ortho-metalated ruthenium complexes with olefins gives complete alkylation of all the ortho positions in the molecule. The

(1) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113.
(2) Flood, T. C.; Statler, J. A. *Organometallics* **1984**, *3*, 1795.
(3) Parshall, G. W. *Chem. Technol.* **1984**, 628.
(4) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327.
(5) Rothwell, I. P. *Polyhedron* **1985**, *4*, 177.
(6) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.
(7) Omae, I. *Coord. Chem. Rev.* **1980**, *32*, 235.
(8) Arlen, C.; Pfeffer, M.; Bars, O.; Granjeau, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.
(9) Barefield, E. K.; Parshall, G. W. *Inorg. Chem.* **1972**, *11*, 964.
(10) Ito, T.; Kitazume, S.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1970**, *92*, 3011.
(11) Parshall, G. W.; Knoth, W. H.; Shunn, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4990.
(12) Lewis, L. N. *Inorg. Chem.* **1985**, *24*, 4433.

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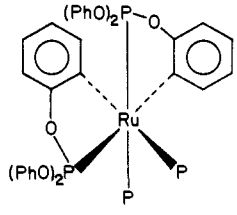
Table I. ^{31}P NMR and Mass Spectral Analyses for III_n

n	isomer	^{31}P NMR	mass spectrum
0	$P(O(C_6H_5))_3$	128.1	310 (M^+), 217-100% peak (M^+ - OPh)
1	$P(O(2\text{-Et-}C_6H_4))(O(C_6H_5))_2$	129.1	338 (M^+), 245 (M^+ - OPh), 217-100% peak (M^+ - O(2-Et-C_6H_4))
2	$P(O(2,6\text{-Et}_2\text{-}C_6H_3))(O(C_6H_5))_2$	129.9	366 (M^+), 273 (M^+ - OPh), 217-100% peak (M^+ - O(2,6-Et_2-C_6H_3))
2a	$P(O(2\text{-Et-}C_6H_4))_2(O(C_6H_5))$	129.3	366 (M^+) not found in GCMS
3	$P(O(2,6\text{-Et}_2\text{-}C_6H_3))(O(2\text{-Et-}C_6H_4))(O(C_6H_5))$	134.09	394 (M^+), 301 (M^+ - OPh), 273 (M^+ - O(2-Et-C_6H_4)), 245-100% peak, (M^+ - O(2,6-Et_2-C_6H_3))
3a	$P(O(2\text{-Et-}C_6H_4))_3$	130.4	394 (M^+) not found in GCMS
4	$P(O(2,6\text{-Et}_2\text{-}C_6H_3))_2(O(C_6H_5))$	139.9	422 (M^+), 329 (M^+ - OPh), 273-100% peak (M^+ - O(2,6-Et_2-C_6H_3))
4a	$P(O(2\text{-Et-}C_6H_4))_2(O(2,6\text{-Et}_2\text{-}C_6H_3))$	134.5	422 (M^+), 301-100% peak (M^+ - O(2-Et-C_6H_4)), 273 (M^+ - O(2,6-Et_2-C_6H_3))
5	$P(O(2,6\text{-Et}_2\text{-}C_6H_3))_2(O(2\text{-Et-}C_6H_4))$	139.16	450 (M^+), 329 (M^+ - O(2-Et-C_6H_4)), 301-100% peak (M^+ - O(2,6-Et_2-C_6H_3))
6	$P(O(2,6\text{-Et}_2\text{-}C_6H_3))_3$	144.76	478 (M^+), 329-100% peak (M^+ - O(2,6-Et_2-C_6H_3))

reaction has been extended to include the first example of selective ortho alkylation of phenol catalyzed by an ortho-metalated complex. The mechanism of these reactions is discussed in detail.

Results and Discussion

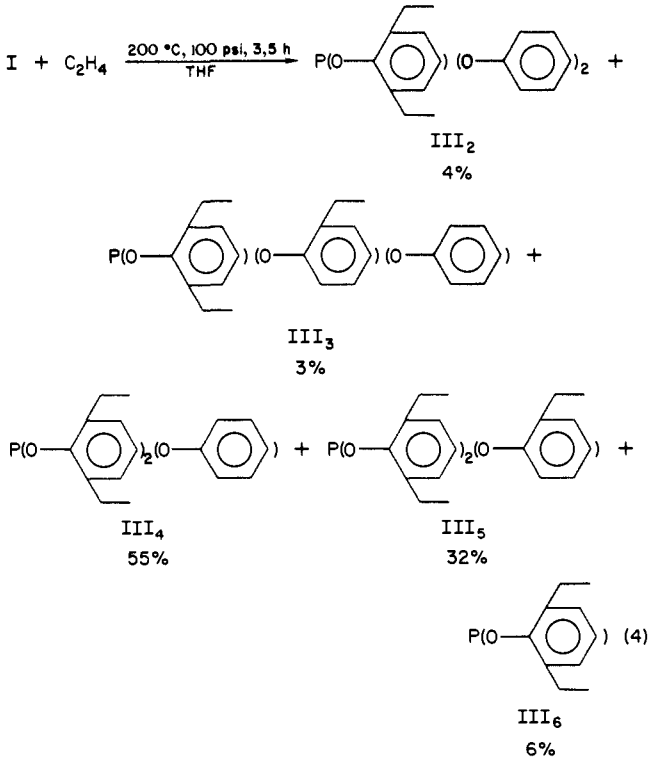
Reactions with Ethylene. Two ruthenium complexes, I and II,[13] were employed in the present alkylation study. Both ruthenium



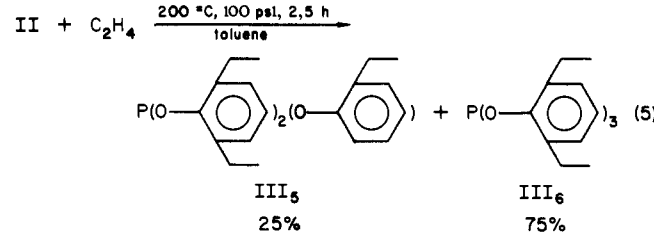
II (P = $P(OPh)_3$)

compounds I and II react above 120 °C with ethylene to give complex product mixtures. The products are of two types: ruthenium complexes containing substituted phosphites and the corresponding free phosphites. Discussion of the ruthenium products will be addressed later in the paper.

Complex I reacts with ethylene according to eq 4 to yield the free phosphites designated as III_n, where n = number of ethyl groups/phosphorus. Complex II reacts with ethylene to give a

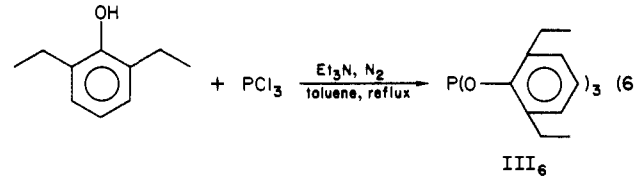


somewhat different product mixture than that obtained for complex I, eq 5. The total phosphite products from eqs 4 and 5



correspond to about 60% yield based on four P/Ru in the starting materials (I and II). The remaining phosphorus atoms and all the ruthenium atoms end up in new ruthenium products (vide infra).

The products III_n were identified on the basis of LC, GC, GCMS, FDMS, and ^1H, ^{13}C, and ^{31}P NMR analyses. Authentic reference compounds are independently prepared by reacting PCl_3 with phenol and ethyl and 2,6-diethylphenol in the presence of triethylamine. Equation 6 shows the synthesis of III_6, $P(O(2,6\text{-Et}_2\text{-}C_6H_3))_3$, by this method, The products were separated by

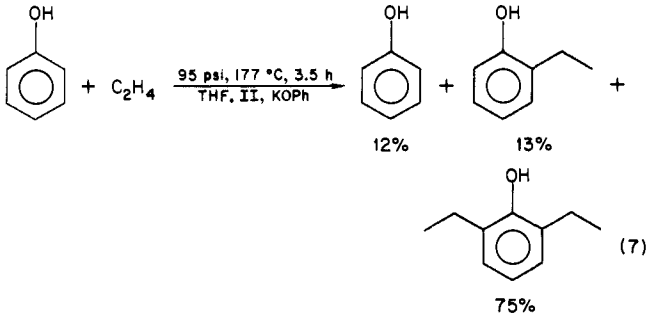


GC and identified on the basis of their mass and ^{31}P NMR spectra. All the compounds give straightforward mass spectra which include the parent ion, The fragmentation pattern clearly distinguishes whether a molecule contains one disubstituted phenoxide $-O(2,6\text{-Et}_2\text{-}C_6H_3)$ or two singly substituted phenoxides $-O(2\text{-Et-}C_6H_4)$. All ten III_n species possess unique ^{31}P NMR resonances which are given in Table I.

As shown in Table I, the phosphites III_2, III_3, and III_4 each occur in two isomeric forms. The products from eq 4 include only III_2, III_3, and III_4: $P(O(2,6\text{-Et}_2\text{-}C_6H_3))(OPh)_2$, $P(O(2,6\text{-Et}_2\text{-}C_6H_3))(O\text{-}(2\text{-Et-}C_6H_4)(OPh)$, and $P(O(2,6\text{-Et}_2\text{-}C_6H_3))_2(OPh)$, respectively. The products III_{2a}, III_{3a}, and III_{4a} were not observed from eq 4. The products III_2, III_3, and III_4 have a higher degree of double substitution on the phenoxide ring ($O(2,6\text{-Et}_2\text{-}C_6H_3)$) as compared to III_{2a}, III_{3a}, and III_{4a}, where single substitution $O(2\text{-Et-}C_6H_4)$ is predominant.

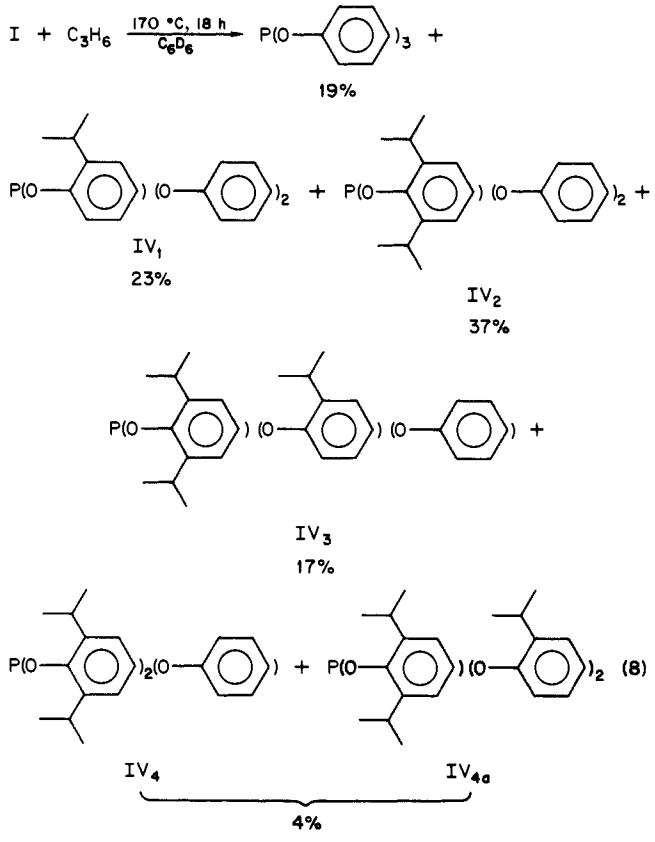
The insertion of ethylene into the Ru–C bond (eq 4 and 5) forms the basis of a catalytic system for selective ortho alkylation of phenol, eq 7. The reaction is analogous to the catalytic ortho deuteration of phenol.[12] Reaction 7 corresponded to about 15 turnovers of phenol per mol of ruthenium. The phenol products were separated by distillation and identified on the basis of their GC and ^{13}C NMR spectra (vs. authentic samples). Phenol was not alkylated in the absence of ruthenium; a THF solution of phenol and phenoxide was heated under ethylene pressure with no alkylation observed.

(13) Garbauskas, M. F.; Kasper, J. S.; Lewis, L. N. *J. Organomet. Chem.* **1984**, *276*, 241.



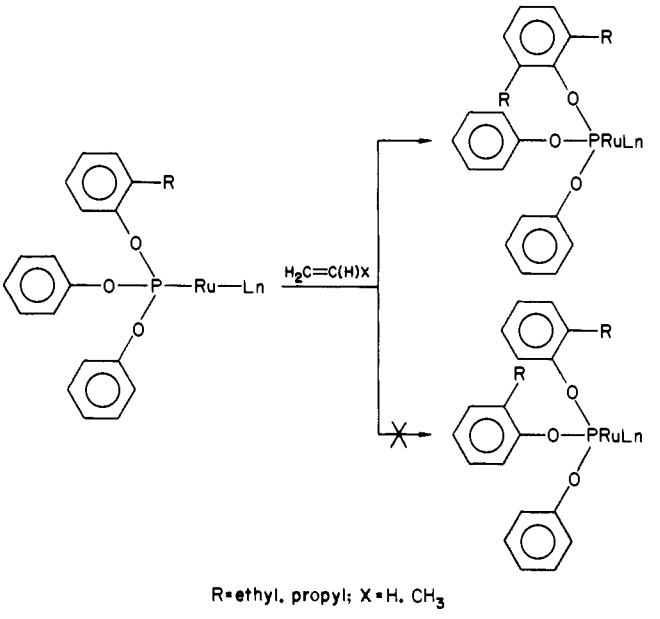
The reactions of I and II with ethylene, eq 4 and 5, demonstrate the first examples of repetitive alkyl substitution on an ortho-metalated complex. In fact, since no free triphenyl phosphite (III_0) was observed from eq 5, this reaction represents greater than 20 substitutions on the same metal. Equation 7 represents the first example of an ortho-metalated complex catalyzing a C–C bond forming reaction. This reaction proceeds with 100% selectivity for the ortho position,

Propylene. I and propylene were reacted under analogous conditions to eq 4 (eq 8) to give the isopropyl-substituted phosphites, IV_n. The products IV_n were separated by GC and analyzed

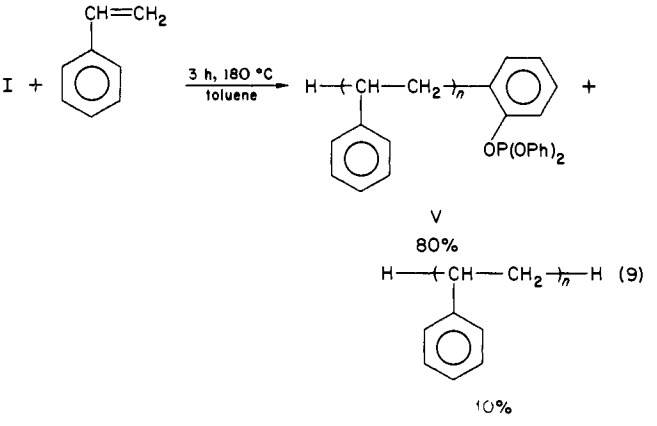


by GCMS and by high-resolution GCMS. It was immediately clear that the total number of ortho positions in triphenyl phosphite alkylated by propylene was much less than that substituted by ethylene (compare eq 4 and 8). One explanation for this result may be the greater steric bulk of the isopropyl group may limit the degree of substitution attainable on the ortho positions within the ortho-metalated complex,

A second set of observations relates to the degree of substitution obtained on the triphenyl phosphite rings. The products IV_2 and IV_3 were observed while their analogues IV_{2a} and IV_{3a} ($P(O(2\text{-}i\text{-}Pr\text{-}C_6H_4))_2(OPh)$ and $P(O(2\text{-}i\text{-}Pr\text{-}C_6H_4))_3$ respectively) were not detected. Trace amounts of IV_4 and IV_{4a} were observed. ^{13}C(APT) analysis of the product mixture from eq 8 shows that isopropyl and not *n*-propyl groups are present in IV_n. The reactions shown in eq 4 and 8 demonstrated that the second substitution event takes place on a ring bearing an alkyl group in preference to an unsubstituted ring,



Styrene. With styrene as the substrate, eq 9, a different type of product was obtained. The toluene product solution from eq

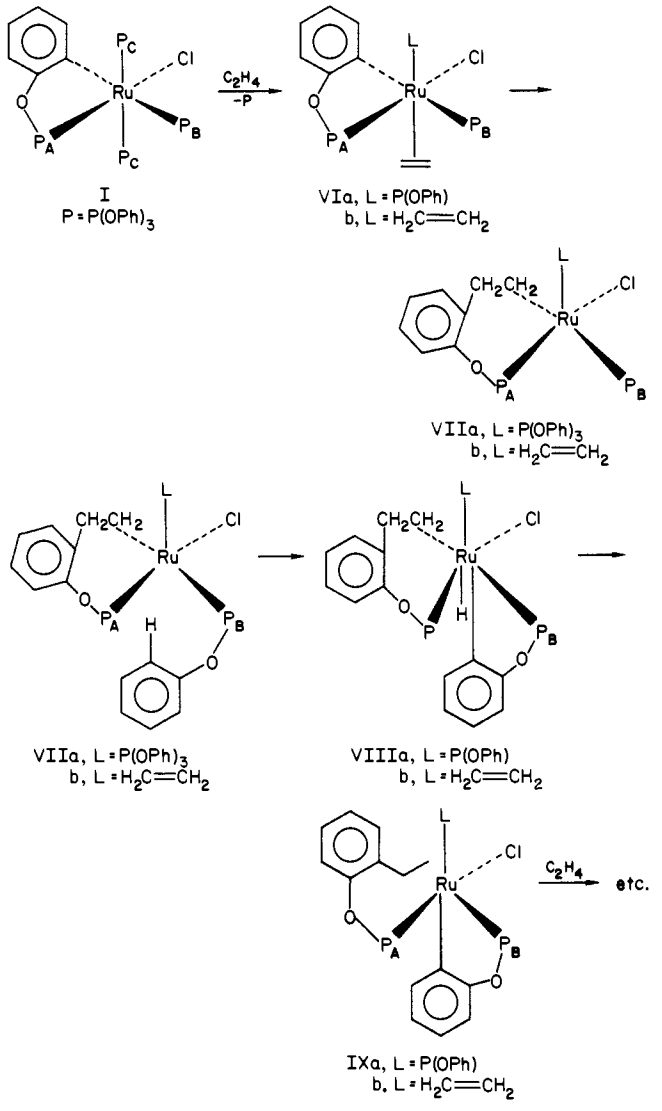


9 was analyzed by LC using UV detectors at 254 and 280 nm and found to contain a mixture of different types of oligomers. It was significant that the major portion of the oligomers absorbed strongly at 280 nm, where polystyrene does not absorb. The polystyrene was isolated and separated from V as a white solid by precipitation into methanol and was identified on the basis of its ^{13}C NMR and by GPC ($\bar{M}_n$ = 100 000). The product V was isolated as an oil from the methanol filtrate; analysis by GPC gave $\bar{M}_n \cong 2000$. A three-dimensional GPC analysis (MW and UV wavelength and absorbance measured simultaneously) showed that the oligomer mixture V had a UV spectrum consistent with the presence of a triphenyl phosphite end group. Analysis by FDMS showed a pattern consistent with $P(OPh)_3$ + (styrene)$_n$, n = 1–5. The ^{31}P NMR had a broad resonance (6 ppm wide at half-height) at 126 ppm assigned to V. In addition, the ^{13}C NMR was consistent with the assigned structure for V, This latter analysis showed that V was atactic with respect to the orientation of the styrene linkages.

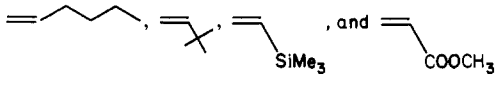
It was of interest to determine if the reaction of eq 9 represented interception of a growing polystyrene chain by ruthenium *or* if the polystyrene grew on ruthenium followed by termination by a phosphite ligand. The reaction of eq 9 was repeated in the presence of 1 mol % phenol which is an inhibitor for thermal styrene polymerization. Under these conditions, only 1% yield of polystyrene was obtained while the yield and spectroscopic properties of V were unaffected by the presence of phenol. These results suggest that oligomerization of styrene may occur within the ruthenium coordination sphere.

Other Substrates. The extension of the insertion reaction described was attempted with other substrates. Carbon monoxide

Scheme I



gives simple substitution products but no insertion vide infra. Phenylacetylene gives cyclotrimerization (triphenylbenzene products). While interesting, this result is not germane to the present investigation and will be described elsewhere,[14] Olefins such as



did not react with I to give insertion products (cf. eq 4, 5, 8, and 9).

Mechanism of Insertion Reaction. Scheme I shows a proposed mechanism for the insertion reaction of olefins into I. The first step in Scheme I consists of the reversible replacement of triphenyl phosphite by olefin and is supported by the fact that triphenyl phosphite completely inhibited the insertion reactions (eq 4, 5, 7, 8, and 9).

There was no reaction at room temperature between I or II and ethylene, In refluxing solvent (toluene, xylene) with ethylene bubbling through the solution, the substitution reactions (eq 4 and 5) proceed with lower efficiency (yields of $III_{1,2,3}$ increase while $III_{4,5,6}$ decrease); however even under these mild conditions no simple ruthenium ethylene phosphite substitution product was observed. These results suggest that the first step of Scheme I

(14) Lewis, L. N., manuscript in preparation. Cyclotrimerization of alkynes catalyzed by ruthenium is well-known. See, for example: James, B. R. *Inorg. Chim. Acta, Rev.* **1970**, 73.

Scheme II

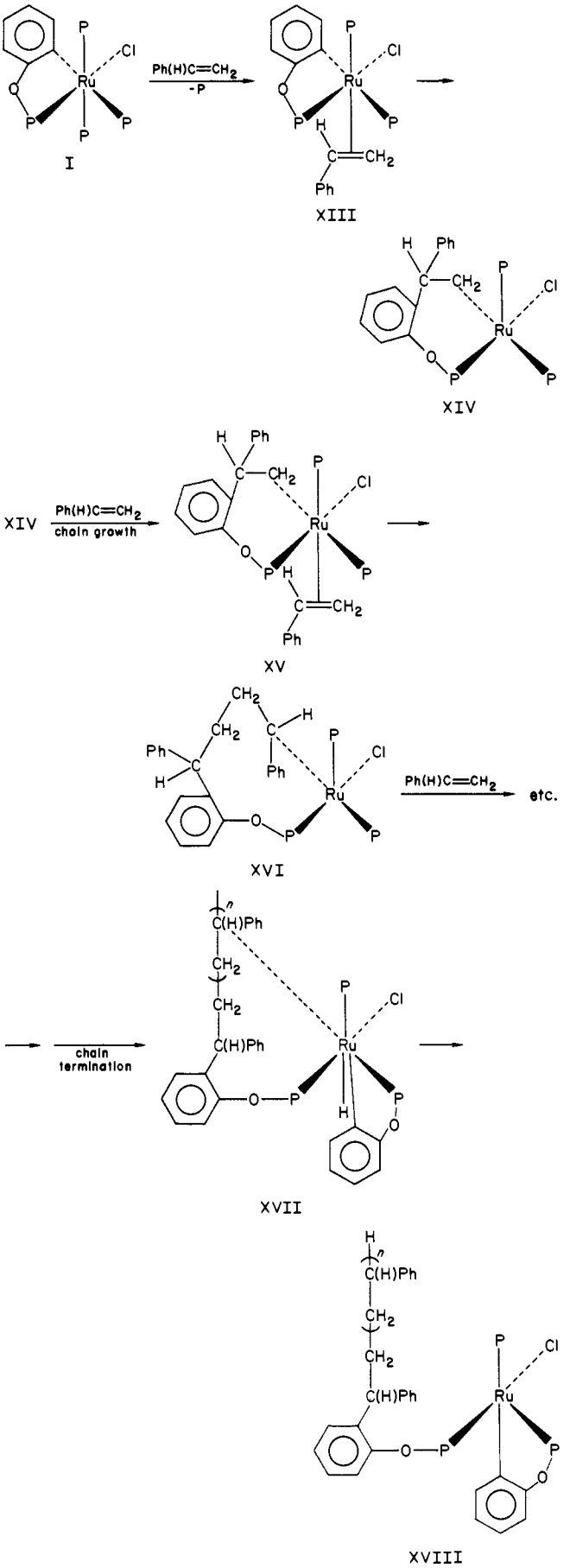


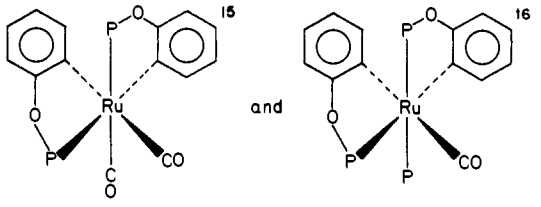
Table II. Spectroscopic Data for acacRh Complexes[a]

complex	^{1}H NMR	^{13}C NMR	^{31}P NMR
X	5.09 (CH), 2.97 (CH_2), 1.77 (CH_3)	99.6 (CH), 59.24 (CH_2, d, J_{C-Rh} = 14), 26.17 (CH_3)	
XI	5.00 (CH), 2.57 (CH_2), 1.57 (CH_3)	100 (CH), 59.1 (CH_2, d, J_{C-Rh} = 11), 26.4 (CH_3)	124.37 (d, J_{P-Rh} = 307)
XII[18]	4.38 (CH), 1.40 (CH_3)	100.32 (CH), 27.38 (CH_3)	118.36 (d, J_{P-Rh} = 300)

[a] Coupling constants in Hz.

(I → VI) is the rate-determining step.

Complex II reacts with CO at 100 psi and 205 °C to give the known compounds



The reaction of II with CO served as a model for simple replacement of a non-ortho-metalated phosphite by a two-electron ligand (CO and ethylene have similar ligating properties). Carbon monoxide did not insert into the ortho-metalated bond of II.

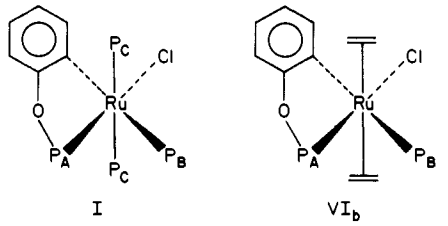
Spectroscopic observation of the other intermediates of Scheme I was accomplished by reacting I with (acacRh(C_2H_4)$_2$) (X), "phosphine sponge",[17] at 25 °C. This rhodium reagent served the dual function of removing triphenyl phosphite from I at 25 °C while providing 1 equiv of ethylene. The substituted rhodium phosphite complexes were made independently by reacting X with $P(OPh)_3$, eq 10, There was no evidence for redistribution of XI

$$\mathrm{X} + \mathrm{P(OPh)_3} \xrightarrow[\mathrm{C_6D_6}]{25\ ^\circ\mathrm{C}} \underset{30\%}{\mathrm{acacRh(C_2H_4)(P(OPh)_3)}}\ (\mathrm{XI}) + \underset{30\%}{\mathrm{acacRh[P(OPh)_3]_2}}\ (\mathrm{XII}) \quad (10a)$$

$$\mathrm{X} + 4\mathrm{P(OPh)_3} \xrightarrow[\mathrm{C_6D_6}]{25\ ^\circ\mathrm{C}} \underset{100\%}{\mathrm{XII}} \quad (10b)$$

(to give X and XII) nor was any reverse reaction between XI or XII and ethylene observed. The ^{1}H, ^{13}C, and ^{31}P NMR parameters for X, XI, and XII are given in Table II.

The spectroscopic data obtained from the reactions of I and X were consistent with the formation of intermediates VI, VII, and IX of Scheme I (eq 11a–c). As phosphine sponge, X (or in this case "phosphite sponge") was added to a benzene solution of I, XI and XII grew in intensity while I was slowly consumed (eq 11a). The ^{31}P NMR spectrum of the first new Ru species formed (3 equiv of X) was consistent with VIb of Scheme I. The ^{31}P NMR spectrum showed a pair of doublets at δ 167.30 (A) and 126.35 (B), J = 97 Hz, as expected for cis coupling, with the former peak assigned as an ortho-metalated phosphite resonance.[19] Comparison of the ^{31}P NMR spectra of starting compound[13] I,



δ 155.24 (A), 123.92 (B), and 116.52 (C), to that for VIb suggested that "P_C" in I is substituted by ethylene to give VIb. The ^{13}C(APT)[20] NMR at this point shows only the resonances for the rhodium complexes (X–XII) and for I. New aromatic resonances and a single broad peak at 59 ppm, C_2H_4 of VIb, further support structure VIb.

Upon further addition of X, XII grew in intensity, I decreased in intensity, and a second set of peaks (attributed to intermediate "VIIb") was observed, eq 11b. The ^{31}P NMR showed an AB (J = 25, 278 Hz) pattern centered at δ 110.45. The ^{13}C(APT) NMR now revealed the presence of new CH_2 resonances at δ 29.2, 35.8, 37.3, and 63.2. In addition, quaternary carbon resonances were observed at δ 126.3 and 126.8, consistent with an ortho point of attachment on an aromatic ring. These results are consistent with structure VIIb (Scheme I). Formation of VIIb is the C–C bond forming step of the mechanism.

A solution containing VIIb was heated at 85 °C for 2 h which resulted in a color change from yellow to maroon (eq 11c). The ^{31}P and ^{13}C(APT) NMR spectra show that the Rh-containing compounds were unchanged after heating but that the ruthenium complex VIIb reacted. A new set of peaks formed after heating which were assigned to intermediate IXb. The ^{31}P NMR showed two pairs of doublets (δ 169.79 (J = 111 Hz) 130.65 (J = 111 Hz), and δ 163,62 (J = 116.5 Hz), 129.12 (J = 116.5 Hz)), including downfield resonances consistent with ortho metalation.[19] In addition, the ^{13}C(APT) spectrum revealed the presence of an ethyl pattern which exactly matched that for III_n (ortho-ethylated triphenyl phosphite).

Intermediate VIIIb was not observed. ^{1}H NMR analysis failed to locate any hydride resonances during the sequences described above. However, there is ample precedence to support the proposal that ortho metalation can occur following loss of a 2-electron ligand from an 18-electron complex.[21] Since VIII is a seven-coordinate Ru complex, this may be a transient intermediate. The conversion of VII to IX may be a concerted process. Finally, note that intermediates VII and IX are five-coordinate. Intermediates VII and IX displayed larger coupling constants in their ^{31}P NMR spectra as compared to I and II ($J \approx 55$ Hz). A general increase in coupling constants from cis (∠PRuP = 90°) to cisoid (∠PRuP from 90 → 120°) to trans is commonly observed in ^{31}P NMR.[22,23]

The rhodium complex, X, efficiently removes phosphorus from the ruthenium complex I so that intermediate VIb formation corresponds to loss of two phosphites from I. In the insertion reaction of eq 4, phosphite loss is the rate-determining step so that the intermediates formed are more likely to be VIa, VIIa, VIIIa, and IXa.

Since no free triphenyl phosphite was observed from the reactions in eq 4 and 5, a step involving replacement of the sterically bulky substituted phosphite, i.e., $P(O(2,6\text{-}Et_2\text{-}C_6H_3))_3$ by $P(OPh)_3$, must occur in the course of the insertion reactions so that all of the phosphites become substituted.

Analysis of the spectroscopic data from the *actual* insertion reactions, eq 4 and 5, shows a complicated mixture of III_n and ruthenium products. The ^{31}P NMR from the reaction solution from eq 5 showed resonances for III_5 and III_6 as well as broad, complicated resonances at δ 162 and 129 (consistent with IX containing a mixture of substituted ligands III_n). The FDMS

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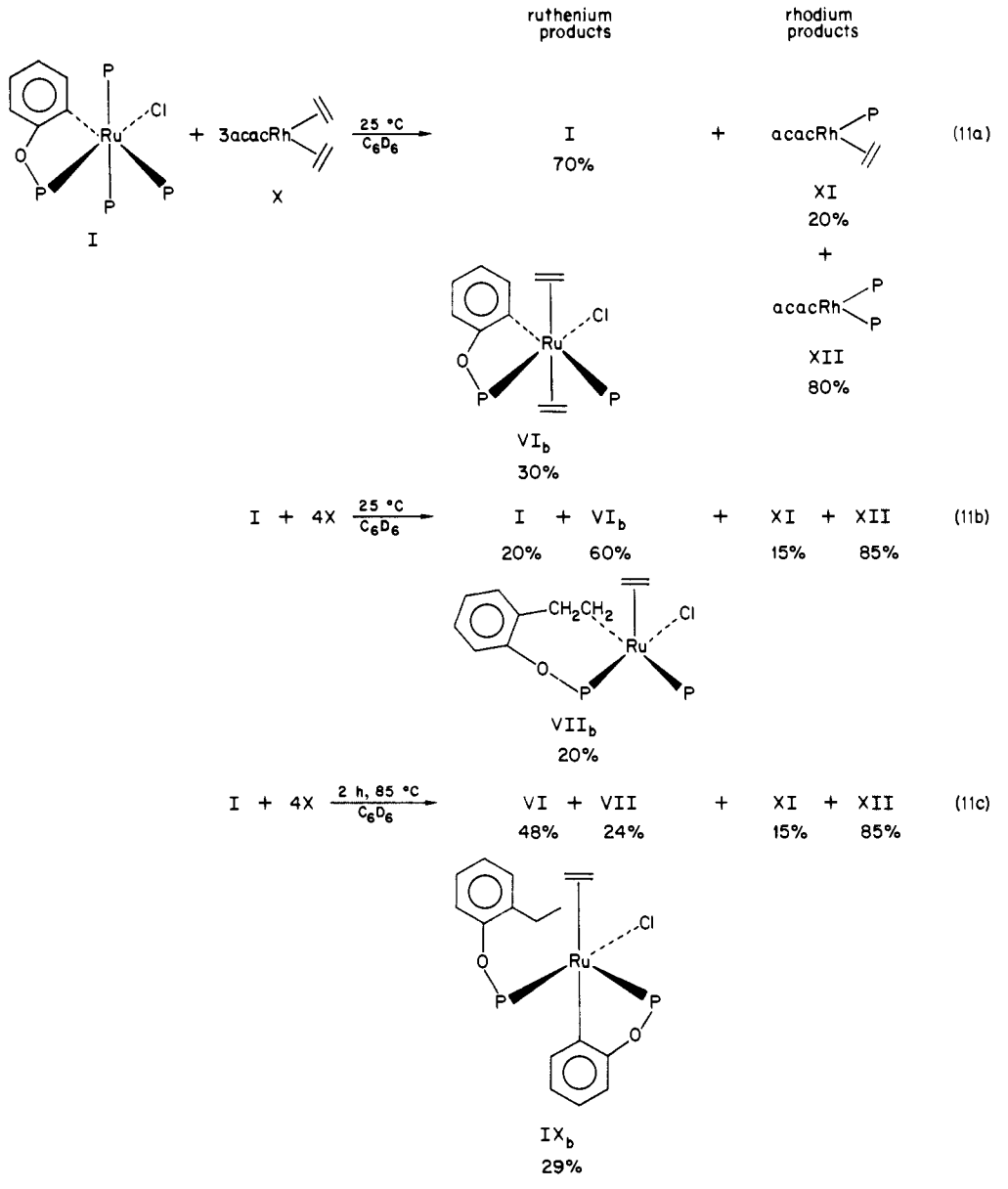

showed the presence of a series of six envelopes (ruthenium isotope pattern) separated by 28 amu $((C_2H_4)_n)$. The masses of these clusters agree with intermediate IX ($M^+ - Cl$[24] + ethyl$_n$, n = 0–6).

The proposed mechanism of Scheme I can explain why the insertion reaction of II (eq 5) proceeds with a higher degree of substitution (III_5 and III_6) than with I, eq 4 (III_3–III_6). With reference to Scheme I, if I is replaced by II in the scheme, then substitution of one of the non-ortho-metalated phosphites by ethylene always results in an ethylene ligand on ruthenium in a cis position relative to a Ru–C bond. However, in complex I if P_B is substituted by ethylene, ethylene is trans to the lone Ru–C bond and no insertion will occur. Thus complex II is more efficient than I for ethylene insertion.

A slight modification of the proposed insertion mechanism explains the styrene results (Scheme II). Conversion of I to XIII and XIV is exactly analogous to conversion of I to VI and VII in Scheme I. However, in Scheme II there is a chain growth step in which the addition of a styrene to XIV is competitive with ortho metalation. The higher concentration of styrene as compared to ethylene may be responsible for this latter fact. The termination step is, as in Scheme I, ortho metalation on a five-coordinate, 16-electron complex. Note that 90% conversion of styrene was observed in eq 9 so that termination occurs only when most of the styrene is consumed; thus this supports the contention that at high olefin concentration chain growth (repetitive olefin insertion) is competitive with ortho metalation (termination).

(24) Work in these labs has shown that the field desorption mass spectra of a number of neutral organometallic halide complexes frequently display the PI-X as the only ion peak observed.

Summary and Conclusion

Ruthenium complexes containing ortho-metalated triphenyl phosphite linkages repetitively react with ethylene to give ortho alkylation on the triphenyl phosphite ligands. The ruthenium complex together with phenoxide catalyze the selective ortho alkylation of phenol.

Alkylation of phenol catalyzed by aluminum and other metals is well-known but often requires higher temperature and pressure and gives mixtures with ortho and para substitution.[25] The present report represents 100% specificity for ortho substitution. This report demonstrates homogeneous, catalytic C–C bond formation. The principle of using ortho-metalated complexes for this purpose has been demonstrated for the first time and a mechanism has been proposed.

The use of other transition-metal ortho-metalated complexes for catalytic synthesis of substituted aromatics by small molecules

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is under continuing investigation.

Experimental Section

General. All operations were carried out under N_2 or argon with use of standard Schlenk techniques or in a Vacuum Atmospheres drybox. THF and toluene were distilled under nitrogen from sodium benzophenone ketyl. Gas chromatography was carried out on an HP 5830A (FID detector) instrument employing 6 ft 3% OV 101 columns. Liquid chromatography was performed on a Waters LC, reverse phase μ Bondapak C-18 column, H_2O–THF solvent system. For preparative LC, a Whatman ODS-51 column was employed. Two UV detectors were employed simultaneously at 254 and 280 nm. ^1H NMR were recorded on a Varian EM 390 NMR spectrometer. ^{13}C and ^{31}P NMR (^1H decoupled, 20 and 32.203 MHz, respectively) were carried out on a Varian FT 80 NMR spectrometer. Additional ^{31}P and ^{13}C NMR spectra (121.42 and 75.43 MHz, respectively) were recorded on a Varian XL 300 NMR spectrometer. Carbon multiplicities in the ^{13}C NMR were determined with use of the Applied Proton Test (APT).[20] Field desorption mass spectra (FDMS) were obtained on a Varian MAT 731 instrument. GCMS were recorded on a Varian MAT 311A instrument. High resolution gas chromatography mass spectra (HRGCMS) were obtained with use of a VG Analytical ZAB high resolution mass spectrometer.

Complexes I,[11] II,[13] and X[26] were prepared as reported. Insertion reactions were carried out in thick-walled glass Fischer-Porter bottles equipped with a pressure gauge and two valves to permit pressurization under inert atmosphere. The bottles were equipped with magnetic stir bars and were uniformly heated with heating tape surrounding a thermocouple in order to monitor reaction temperature.

Insertion Reactions. I + C_2H_4 (Equation 4). Complex I (0.186 g, 0.135 mmol) was dissolved in 10 mL of toluene under N_2 in a 90-mL thick-walled bottle. The bottle was pressurized with ethylene 80 psi, 17.8 mmol) and heated to 194 °C with stirring for 3.5 h. The reaction was cooled to room temperature, vented, and then analyzed by GC and LC which gave the products shown in eq 4. ^1H NMR: δ 7.07 (m, 9 H), 2.73 (q, 7 Hz, 5 H), 1.16 (t, 7 Hz, 8.5 H). ^{13}C NMR: δ 14.35, 23.91, 120.31, 123.90, 124.67, 126.94, 129.5, 136.6. ^{31}P NMR resonances for III_4 and III_5 (see Table I) and broad resonances at 155 and 118 ppm. FDMS: (major) III_4 (m/e 422, M^+) and III_5 (m/e 450, M^+); (minor) III_3 (m/e 394, M^+) and III_6 (m/e 476, M^+).

II + C_2H_4 (Equation 5). Complex II (0.021 g, 0.16 mmol) was dissolved in 10 mL of toluene under N_2 in a 90-mL thick-walled glass bottle. The bottle was pressurized with ethylene (90 psi, 22 mmol) and stirred at 25 °C for 10 min (P = 70 psi due to dissolved gas). The tube was heated to 190 °C with stirring for 2.5 h (final P at 25 °C 58 psi or 24 mol of ethylene/mol of Ru consumed). The product ratio was determined by GC and LC (see eq 5). Absolute yield of III_n was ca. 60% based on II. GCMS and ^{31}P NMR (see Table I) additional broad ^{31}P NMR resonances: δ 162 and 129. ^1H NMR ($CDCl_3$): δ 6.97 (m, 9 H), δ 2.70 (q, 7 Hz, 4.3 H), 1.10 (t, 7 Hz, 5.7 H). ^{13}C NMR (APT) ($CDCl_3$): δ 14.28 (CH_3), 23.85 (CH_2), 70.43 (CH_2). Aromatic CH: 119.95, 124.41, 125.48, 126.76, 128.90, 129.29, 129,40, 129.72; 136.45 (ortho >C<), 146.4 (ipso >C<), 155.4 (ipso >C<). FDMS: major peaks III_5 (m/e 450, M^+) and III_6 (m/e 476, M^+); "ruthenium isotope envelope" M = $Cl^{101}Ru[P(OPh)_3]_2$ m/e 812 ($M^+ + Et_2$), 840 ($M^+ + Et_3$), 868 ($M^+ + Et_4$), 896 ($M^+ + Et_5$), 924 ($M^+ + Et_6$).

Synthesis of $P(O(2,6\text{-}Et_2\text{-}C_6H_3))_3$ (III_6) (equation 6). PCl_3 (0.55 mL, 6.3 mmol) was added to a refluxing toluene solution (50 mL) which contained freshly distilled (65 °C (0.25 mmHg)) 2,6-diethylphenol (2.87 g, 0.019 mol). NEt_3 (3.5 mL) was added and then reflux was continued for 1 h. The toluene was removed in vacuo, and the remaining oily solids were then extracted with diethyl ether. The diethyl ether was removed in vacuo to leave an oil, bp 165–8 °C (0.25 mmHg), which was shown by GCMS to be $P(O(2,6\text{-}Et_2\text{-}C_6H_3))_3$ (isolated yield 1.3 g, 54%). ^1H NMR: δ 7.09 (m, 9 H), 2.77 (q, 8 Hz, 12 H), 1.24 (t, 8 Hz, 18.8 H). $^{31}P\{^1H\}$ NMR: 144.5 ppm. $^{13}C\{^1H\}$ NMR: δ 147.6 (ipso C), 136.5 (C-Et, $J_{P\text{-}C}$ = 2 Hz), 127.0 (meta), 124.7 (ortho), 24.1 (CH_2CH_3, $J_{P\text{-}C}$ = 6 Hz), 14.5 (CH_2CH_3). EIMS: m/e 478 (M^+), 329 ($M^+ - O(2,6\text{-}Et_2\text{-}C_6H_3)$), 150 ($HO(2,6\text{-}Et_2\text{-}C_6H_3)^+$). HRMS calcd for $C_{30}H_{39}O_3P$, 478.2637, found 478.2642.

Preparation of III_0–III_5. PCl_3 (0.75 mL, 25.5 mmol) was added to a refluxing toluene solution (50 mL) which contained phenol (1.001 g, 10.6 mmol), 2-ethylphenol (1.015 g, 8.32 mmol), and 2,6-diethylphenol (0.99 g, 6.59 mmol). NEt_3 (3.5 mL) was added and reflux was continued for 1 h. The toluene was removed in vacuo and the resulting oily mass was extracted with diethyl ether. The ether was removed in vacuo which left an oil. GC and GCMS analysis (see Table I): III_0 (9.2%), III_1 (21.5%), III_2 (26.2%), III_3 (21.3%), III_4 (17.1%), and III_5 (4.6%). ^{31}P NMR (relative % from integrated intensities in parentheses): δ 128.1 (III_0 9), 129.1 (III_1 15.7), 129.9 (III_2 7.2), 129.3 (III_{2a} 16.9), 134.1 (III_3 15.7), 130.4 (III_{3a} 7.2), 139.9 (III_4 3.6), 134.5 (III_{4a} 5.4), 139.2 (III_5 3.6).

Ethylation of Phenol (Equation 7). Phenol (0.23 g, 2.45 mmol), II (0.203 g, 0.15 mmol), and KOPh (0.029 g, 0.22 mmol) were dissolved in 10 mL of THF and placed in a 90-mL thick-walled bottle under N_2. The bottle was pressurized with ethylene (95 psi, 21 mmol) and then heated to 177 °C for 3.5 h with stirring. The bottle was cooled to room temperature and then vented. Analysis of the contents by GC and LC showed unreacted phenol (0.27 mmol) and 89% conversion to o-ethylphenol (15%, 0.33 mmol) and 2,6-diethylphenol (85%, 1.85 mmol). The products were partially separated by distillation (0.5 mmHg) at 42 °C (first fraction, mostly phenol, second fraction, phenol and ethylphenol) and at 56–57 °C (2,6-diethylphenol). ^1H and ^{13}C NMR agreed with authentic samples. ^{13}C NMR of 2,6-diethylphenol: δ 14.03 (CH_3), 23.10 (CH_2), 120.49 (para), 126.72 (meta), 129.24 (ortho point of attachment, reduced NOE), 151.51 (ipso).

Control. Phenol (0.95 g, 0.1 mmol) and KOPh (0.94 g, 7.12 mmol) were dissolved in 10 mL of THF and placed in a 90-mL thick-walled glass bottle under N_2. The bottle was pressurized with ethylene (90 psi, 20.0 mmol) and then heated to 177 °C for 4 h with stirring. After the reaction vessel was cooled and vented, GC analysis showed only phenol (no ethylated phenol) was present.

I + C_3H_6 (Equation 8). Complex I (0.100 g, 0.073 mmol) was dissolved in 5 mL of C_6D_6 under N_2), in a 90-mL thick-walled bottle. The bottle was pressurized with propylene (60 psi, 14 mmol) and then heated to 170 °C for 18 h with stirring. After the reaction vessel was cooled to room temperature and vented, the solution was analyzed by GC (see eq 8) and GCMS: IV_0 m/e 310 ($P(OPh)_3$), 217 (100% peak, M^+ – OPh); IV_1 m/e 352 (M^+), 259 (100% peak, M – OPh), 217 ($M^+ - O(2\text{-}i\text{-}Pr\text{-}C_6H_4)$); IV_2 394 (M^+), 301 (100% peak, M^+ – OPh), 217 ($M^+ - O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)$); IV_3 436 (M^+), 343 (M – OPh), 301 (100% peak, $M^+ - O(2\text{-}i\text{-}Pr\text{-}C_6H_4)$), 259 ($M^+ - O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)$); IV_4 478 (M^+), 385 (M^+ – OPh), 301 (100% peak, $M^+ - O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)$); at higher retention time IV_{4a} 478 (M^+), 343 ($M^+ - O(2\text{-}i\text{-}Pr\text{-}C_6H_4)$), 301 (100% peak, $M^+ - O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)$). ^{13}C NMR (in C_6D_6): δ 22.5, 23.4, 23.7, 26.7, 27.1, 30.4, 30.9, aromatic 115.3, 121.2, 126.3, 126.6, and 120.2–129.8 (several peaks), 132.1, 137.5, 139.3, 140.68 152.5. Cf. 2-isopropylphenol: 22.6 (CH_3), 27.1 (CH), 115.4 (ortho, CH), 121.1 (para), 126.5 (meta), 126.7 (meta), 134.6 (ortho, >C<), 152.8 (ipso). HRGCMS were obtained for IV_3, $O{=}P(OPh)_3$, and the phosphates of $IV_{1\text{-}3}$. $O{=}P(OPh)_3$ calcd 326.0708, found 326.0701 (M^+); calcd 233.0368, found 233.0368 (M^+ – OPh). $O{=}P(OPh)_2(O(2\text{-}i\text{-}Pr\text{-}C_6H_4))$ calcd 368.1177, found 368.1168 (M^+); calcd 353.0943, found 353.0930 ($M^+ - CH_3$). $O{=}P(OPh)_2(O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3))$ calcd 410.1647, found 410.1647 (M^+); calcd 367.1099, found 367.1101 ($M^+ - C_3H_7$). $P(O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3))(O(2\text{-}i\text{-}Pr\text{-}C_6H_4))(O(C_6H_5))$, ($IV_3$) calcd 436.2167, found 436.2152 (M^+); calcd 343.1827, found 343.1816 (M^+ – OPh); calcd 301.1357, found 301.1364 ($M^+ - O(2\text{-}i\text{-}Pr\text{-}C_6H_4)$); calcd 259.0888, found 259.0886 ($M^+ - O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)$). $O{=}P(O(2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3))(O(2\text{-}i\text{-}Pr\text{-}C_6H_4))(O(C_6H_5))$ calcd 452.2116, found 452.2102 (M^+); calcd 409.1569, found 409.1576 ($M^+ - C_3H_7$). FDMS: see M^+ for $IV_{0\text{-}3}$, M = $^{101}Ru[P(OPh)_3]_2$, "ruthenium envelope" 721 (M^+), 763 (M^+ + propyl), 805 (M^+ + $propyl_2$), 847 (M^+ + $propyl_3$).

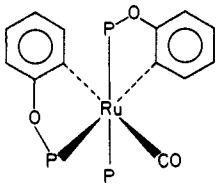
I + Styrene (Equation 9). Complex I (0.42 g, 0.31 mmol) and freshly distilled styrene (2 mL, 17.4 mmol) were combined in 20 mL of toluene in a 300-mL stainless steel bomb under N_2. The bomb was heated to 230 °C for 18 h with stirring. After the reaction mixture was cooled to room temperature, 50 mL of methanol was added which resulted in precipitation of a white solid (polystyrene vide 0.22 g); the filtrate contained V. GPC analysis showed that the white solid had $\bar{M}_n$ = 111 000. LC analysis showed 10% unreacted styrene and that the polystyrene oligomers had UV absorbance at 254 nm but not at 280 nm. The polystyrene had a ^{13}C NMR which was identical with the ^{13}C NMR obtained from thermally polymerized polystyrene. GPC analysis of the MeOH soluble fraction, V, gave $\bar{M}_n$ = 2000. LC analysis of V showed UV absorbance at both 254 and 280 nm.

The above reaction was repeated in the presence of 1 mol % phenol. Styrene (undistilled with 10–15 ppm p-TBC, 2 mL, 17.4 mmol), phenol (0.015 g, 0.16 mmol), and complex I (0.306 g, 0.22 mmol) were combined in 20 mL of toluene and placed in the 300-mL bomb under N_2. The bomb was heated to 206 °C for 3.5 h with stirring. The bomb was then cooled and vented. MeOH (100 mL) was added to the toluene reaction solution, and the resulting white solid (polystyrene) was collected on a fine fritted funnel (0.03 g). The filtrate (V) was analyzed as above and gave the same results. Additionally, ^{13}C NMR analysis of V showed δ 23.8, 28.0, 32.5, 129.5 (large, br), 145.3 consistent with an atactic arrangement in the polystyrene chain. Three-dimensional GPC analysis, which plotted molecular weight and the UV absorbance and wavelength simultaneously, showed low molecular weight ($\bar{M}_n \approx 2000$) with $\lambda_{max} \approx$ 280 nm consistent with a triphenyl phosphite group present in the oli-

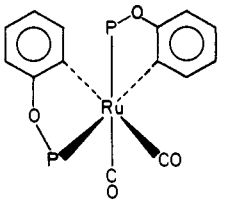
(26) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14.

gomers. ^{31}P NMR analysis of the white precipitates from the styrene reactions showed no resonances (no phosphorus in sample). The ^{31}P NMR of V showed a broad resonance at ca. 126 ppm (6-ppm wide). FDMS analysis showed M = $P(OPh)_3$, m/e 415 (M^+ + styrene), 518 (M^+ + styrene$_2$), 622 (M^+ + styrene$_3$), 726 (M^+ + styrene$_4$), 830 (M^+ + styrene$_5$).

Reaction of II with CO. Complex II (0.026 g, 0.019 mmol) was dissolved in 10 mL of toluene and placed in a 90-mL thick-walled bottle under N_2. The bottle was charged with CO (100 psi, 0.025 mol) and then heated to 205 °C for 4 h with stirring. The bottle was cooled to room temperature and vented. The contents of the bottle were completely extracted with THF. LC analysis showed that quantitative conversion of II to two new products had occurred. The prep LC column was used to separate the products.



IR ν_{CO} (CH_2Cl_2) 2044 cm^{-1}.[16] FDMS: m/e 1061 (M^+, Ru isotope pattern).



IR ν_{CO} (CH_2Cl_2) 2055, 2010 cm^{-1}.[15] FDMS: m/e 776 (M^+, Ru isotope pattern).

Reaction of X with $P(OPh)_3$ (Equation 10a). Complex X (0.037 g, 0.14 mmol) was dissolved in 2 mL of C_6D_6 under N_2 in a septum-capped 10-mm NMR tube. $P(OPh)_3$ (37 mL, 0.14 mmol) was then added by syringe. The solution was analyzed by ^1H, ^{13}C, and ^{31}P NMR (see Table II and eq 10a) and yield established by ^1H and ^{31}P NMR. FDMS analysis showed X m/e 258 (M^+), XI m/e 540 (M^+), and XII m/e 822 (M^+).

Reaction of I and X (Equations 11a-c). A C_6D_6 solution (1 mL) of complex I (0.054 g, 0.039 mmol) was combined with a C_6D_6 solution (1 mL) of X (0.013 g, 0.050 mmol) under N_2. ^{31}P NMR analysis indicated that I was unchanged and that only trace quantities of XI and XII were produced. Incremental amounts of solid X were added to the solution under N_2. When the Ru:Rh ratio was 1:3 (eq 11a), the ^{31}P NMR showed resonances for XI and XII (relative intensity of XI:XII was 1:4) as well as resonances for I and VI (see text). There were about equal amounts of I and XII at this point, which indicated about 60-70% unreacted X. An additional equivalent of solid X was added under N_2 (eq 11b). The ^{31}P NMR spectrum at this time showed that the relative ratio of XI to XII was 1:5 while I was consumed; VI and VII grew in intensity. The solution was heated in an oil bath at 85 °C for 2 h. The color of the solution changed from yellow to maroon but no precipitate was observed. ^{31}P NMR showed complete consumption of I had occurred.

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Registry No. I, 25839-18-3; II, 59634-28-5; III_0, 101-02-0; III_1, 100814-87-7; III_2, 100814-86-6; III_3, 100814-84-4; III_4, 100814-82-2; III_{4a}, 100814-93-5; III_5, 100814-83-3; III_6, 100814-85-5; IV_1, 100814-88-8; IV_2, 100814-89-9; IV_3, 100814-90-2; IV_4, 100814-91-3; IV_{4a}, 100814-92-4; VI_b, 100814-96-8; VII_b, 100814-97-9; IX_b, 100839-15-4; X, 12082-47-2; XI, 100814-95-7; XII, 25966-19-2; $Ru(P(OPh)_3)(P(OPh)_2(O\text{-}o\text{-}C_6H_4))CO$, 100814-94-6; $Ru(P(OPh)_2(O\text{-}o\text{-}C_6H_4))_2(CO)_2$, 100897-56-1; C_2H_4, 74-85-1; PCl_3, 7719-12-2; $Ph(H)C{=}CH_2$, 100-42-5; C_3H_6, 115-07-1; polystyrene, 9003-53-6; 2,6-diethylphenol, 1006-59-3; phenol, 108-95-2; 2-ethylphenol, 90-00-6.

Metal Carbonyl ν(CO) Force Constants as Predictors of π-Ethylene and π-Benzene Complex Reactivity with Nucleophiles

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Abstract: Nucleophilic attack on π-ethylene and π-benzene organometallic compounds, resulting in β-substituted ethyl and exo-substituted cyclohexadienyl complexes, respectively, is examined in terms of a new reactivity parameter, k_{CO}*. This parameter represents the Cotton-Kraihanzel (C-K) C-O stretching force constant of a hypothetical compound in which CO ligands replace the unsaturated hydrocarbon of interest. For example, k_{CO}* for ethylene in $L_nM(C_2H_4)$ is simply the C-O force constant of $L_nM(CO)$. The C-K force constants may be calculated from available IR data, or they may be conveniently estimated by using the ligand effect constants described by Timney. A survey of reported reactions of nucleophiles with π-ethylene and π-benzene complexes reveals a definite correlation between the magnitude of k_{CO}* and the likelihood of addition to the hydrocarbon ligand; a reactivity index utilizing k_{CO}* is established for several nucleophiles. For coordinated ethylene, attack by PPh_3 or most amines is not observed for complexes with k_{CO}* $\leq$ 16.8 mdyn/Å. Trialkylphosphines react with complexes that have k_{CO}* values as low as 15.5 mdyn/Å. Attack on coordinated benzene by PPh_3 does not occur for complexes with k_{CO}* $\leq$ 18.3 mdyn/Å, and trialkylphosphines do not add to benzene in complexes with k_{CO}* below a value of 17.7 mdyn/Å. Carbanions, such as alkyllithium reagents and CH_2X^- (X = CN, NO_2), successfully add to benzene complexes with k_{CO}* values as low as 16.5 mdyn/Å. The results indicate that the k_{CO}* parameter provides a simple means of gauging the activation of coordinated ethylene and benzene toward nucleophilic attack.

Nucleophilic attack on unsaturated hydrocarbons which are coordinated to transition metals has been studied extensively and continues to be a subject of considerable interest.[1] Two reactions of this type involving attack on π-ethylene and π-benzene ligands are shown in eq 1 and 2. Such reactions are important in certain industrial processes, such as the Wacker acetaldehyde synthesis,[2] and are also useful in a variety of laboratory scale syntheses.[3] In

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(2) Bäckvall, J. E.; Åkermark, B.; Ljunggren, S. O. *J. Am. Chem. Soc.* **1979**, *101*, 2411.

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