Alkyl− and Aryl−Oxygen Bond Activation in Solution by Rhodium(I), Palladium(II), and Nickel(II). Transition-Metal-Based Selectivity

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Abstract: Reaction of $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) with 2 equiv of the aryl methyl ether phosphine **1** in C_6D_6 results in an unprecedented metal insertion into the strong sp^2-sp^3 aryl−O bond. This remarkable reaction proceeds even at *room temperature* and occurs directly, with no intermediacy of C−H activation or insertion into the adjacent weaker $ArO-CH_3$ bond. Two new phenoxy complexes (**8** and **9**), which are analogous to the product of insertion into the $ArO-CH_3$ bond (had it taken place) were prepared and shown not to be intermediates in the $Ar-OCH_3$ bond cleavage process. Thus, aryl−O bond activation by the nucleophilic Rh(I) is kinetically preferred over activation of the alkyl−O bond. The phenoxy Rh(I)−η^1-N_2 complex (**8**) is in equilibrium with the crystallographically characterized Rh(I)−μ-N_2−Rh(I) dimer (**12**). Reaction of $[RhCl(C_8H_{14})_2]_2$ with 2 equiv of the aryl methyl ether phosphine **2**, PPh_3, and excess $HSiR_3$ (R = OCH_2CH_3, CH_2CH_3) results also in selective metal insertion into the aryl−O bond and formation of $(CH_3O)SiR_3$. Thus, transfer of a OCH_3 group from carbon to silicon was accomplished, showing that hydrosilation of an unstrained aryl−O single bond by a primary silane is possible. The selectivity of C−O bond activation is markedly dependent on the transition-metal complex and the alkyl group involved, allowing direction of the C−O bond activation process at either the aryl−O or alkyl−O bond. Thus, contrary to the reactivity of the rhodium complex, reaction of NiI_2 or $Pd(CF_3CO_2)_2$ with 1 equiv of **1** in ethanol or C_6D_6 at elevated temperatures results in exclusive activation of the sp^3-sp^3 $ArO-CH_3$ bond, while reaction of the analogous aryl ethyl ether **4** and $Pd(CF_3CO_2)_2$ results in both sp^3-sp^3 and sp^2-sp^3 C−O bond activation. The resulting phenoxy Pd(II) complex (**18**) is fully characterized by X-ray analysis. Heating the latter under mild dihydrogen pressure results in hydrodeoxygenation to afford an aryl−Pd(II) complex (**19**).

Introduction

Activation processes of unstrained C−O single bonds by metal complexes are proposed as key steps in the hydrodeoxygenation (HDO) of crude oil and may lead to the design of novel catalytic reactions.[1−4] Cleavage of C−O bonds is applied in the manufacture of drugs, pharmaceuticals, and other fine chemicals. Direct activation of unstrained C−O bonds by metal complexes in solution is rare, and mechanistic information regarding these processes is scarce.[5−15] C−O bond cleavage by transition-metal complexes which involve either strained systems or relatively weak C−O bonds, or systems driven by aromatization, are well-known.[16−21] For example, C−O bond activation of strained cyclic ethers by transition metals has been applied to catalysis of isomerization to carbonyl compounds, coupling to form esters, and carbonylation to lactones.[16,19,22]

Only a few examples of CH_3-O bond cleavage in aryl alkyl ethers have been reported with soluble metal complexes.[7−9,23] Activation of the sp^3-sp^3 C−O bond results in the formation of phenoxy metal complexes (Scheme 1). For instance, reaction of anisole with Fe(0) complexes results in activation of the CH_3-O bond,[7,8] while the stronger aryl−O bond remains intact.

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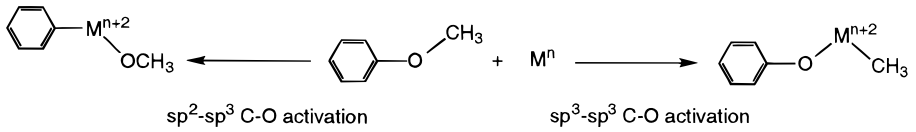
Scheme 1



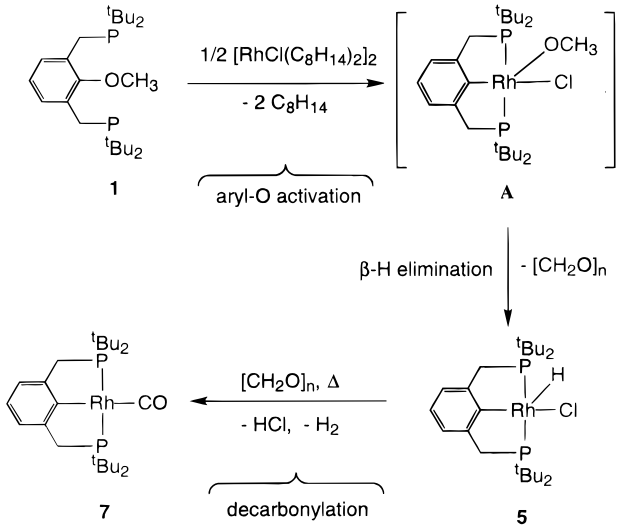
Metal insertion into aryl−O bonds is unprecedented. Such a process is expected to be followed by facile β-hydrogen elimination of the generated alkoxy metal complexes.[24,25] In recent years, we reported the activation of unstrained aryl−C bonds by Rh(I), Ir(I), and Pt(II) and studied the mechanism involved.[26−32] Cleavage of an aryl−Si bond by Pt(II)[33,34] and insertion of a Ta(III) complex into an aryl−N bond were published recently.[5]

We report here the first examples of metal insertion into the strong aryl−O bond of an aryl alkyl ether under mild conditions in solution. These unique processes occur directly, with no intermediacy of C−H activation or insertion into an adjacent weaker alkyl−O bond. The alkoxy group can be transferred to primary silanes, providing the first example of hydrosilation of an unstrained C−O single bond. Moreover, we demonstrate that the C−O bond activation process can be directed at either an aryl−O or alkyl−O bond depending on the metal complex employed and the alkyl group. Thus, reaction of the methyl phenyl ether **1** with Rh(I) results in direct Ar−O activation, while with Pd(II) or Ni(II) exclusive activation of the sp^3-sp^3 $ArO-CH_3$ bond takes place. On the other hand, reaction of the analogous ethyl phenyl ether **4** and Pd(II) results in both sp^3-sp^3 and sp^2-sp^3 C−O bond cleavage. We report also an example of hydrodeoxygenation (HDO) of an alkoxy metal complex. Part of this study has been communicated previously.[13]

Results and Discussion

Preparation of Substrates. To probe the possibility of activation of unstrained C−O single bonds, we prepared the new phosphine aromatic ethers **1**, **2**, **4**, and the phenol **3**. Phosphine coordination is expected to direct a metal to the vicinity of both aryl and alkyl ether bonds. The preparation of substrates **1**−**4** is similar to the synthesis of PCP-based ligands.[6] Our synthetic route for **1** and **2** consists of reaction of $HP(^tBu)_2$ or $LiPPh_2$ with α,α'-dibromo-2-methoxy-*m*-xylene, which is readily obtained by bromination of 2-methoxy-*m*-xylene. Alkylation of *p*-cresol resulted in the formation of oxyuvitin alcohol;[35] halide and phosphine exchange afforded the new diphosphine **3**.[6] The ethyl phenyl ether **4** was prepared from 2,6-dimethylphenol via the Williamson reaction,[36] followed by bromination and phosphine exchange.[6] Compounds **1**−**4** were obtained in good yields as white powders and were fully characterized by ^1H, $^1H\{^{31}P\}$, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^{13}C-DEPT-135 NMR, MS, and elemental analysis.

Scheme 2



Ar−O Activation by Rhodium(I). Reaction of the complex $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) with 2 equiv of **1** in C_6D_6 at 85 °C for 3 h (in a sealed vessel) resulted in quantitative formation of the known Rh(III) hydride complex **5**, which was unambiguously identified by various NMR techniques and by comparison to an authentic sample (Scheme 2).[6,37]

This unprecedented Ar−O bond activation, proceeds even at *room temperature* (20% conversion into **5** was observed by $^{31}P\{^1H\}$ NMR after 24 h). Former studies in our group have shown that coordination of the di-*tert*-butyl phosphine to Rh and Ir alkene dimers controls the overall rate in the activation of an Ar−C bond.[30] Likewise, the substitution of the olefin by **1** is probably slow relative to Ar−O bond activation. Using deuterated solvents, no Rh(III)−D formation was observed by ^2H NMR, indicating that the solvents do not contribute to the Rh−H formed. The presumably formed (unobserved) Rh(III)−OCH_3 intermediate **A** undergoes readily β-hydrogen elimination to afford complex **5** and formaldehyde.[24] Very recently, we prepared the analogous Rh(III)-CH_2CH_3 complex **6**, which upon heating gives complex **5** and ethylene.[38]

Although we have not directly detected formation of formaldehyde in the Ar−O bond activation reaction (**1** → **5**; Scheme 2), heating the orange product solution at 140 °C or performing the reaction at this temperature leads also to formation of complex **7**,[6] presumably by decarbonylation of the initially formed formaldehyde. In support of this, heating of complex **5** at 140 °C in a sealed vessel with paraformaldehyde (10 equiv) results in decarbonylation to yield complex **7** quantitatively. The

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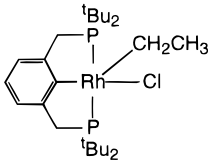

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yellow complex **7** exhibits identical ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR and IR spectra to those reported in the literature.[6] Aldehyde decarbonylation by rhodium is well-known.[39] Products resulting from metal insertion into the adjacent ArO−CH_3 bond, if it occurs at all, are not observed.

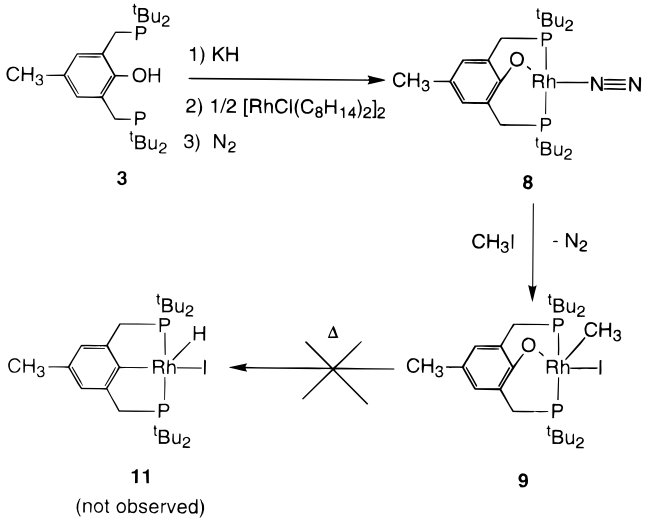
The phenoxy complexes **8** and **9** (Scheme 3) were prepared in order to evaluate whether activation of the weaker CH_3−O bond (compare bond dissociation energy (BDE) values of Ph−OCH_3 = 91 kcal/mol, PhO−CH_3 = 80 kcal/mol)[40,41] precedes the observed aryl−O bond activation step (**1** → **5**; Scheme 2), or perhaps it is a reversible parallel process. Complex **9** is the iodide analogue of the expected product of Rh(I) insertion into the ArO−CH_3 bond (**10**; Scheme 4). Deprotonation of the aromatic phosphine alcohol **3** with KH or NaH in THF, followed by reaction with $[RhCl(C_8H_{14})_2]_2$ (0.5 equiv) in THF under a nitrogen atmosphere at room temperature leads to quantitave formation of complex **8** as proven spectroscopically by ^{1}H, ^{1}H-{^{31}P}, and ^{31}P{^{1}H} NMR, IR, and FD-MS. The latter exhibits the molecular ion (M^+ 554) having the expected isotope pattern. The ^{31}P{^{1}H} NMR shows a characteristic resonance at δ 91.4 (d, $^1J_{RhP}$ = 163.1 Hz), indicating that both phosphorus atoms are magnetically equivalent and coordinated to the Rh(I) center. The frequency of the N≡N stretch in the IR (ν = 2095 cm^{-1}) is very close to those observed for $RhCl(PCy_3)_2$−η^1-N_2 (Cy = cyclohexyl)[42] and (PCP)RhN_2 complexes,[43,44] and it is indicative for an "end-on" coordinated dinitrogen molecule.

Interestingly, no THF or cyclooctene coordination is observed in the ^{1}H NMR. N_2 competes favorably with the solvent and the olefin, probably as a result of the bulky *tert*-butyl substituents on the phosphorus atoms. η^1-N_2 binding to a sterically crowded T-shaped Rh(I) center competes favorably with coordination of CO_2 and even with ethylene.[44]

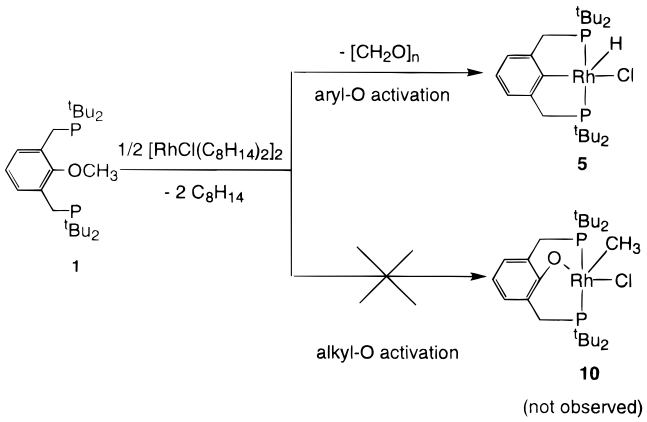
Oxidative addition of $^{13}CH_3I$ (1 equiv) to complex **8** in C_6D_6 at 80 °C in a sealed tube leads within 10 min to quantitative formation of complex **9**, which was characterized by various NMR techniques and FD-MS (Scheme 3). The ^{13}C{^{1}H} NMR shows clearly the presence of the Rh(III)−$^{13}CH_3$ moiety, which appears as a doublet of triplets at δ 10.0 ($^1J_{RhC}$ = 27.4 Hz and $^2J_{PC}$ = 2.7 Hz), and in the ^{13}C-DEPT-135 NMR, a positive signal is observed indicative of an odd number of protons. The FD-MS shows the molecular ion (M^+ 668) and a correct isotope pattern. Complex **9** exhibits similar spectroscopic features to analogous phenoxy Rh(III)(Me)(Cl), Rh(III)(H)(Cl), and Ir(III)-(H)(Cl) complexes.[45] No intermediate products were detected by monitoring this reaction at room temperature by ^{1}H, ^{1}H-{^{31}P}, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR. Continued heating of **8** and **9** at 100 °C results eventually in the formation of unidentified products, while **11** or other products indicative of aryl−O bond cleavage are not observed. Importantly, complexes **8** and **9** are stable under conditions in which **1** readily undergoes aryl−O bond cleavage with $[RhCl(C_8H_{14})_2]_2$. This constitutes strong evidence that the observed sp^2−sp^3 C−O bond activation by Rh(I) is a direct process (**1** → **5**; Scheme 4).

Thus, cleavage of the ArO−CH_3 bond is not involved either on the reaction coordinate or as a side equilibrium, even though this bond is substantially weaker than the adjacent aryl−O bond. Direct sp^2−sp^3 aryl−C oxidative addition *at room temperature* to Rh(I) and Ir(I) was reported recently.[30,31]

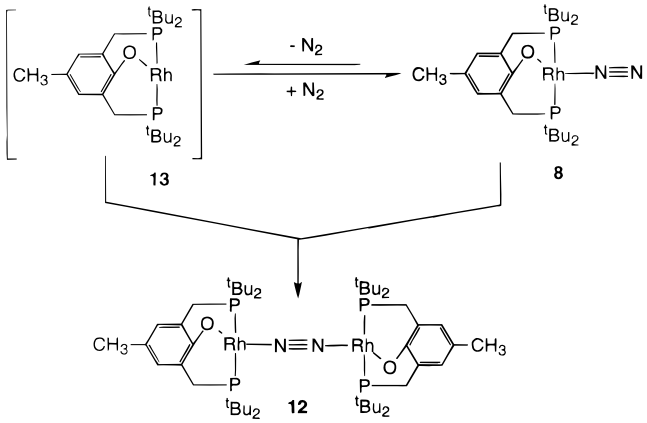
Scheme 3



Scheme 4



Scheme 5



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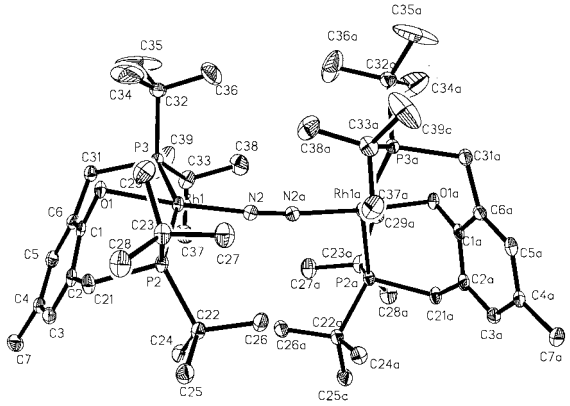
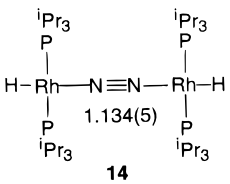


Figure 1. ORTEP view of complex **12**. Selected bond lengths (Å): Rh(1)−N(2) = 1.912(2); Rh(1)−O(1) = 2.041(2); Rh(1)−P(2) = 2.3847(8); Rh(1)−P(3) = 2.3512(7); N(2)−N(2a) = 1.129(4); C(1)−O(1) = 1.343(3); Rh(1)···C(1) = 2.610(2). Selected bond angles (deg): N(2)−Rh(1)−O(1) = 175.88(8); P(2)−Rh(1)−P(3) = 155.64(2); N(2)−Rh(1)−P(2) = 103.12(7); N(2)−Rh(1)−P(3) = 98.52(7); O(1)−Rh(1)−P(2) = 79.41(6); O(1)−Rh(1)−P(3) = 79.68(6); N(2)−Rh(1)−C(1) = 152.85(8); Rh(1)−N(2)−N(2a) = 175.25(7); C(1)−O(1)−Rh(1) = 98.85(14); O(1)−Rh(1)···C(1) = 30.56(7); O(1)−C(1)−C(2) = 119.9(2); O(1)−C(1)−C(6) = 119.7(2).

Orange prismatic crystals of complex **12** were obtained upon slow concentration of a THF solution of **8** under a nitrogen atmosphere at room temperature (Scheme 5). $^{31}P\{^1H\}$ NMR of the THF solution after precipitation of **12** (δ 88.2, $^1J_{RhP}$ = 168.0 Hz and $^4J_{RhP}$ = 24.5 Hz) shows the presence of complexes **8** and **12** in an approximately 4:1 ratio. Thus, **12** crystallizes more readily than the monomeric analogue (**8**). Performing the synthesis of complex **8** in a concentrated solution or bubbling argon for 3 h through a benzene solution of **8** at room temperature results also in the formation of complex **12** (30% yield by $^{31}P\{^1H\}$ NMR). This indicates that the monomeric dinitrogen precursor (**8**) is in equilibrium with a 14-electron species (**13**), which might be stabilized by the bulky, basic phosphine ligands. Subsequentially recombination of **8** and **13** affords **12** (Scheme 5). Reversible dissociation of N_2 to form unsaturated, three-coordinated Rh(I) complexes has been observed.[43,44,46] Stabilization of reaction intermediates with N_2 in PCP-based Rh(I) complexes was recently reported.[43]

X-ray Crystal Structure Analysis of Complex 12. A single-crystal analysis was performed, clearly showing that one dinitrogen molecule linearly bridges two Rh(I) atoms and indirectly supporting the structures of precursors **8** and **13**. An ORTEP view of the molecular structure of **12** and the adopted numbering scheme is shown in Figure 1. Table 1 gives details of the crystal structure determination. Complex **12** is a crystallographic dimer which packs with 1/2 a molecule per asymmetric unit. An X-ray diffraction study of a dinuclear Rh(I)−μ-N_2 complex **14** was reported.[47]



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The N(2)−N(2a) distance (1.129(4) Å) is only slightly shorter than that reported for $[RhH(P^iPr_3)_2]_2(\mu$-$N_2)$ **14** (1.134(5) Å)[47] and comparable with those found in Rh(I) complexes with terminally bound dinitrogen ligands.[43,44,48−50] It is close to that of molecular nitrogen (1.0968 Å) and almost identical to N_2^+ (1.116 Å; bond order $2^1/_2$) suggesting small π-delocalization in the collinear Rh(I)−N≡N−Rh(I) moeity compared to other μ-N_2-bimetallic complexes.[51] Complexes **12** and **14** have an almost linear X−Rh−N≡N−Rh−X linkage (X = O or H) and two trans bulky phosphorus groups with comparable cone angles (e.g., compare cone angles θ, $EtP(^tBu)_2$ = 162° vs P^iPr_3 = 160°).[52,53] The Rh(1)−O(1) and Rh(1)−N(2) distances of 2.041(2) and 1.912(2) Å, respectively, are normal. The nitrogen and oxygen atoms are mutually trans with an almost linear N(2)−Rh(1)−O(1) angle of 175.88(8)°. Least-squares plane analysis through the atoms Rh(1), P(2), P(3), O(1), and N(2) shows that the mean deviation from planarity is 0.1322 Å. The C(1)−O(1) distance (1.343(3) Å) is comparable with the Ph−OH distance of phenol (1.362 Å), and thus, it is hardly affected by binding of the oxygen atom to the metal center.[54] The C(1)−O(1)−Rh(1) angle of 98.85(14)° is indicative of a sp^3-hybridized oxygen atom, which fits well with the observed C(1)−O(1) and Rh(1)−O(1) distances. The P(2)−Rh(1)−P(3) angle of 155.64(2)° is similar to those recently observed in the structures of two monomeric benzylic PCP-based Rh(I) and Rh(III) complexes.[26,28] The expected steric hindrance between the two rhodium moieties is significantly reduced by bending of the bulky phosphorus groups, as is observed for **14**, allowing the formation of complex **12**. However, there is still considerable steric hindrance between the *tert*-butyl groups as indicated by the relatively short intermolecular distances of C(26)···C(24a) = 3.691 Å and C(36)···C(36a) = 3.308 Å. The rhodium−phosphorus distances (2.3512(7) and 2.3847(8) Å) are similar to those observed in other rhodium complexes.[26,28,30,37,55] The ipso carbon of the aromatic ring is close to the metal center (C(1)···Rh(1) = 2.610(2) Å), but no additional evidence for any bonding interaction is observed. The aromaticity is not distorted as indicated by the normal sp^2−sp^2 C−C distances (range 1.391(4)−1.401(3) Å)[54] and the ring planarity (mean deviation from plane = 0.0196 Å).

Table 1. Crystal Data for Complexes **12** and **18**

compd	**12**	**18**
formula	$^1/_2$ ($C_{50}H_{90}N_2P_4O_2Rh_2$)	$C_{26}H_{43}P_2F_3O_3Pd$
fw	540.7	628.9
space group	*C*2/*c* (No. 15)	$P\bar{1}$ (No. 2)
cryst syst	monoclinic	triclinic
a, Å	25.575(5)	10.714(2)
b, Å	18.219(4)	15.988(3)
c, Å	11.656(2)	19.420(4)
α, deg	90	68.96(3)
β, deg	103.99(3)	74.09(3)
γ, deg	90	70.47(3)
V, Å^3	5270(2)	2880.9(10)
Z	8	4
D_{calcd}, g cm^{-3}	1.362	1.450
μ(Mo Kα), mm^{-1}	0.786	0.799
T (K)	110	110
cryst size, mm^3	0.25 × 0.25 × 0.3	0.1 × 0.1 × 0.05

Methoxy Group Transfer to Silanes Promoted by Rh(I). The new ligand **2** was prepared in order to evaluate the role of

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(53) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313−348.
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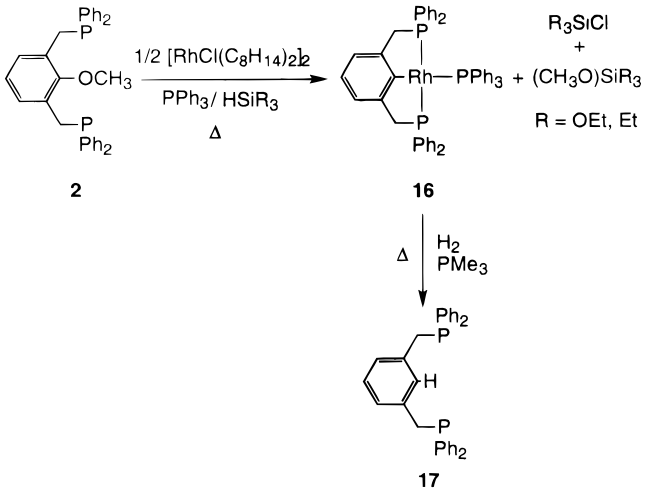
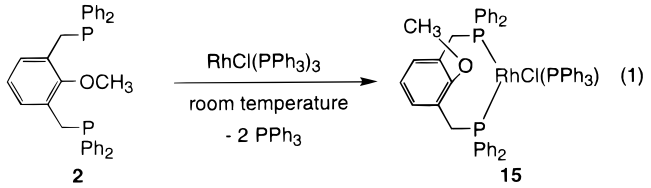
Scheme 6



the subsituents on the phosphorus atoms on the C−O bond activation process. Reaction of $RhCl(PPh_3)_3$ with 1 equiv of **2** in C_6D_6 at room temperature for 0.5 h suggests the formation of **15** as indicated by ^1H and $^{31}P\{^1H\}$ NMR, although characterization is not conclusive (eq 1). The ^1H NMR shows free

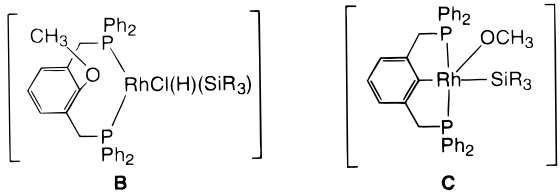


cyclooctene and broad signals for coordinated **2**; the singlet resonance of the OCH_3 group (δ 3.61) is broadened but appears in almost the same chemical shift as in the free ligand (δ 3.58), showing that the C−O bonds are not preactivated by the metal center in the coordinated ligand. The $^{31}P\{^1H\}$ NMR shows two broad signals at δ 49.0 and 40.5 (ratio 2:1), consistent with the proposed structure **15**. Similar features have been observed previously for related eight-membered PCP-based Pt(II) complexes.[56]

Performing the same reaction with **2** and various Rh(I) precursors such as $HRh(PPh_3)_4$ or $PhRh(PPh_3)_3$ at elevated temperatures, or thermolysis of the postulated **15** in benzene at 120 °C in a sealed vessel, afforded mixtures of unknown products. No products indicative of aryl−O or alkyl−O bond activation were observed either by ^1H or $^{31}P\{^1H\}$ NMR.

Significantly, reacting $[RhCl(C_8H_{14})_2]_2$ with 2 equiv (each) of **2** and PPh_3 in the presence of a 7-fold excess of $HSiR_3$ (R_3 = $(OEt)_3$ or Et_3) for 0.5 h at 130 °C in benzene or dioxane (in a pressure bottle) results in the formation of the previously reported aryl−Rh(I) complex **16** as a major organometallic product (~95%) and $(MeO)SiR_3$ (Scheme 6).[32] $RhCl(PPh_3)_3$ can be used as well. Formation of the methoxysilanes is unambiguous based on ^{29}Si NMR and GC-MS (CI and EI) analysis of the product solution, showing the molecular peaks and expected fragmentation patterns.[57−59] Complex **16** was characterized spectroscopically and by comparison to an authentic sample. PPh_3 was used to stabilize the organometallic product **16**. The demethoxylated arene **17** can be readily released from complex **16** by mild heating under H_2 (20 psi) in the presence of excess PMe_3.[27,60]

Mechanistically, the first step is probably coordination of **2** by both phosphine arms to afford **15**, followed by oxidative addition of the H−Si bond to afford intermediate **B**. Formation of the strong Cl−Si bond would yield a Rh(I)-H species. A



second oxidative addition of Si−H followed by H_2 elimination and by aryl−O bond cleavage may afford the unobserved Rh(III)$(OMe)(SiR_3)$ complex (**C**; the silane analogue of **A**). Formation of $ClSiEt_3$ was detected by GC-MS analysis of the product solution, showing the molecular ion and the expected fragmentation pattern.[58] Intermediate **C** may undergo facile irreversible O−Si reductive elimination to afford the observed CH_3OSiR_3 and complex **16** from which the organic product (**17**) can be liberated.[27,60]

Regardless of the exact mechanism involved, unprecedented transfer of an alkoxy group from carbon to silicon was observed, showing that functionalization of an unstrained aryl−O single bond by a silane is possible. We are unaware of other examples of hydrosilation of an unstrained ether. Moreover, the reaction is selective toward the stronger Ar−O bond. Formation of the very strong O−Si single bond provides a large contribution to the driving force of this reaction. No β-hydrogen elimination products resulting from the presumed Rh(III)−OCH_3 intermediate (**C**) were observed. The selective transfer of the OCH_3 group to the silane fits well with our observations that aryl−O bond activation with **1** and Rh(I) is a direct process (vide supra; Schemes 3−5). Products indicative of sp^3−sp^3 C−O bond activation were not formed. $MeSiR_3$ was not detected either by ^1H and ^{29}Si NMR or by GC-MS analysis of the reaction mixture, and only traces of methane (<3%) were detected by GC analysis of the gas phase, ruling out a consecutive C−O bond activation process or a side equilibrium involving sp^3−sp^3 C−O bond cleavage. In both systems **1** and **2**, exclusive aryl−O bond cleavage with Rh(I) was observed, showing that this unusual bond activation process can take place with significantly different electron density and bulk at the metal center.

Mechanistically, following coordination of the chelating diphosphines (**1** and **2**) coordination of the OCH_3 group to the metal center might take place,[61−64] although we did not see any evidence for it. The Rh(I) insertion into the aryl−O bond may proceed via an η^2-arene complex **E** (Scheme 7), followed by

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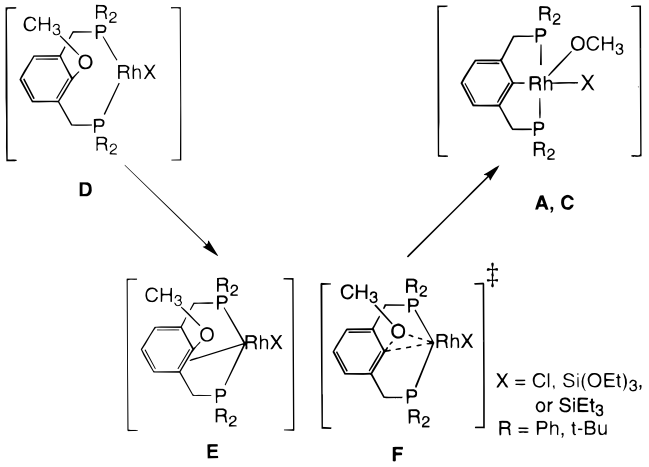
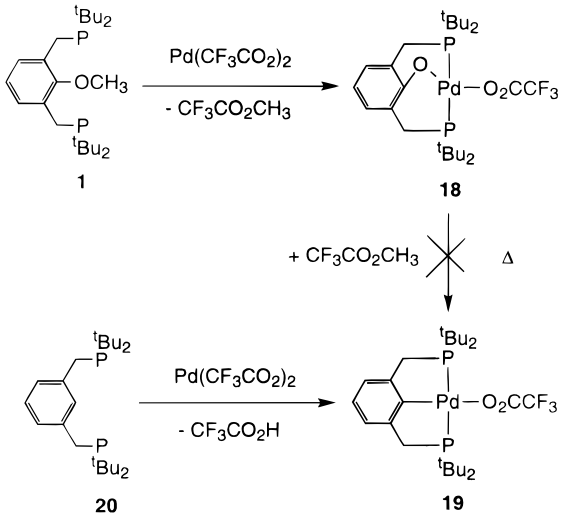
Scheme 7



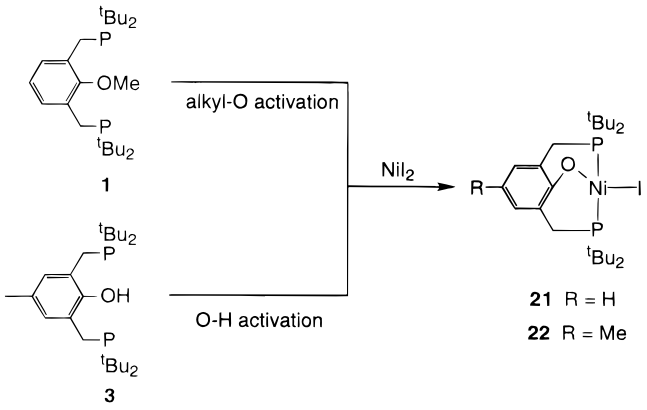
Scheme 8



1,2-migration of the methoxy group from carbon to the metal center, or via a concerted, tri-centered transition state **F**, as observed for Rh(I) and Ir(I) insertion into an Ar−C bond in an analogous system.[30] The kinetic preference leading exclusively to the aryl−O bond activation might indeed be a result of **E**. In the C−C activation process, competitive C−H activation is observed.

ArO−CH$_3$ Activation by Palladium(II) and Nickel(II). Interestingly, it is possible to direct the bond activation process toward the CH$_3$−O bond by employing Pd(II) or Ni(II). Thus, upon reaction of Pd(CF$_3$CO$_2$)$_2$ with a stoichiometric amount of **1** in C$_6$D$_6$ at 85 °C for 3 h (in a sealed vessel), exclusive activation of the sp^3−sp^3 C−O bond took place, leading to quantitative formation of the phenoxy Pd(II) complex **18** (Scheme 8). The reaction proceeds even at room temperature, resulting in 40% conversion to **18** after 24 h. No intermediates were observed, compatible with rate-determining phosphine coordination. No other products were formed even at higher temperatures (130 °C). Complex **18**, which was isolated and fully characterized by ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR, FD-MS, and X-ray analysis, exhibits similar spectroscopic features to two analogous benzylic and phenoxy Pd(II) complexes (**23**; vide infra).[65] CF$_3$CO$_2$CH$_3$ was also formed, as detected by ^{1}H NMR by comparison with an added authentic sample. Complex

Scheme 9



19, which is the expected product of aryl−O bond cleavage, is neither observed nor formed upon treatment of **18** with a 10-fold excess of CF$_3$CO$_2$CH$_3$ at 85 °C, suggesting that the sp^3−sp^3 C−O bond cleavage is thermodynamically preferred in this system. The thermally stable complex **19** is readily obtained by heating the disphosphine **20** with Pd(CF$_3$CO$_2$)$_2$ in toluene at 130 °C for 1 h in a sealed vessel and exhibits similar spectroscopic features in ^{1}H, ^{1}H{^{31}P}, ^{31}P{^{1}H}, and ^{13}C-DEPT-135 NMR as its chloride, iodide, and hydride analogues.[6,65]

Likewise, the reaction of **1** with 1 equiv of NiI$_2$ in ethanol for 12 h at 120 °C in a closed vessel affords complex **21** (R = H) and presumably CH$_3$I (Scheme 9). No products of aryl−O bond activation were observed by ^{1}H and ^{31}P{^{1}H} NMR. An analogous phenoxy complex (**22**; R = CH$_3$) was obtained by reacting **3** with NiI$_2$ under the same reaction conditions. Both Ni(II) complexes, which were characterized by various NMR techniques and by FD-MS, exhibit very similar spectroscopic properties. The ^{1}H NMR spectra of complexes **21** and **22** show that the resulting geometry render the four hydrogen atoms of the CH$_2$P groups (AB quartet) and the *tert*-butyl substituents magnetically nonequivalent. The ^{31}P{^{1}H} NMR exhibits a singlet resonance, indicating that the two phosphorus atoms are identical.

Thus, in striking contrast to the reactivity of **1** with Rh(I), alkyl−O bond activation takes place with Pd(CF$_3$CO$_2$)$_2$ or NiI$_2$. Few other examples of sp^3−sp^3 C−O bond cleavage by transition metals were reported, including metal insertion into unstrained ArO−CH$_3$ bonds.[7−9,23,63,66,67] It was suggested that CH$_3$−O bond cleavage with Pt(II) might occur via a polar four-centered transition state.[66,67]

Aromatic ethers, such as anisole (Scheme 1), undergo exclusive sp^3−sp^3 C−O cleavage upon reaction with HI or HBr at elevated temperatures to give an alkyl halide and an aromatic alcohol (eq 2).[68] Lewis acids such as AlCl$_3$ or BF$_3$ are also effective. The reaction proceeds by protonation of (or Lewis

$$\mathrm{ArO\text{–}CH_3 + HX \rightarrow ArOH + CH_3X} \qquad (2)$$

acid binding to) the oxygen followed by an external nucleophilic attack of the anion on the alkyl group (S$_N$2 mechanism). It is likely that the electrophilic Pd(II) and Ni(II) centers react as Lewis acids and coordinate to the ether oxygen, forming an intermediate such as **G**.[69−71] Such an interaction could promote the loss of the alkyl group by an internal interaction with a

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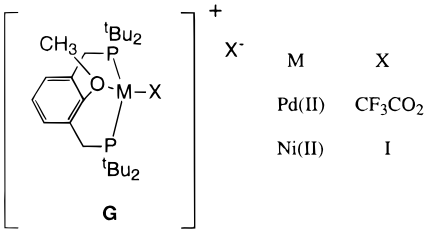


G

coordinated anion, as suggested by Shaw,[66] or by an external nucleophilic attack affording **18** or **21** and an alkyl halide.

X-ray Crystal Structure of 18. The structure of complex **18** was determined by single-crystal X-ray diffraction. Orange crystals (plates) were obtained upon slow concentration of a benzene solution of **18** under nitrogen at room temperature. An ORTEP view of **18** and the adopted numbering scheme is shown in Figure 2. Table 1 gives details of the crystal structure determination. The overall features are similar to the phenoxy Rh(I) complex **12** and will be discussed only briefly. The Pd(II) center has a distorted square planar coordination geometry. Least-squares planar analysis through the atoms Pd(1), P(3), P(4), O(1), and O(5) shows a mean deviation from planarity of 0.1573 Å. The bulky phosphines P(2) and P(3) as well as the phenoxy group O(11) and the trifluoracetate anion O(4) are in a trans arrangement with a rather acute angle of P(2)−Pd(1)−P(3) (157.06(10)°) and an almost linear angle of O(11)−Pd−O(10) (176.6(3)°). The Pd(1)−P(2) (2.354 Å), Pd(1)−P(3) (2.360 Å), Pd(1)−O(1) (1.981 Å), and Pd(1)−O(4) (2.057 Å) distances are in the range normally found for such bonds.[54] The second oxygen of the CF_3CO_2 anion is relatively close to the metal center (Pd(1)···O(52) = 3.014 Å). The sp^2-sp^3 C−O bond length (1.344 Å) is not weakened by bonding of O(1) to the metal center. The intramolecular Pd(1)···C(1) distance is relatively short (2.629 Å) as observed for **12** (Rh(1)···C(1) = 2.610 Å), but as in the latter case, there is no spectroscopic evidence for any metal−carbon interaction. The C(11)−O(1)−Pd(1) angle (102.8(5)°) is a little larger compared to the one observed in **12** (98.85°) and indicates an approximate tetrahedral geometry around O(1).

Competitive sp^3-sp^3 and sp^2-sp^3 C−O Bond Activation with Palladium(II). Reaction of the aryl ethyl ether **4** with a stoichiometric amount of $Pd(CF_3CO_2)_2$ in toluene for 3 h at 130 °C (in a closed vessel) led to the formation of complexes **18** and **19** in a ratio of 9:1, respectively (Scheme 10). Quantitave formation of CF_3CO_2Et (based on **18**) was observed by ^1H, $^{13}C\{^1H\}$, and ^{13}C-DEPT-135 NMR and GC-MS analysis of the reaction mixture.[58,72] Heating the yellow reaction solution overnight at 130 °C did not change the product distribution, suggesting that complexes **18** and **19** are formed independently and do not intercovert. Thus, both C−O bonds are readily accessible to the metal center, and *the overall C−O bond activation processes are probably kinetically controlled.* A rough estimation of the *overall* relative rates is $k_{alkyl-O}/k_{aryl-O} \approx 9$.

These observations indicate that there is only a small difference in the kinetic barriers of sp^3-sp^3 and sp^2-sp^3 C−O bond cleavage. The sp^3-sp^3 C−O bond activation process with M(II) (M = Pd, Ni) is kinetically more favorable than the competitive sp^2-sp^3 C−O bond cleavage, while with Rh(I) the opposite is true. Interestingly, the balance between aryl−O and alkyl−O is not only readily influenced by the metal but also by the nature of the alkyl group. This is in line with our postulated mechanism for the sp^3-sp^3 CH_3−O bond activation with compound **1** and $Pd(CF_3CO_2)_2$ or NiI_2, which probably involves a S_N2 attack on the methyl group by the anion (**G**; vide supra). Apparently a nucleophilic attack by a $CF_3CO_2^-$ anion on the α carbon of the ethyl moiety of **4** is less favorable than on the methyl group, mainly due to steric hindrance, rendering the Ar−O activation to afford **19** more competitive. This latter process can proceed by a concerted oxidative addition process or indirectly by formation of an arenium intermediate.[73]

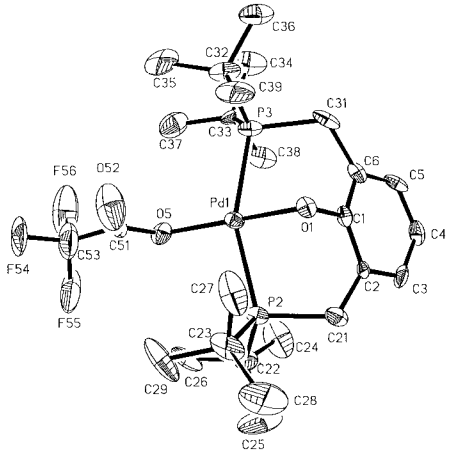
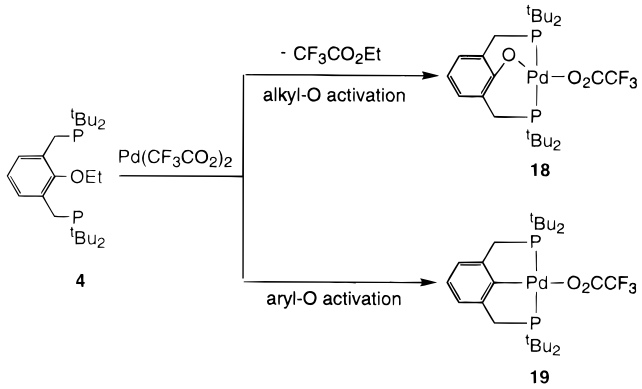


Figure 2. ORTEP view of complex **18**, showing that the Pd(II) atom has selectively inserted into the sp^3-sp^3 C−O bond, with overall retention of the metal oxidation state. Selected bond lengths (Å): Pd(1)−O(1) = 2.041(2); Pd(1)−O(1) = 2.041(2); Pd(1)−P(2) = 2.3847(8); Pd(1)−P(3) = 2.3512(7); Pd(1)···C(1) = 2.610(2); C(1)−O(1) = 1.343(3). Selected bond angles (deg): O(1)−Pd(1)−O(5) = 175.88(8); P(2)−Pd(1)−P(3) = 155.64(2); O(2)−Pd(1)−P(2) = 103.12(7); O(2)−Pd(1)−P(3) = 98.52(7); O(1)−Pd(1)−P(2) = 79.41(6); O(1)−Pd(1)−P(3) = 79.68(6); C(1)−O(1)−Pd(1) = 98.85(14); O(1)−Pd(1)···C(1) = 30.56(7).

Scheme 10



Ar−O Hydrodeoxygenation (HDO) by Palladium(II). Reaction of the diphosphine **3** with a stoichiometric amount of $Pd(CF_3CO_2)_2$ in toluene at room temperature led to the quantitative formation of the phenoxy palladium(II) complex **23** and CF_3CO_2H by selective cleavage of the O−H bond (eq 3). Prolonged stirring for 5 days or performing this reaction at various temperatures resulted in the same product. The thermally stable complex **23** exhibits similar spectroscopic

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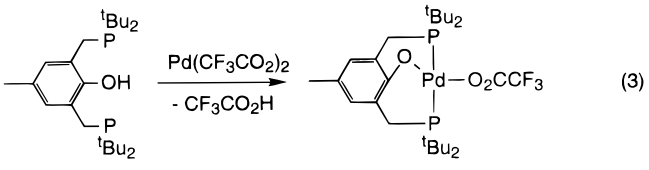
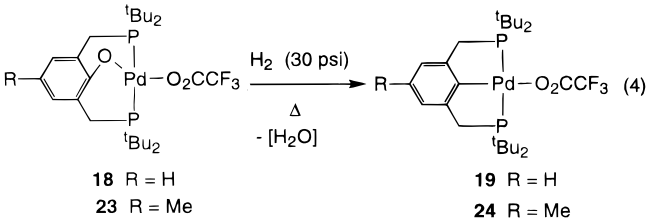


3 **23**

features as the isostructural Pd(II) and Ni(II) complexes **18**, **21**, and **22** and was also characterized by preliminary X-ray analysis. Complex **24**, which is the expected product of aryl−O bond cleavage, is neither observed by ^{1}H or ^{31}P{^{1}H} NMR nor formed upon heating the product solution up to 180 °C for 24 h in a sealed vessel. This suggests that the ArO−H bond activation generating CF_3CO_2H is thermodynamically more favorable than the competing Ar−OH bond activation process.

Remarkably, heating the orange product solution or the isolated thermally stable complexes **18** or **23** (lacking the *p*-methyl group on the aromatic ring) at 180 °C in toluene under H_2 (30−35 psi) resulted, within 8 h, in the formation of the colorless aryl−Pd(II) complexes **19** or **24** as the only organometallic products in approximately 55% yield (by ^{31}P{^{1}H} NMR; eq 4).



18 R = H
23 R = Me

19 R = H
24 R = Me

The reaction proceeded also at lower temperatures at longer reaction times (e.g., 16 h at 140 °C). Formation of **19** and **24** was clearly observed by ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H}, ^{13}C-DEPT-135 NMR and FD-MS. The spectroscopic properties are fully in accord with a C_2 symmetry. The structure of **19** was confirmed by comparison with an authentic sample (vide supra). Complex **24** shows very similar spectroscopic properties. For instance, the well-resolved ^{1}H NMR spectrum of **24** clearly shows the characteristic *tert*-butyl and CH_2P 1:2:1 triplets at δ 1.19 (J_{PH} = 6.9 Hz) and δ 2.81 (J_{PH} = 4.0 Hz), which collapse into singlets in the ^{1}H{^{31}P} NMR.

Hydrodeoxygenation of a strong aryl−O bond by a transition metal in solution is unprecedented. Kubiak reported deoxygenation of phenols by Pt(II) under mild CO pressure.[74] Further studies are underway to explore the mechanism of this unique transformation. We believe that the ArO−M σ bond is cleaved upon treating **18** or **23** with an excess of H_2 to afford an Ar−OH moeity. Competitive, reversible O−H activation and irreversible activation of the Ar−OH bond yields **19** or **24**. Water was presumably formed, although we could not detect it.

Summary and Conclusions

We have demonstrated, for the first time, that metal insertion (Rh(I), Pd(II)) into the strong aryl−oxygen single bond of an aromatic ether and a phenol under mild homogeneous conditions is possible. These fascinating processes occur directly without prior activation of the substantially weaker alkyl−O bond. Moreover, the alkoxy group can be transferred to silanes (eq 5), providing a rare example of hydrosilation of an unstrained C−O bond.

$$\text{Ar-OCH}_3 + \text{HSiR}_3 \xrightarrow{\text{Rh(I)}} \text{Ar-H} + (\text{MeO})\text{SiR}_3 \quad (5)$$

(R = OEt, Et)

It is possible to influence the selectivity of the kinetically controlled sp^2-sp^3 vs sp^3-sp^3 C−O bond activation by proper choice of metal precursor or the alkyl group. Our observations clearly show that a nucleophilic metal favors direct aryl−O bond activation, while electrophilic metals are likely to promote alkyl−O bond cleavage. Although in all cases studied a d^8 metal is used, the nucleophilic Rh(I) complex selectively activates the very strong aryl−O bond, whereas the more electrophilic Pd(II) or Ni(II) complexes preferentially cleave the alkyl−O single bond.

Significantly, the phenoxy complexes are clearly neither intermediates in the sp^2-sp^3 C−O bond activation processes nor involved in side equilibria. Unprecedented hydrodeoxygenation of an aryl−O bond by Pd(II) has been observed. Our results provide evidence that metal complexes might be designed to selectively activate and functionalize unstrained C−O single bonds under mild homogeneous conditions. The bond activation processes proceed even at *room temperature*. We believe that the observed C−O bond cleavage, which is based on model systems, indicates that the development of a general strategy for activation of unstrained C−O single bonds under mild conditions in solution may be possible. Noteworthy, methylene transfer from benzylic metal complexes to H−C, H−Cl, H−Si, and even to Si−Si bonds was communicated by us.[27,29] The formation of isostructral phenoxy complexes might lead to selective oxygen transfer to various substrates, which is a subject of further studies.

Experimental Section

General Procedures. All reactions were carried out under nitrogen in a Vacuum Atmospheres glovebox (DC-882) equipped with a recirculation (MO-40) "Dri Train" or under argon using standard Schlenk techniques. Oxygen levels (≤2 ppm) were monitored with Et_2Zn (1 M solution in hexane, Aldrich), water levels (≤2 ppm) were monitored with $TiCl_4$ (neat, BDH chemicals). Solvents were reagent grade or better, dried, distilled, and degassed before introduction into the glovebox, where it was stored over activated 4 Å molecular sieves. Deuterated solvents were purchased from Aldrich and were degassed and stored over 4 Å activated molecular sieves in the glovebox. [RhCl-$(C_8H_{14})_2]_2$ was prepared by a published procedure.[75] NiI_2 and Pd$(CF_3$-$CO_2)_2$ were obtained from Aldrich. Reaction flasks were washed with dionized water, followed by acetone, and then oven dried prior to use. GC analyses were performed on a Varian 3300 gas chromatograph equipped with a molecular sieve column. Field desorption (FD) mass spectra were measured at the Institute of Mass Spectrometry, University of Amsterdam, The Netherlands. Elemental analyses were carried out at the Hebrew University, Jerusalem, Israel.

Spectroscopic Analysis. The ^{1}H, ^{31}P, ^{13}C, and ^{29}Si NMR spectra were recorded at 400.19, 161.9, 100.6, and 79.5 MHz, respectively, on a Bruker AMX 400 NMR spectrometer. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were also recorded at 250.17, 101.3, and 62.9 MHz, respectively, on a Bruker DPX 250 NMR spectrometer. All chemical shifts (δ) are reported in ppm, and coupling constants (J) are in hertz (Hz). The ^{1}H and ^{13}C NMR chemical shifts are relative to tetramethylsilane; the resonance of the residual protons of the solvent was used as an internal standard h_1 (7.15 ppm benzene; 7.26 chloroform) and

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all-d solvent peaks (128.0 ppm benzene; 77.0 chloroform), respectively. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 in D_2O at δ 0.0 (external reference), and ^{29}Si NMR chemical shifts are relative to $HSiEt_3$ (internal reference) with shifts downfield of the reference considered positive. Assignments in the ^{1}H and ^{13}C{^{1}H} NMR were made using ^{1}H{^{31}P}, ^{1}H−^{1}H COSY, and ^{13}C-DEPT-135 NMR. All measurements were carried out at 298 K unless otherwise specified. Ph_3PO was used as an internal standard for integration. IR spectra were recorded as films between NaCl plates on a Nicolet 510 FT spectrometer. Field desorption (FD) mass spectrometry was carried out using a JEOL JMS SX/SX 102A four-sector mass spectrometer, coupled to a JEOL MS/MP7000 data system; 10 μm tungsten wire FD emitters containing carbon microneedles with an average length of 30 mm were used. The samples were dissolved in methanol/water and then loaded onto the emitter with the dipping technique. An emitter current of 0−15 mA was used to desorb the sample. The ion source temperature was generally 90 °C.

Synthesis of α,α′-Dibromo-2-methoxy-*m*-xylene. 2-Methoxy-*m*-xylene (13.6 g, 100 mmol), *N*-bromosuccinimide (35.5 g; 200.0 mmol), AIBN (∼0.1 g) and CCl_4 (250 mL) were placed in a 500 mL three-necked round-bottom flask equipped with an argon inlet, condenser, and a stirring bar. The reaction mixture was heated to 80 °C and refluxed overnight. The mixture was slowly cooled and filtered, and the resulting solution was washed with H_2O (3 × 25 mL), dried over Na_2SO_4, and concentrated by rotary evaporation. The residue was kept overnight at −20 °C to recrystallize and filtered, and the resulting lachrimating solid was washed with cyclohexane (3 × 25 mL) to give a white solid (22.3 g; 76%). ^{1}H NMR ($CDCl_3$): δ 7.31 (d, 2H, J_{HH} = 7.6 Hz, *m*-C_6H_3), 7.06 (t, 1H, J_{HH} = 7.6 Hz, *p*-C_6H_3), 4.50 (s, 4H, CH_2Br), 3.97 (s, 3H, OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 157.2 (C_{ipso}), 132.8 (C_{meta}), 132.5 (C_{ortho}), 125.7 (C_{para}), 62.9 (s, OCH_3), 28.1 (s, CH_2-Br). Anal. Calcd for $C_9H_{10}O_1Br_2$: C, 36.77; H, 3.43; Br, 54.36. Found: C, 36.85; H, 3.33; Br 54.66.

Synthesis of 1. α,α′-Dibromo-2-methoxy-*m*-xylene (1.0 g, 3.4 mmol) and di-*tert*-butylphosphine (1.0 g, 6.8 mmol) in 5 mL of acetone were refluxed with stirring for 40 min under argon to afford a white precipitate. The solid was filtered and washed with ether, and the resulting diphosphonium salt was dissolved in distilled degassed water (10 mL) and treated with a solution of sodium acetate (4 g, 48 mmol) in water (10 mL). The precipitated diphosphine **1** was extracted with ether (3 × 50 mL) and dried over Na_2SO_4, and the ether solution was filtered via a sinter tube under argon pressure. The solvent was evaporated under vacuum, and the solid was extracted with ether. The ether extract was filtered, and the solvent was evaporated, giving 0.86 g (60%) of **1** as a white solid. ^{1}H NMR (C_6D_6): δ 7.62 (d, 2H, J_{HH} = 7.7 Hz, *m*-C_6H_3), 7.01 (t, 1H, J_{HH} = 7.6 Hz, *p*-C_6H_3), 3.58 (s, 3H, OCH_3), 2.92 (d, 4H, J_{PH} = 9.4 Hz, CH_2P), 1.13 (d, J_{PH} = 10.5 Hz, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (C_6D_6): δ 155.6 (t, J_{PC} = 4.2 Hz, C_{ipso}), 134.4 (d, J_{PC} = 11.9 Hz, C_{meta}) 129.1 (dd, J_{PC} = 15.2 Hz, J_{PC} = 1.8 Hz, C_{ortho}), 124.0 (s, C_{para}), 61.1 (s, OCH_3), 31.9 (d, J_{PC} = 11.9 Hz, C(CH_3)$_3$), 29.8 (d, J_{PC} = 13.2 Hz, C(CH_3)$_3$), 21.1 (d, J_{PC} = 22.4 Hz, CH_2P). ^{31}P{^{1}H} NMR (C_6D_6): δ 34.3 (s). Anal. Calcd for $C_{25}H_{46}P_2O_1$: C, 70.72; H, 10.92. Found: C, 70.43; H 10.73.

Synthesis of 2. In a 250 mL three-necked round-bottom flask equipped with an argon inlet, dropping funnel, and stirring bar was added 1.6 M *n*-BuLi in *n*-hexane (8.81 mL; 14.1 mmol) under argon, and the flask was then cooled to −40 °C. A solution of $HPPh_2$ (2.62; 14.1 mmol) in 30 mL of THF was added dropwise under vigorous stirring. Subsequently the reaction mixture was cooled to −78 °C and a THF (120 mL) solution of α,α′-dibromo-2-methoxy-*m*-xylene (2.07 g, 7.05 mmol) was added dropwise under vigorous stirring. The reaction mixture was allowed to warm to room temperature and was stirred overnight and concentrated on a rotary evaporator. Toluene (100 mL) was added, and the mixture was filtered and concentrated again. After addition of $CHCl_3$ (100 mL), the mixture was filtered again, concentrated, and recrystallized from toluene at −30 °C to give **2** as a white solid (3.23 g, 91%). ^{1}H NMR (C_6D_6): δ 7.41 (td, 8H, J_{HH} = 7.1 Hz, J_{PH} = 1.9 Hz, PPh_2), 7.03 (m, 12H, J_{HH} = 7.0 Hz, PPh_2), 6.83 (dt, 2H, J_{HH} = 7.6 Hz, J_{PH} = 1.4 Hz, *m*-C_6H_3), 6.58 (t, 1H, J_{HH} = 7.6 Hz, *p*-C_6H_3), 3.58 (s, 3H, OCH_3), 3.46 (s, 4H, CH_2P). ^{13}C-{^{1}H} NMR (C_6D_6): δ 157.1 (t, J_{PC} = 4.2 Hz, C_{ipso}), 139.4 (d, J_{PC} = 16.7 Hz, PPh_2), 133.3 (d, J_{PC} = 18.8 Hz, PPh_2), 131.3 (d, J_{PC} = 8.9 Hz, C_{meta}), 129.3 (dd, J_{PC} = 9.8 Hz, J_{PC} = 2.4 Hz, C_{ortho},), 128.7 (s, PPh_2), 128.6 (d, J_{PC} = 6.4 Hz, PPh_2), 123.8 (s, C_{para}), 61.4 (t, J_{PC} = 4.5 Hz, OCH_3), 30.0 (d, J_{PC} = 16.5, CH$_2$P). ^{31}P{^{1}H} NMR (C_6D_6): δ −11.4 (s). Anal. Calcd for $C_{33}H_{30}P_2$: C, 78.56; H, 5.46. Found: C, 78.20; H 5.76.

Synthesis of 3. (a) Synthesis of Oxyuvitin Alcohol. An aqueous formaldehyde solution (215 g, 37%) was added to a solution of *p*-cresol (108 g, 1 mol) and NaOH (50 g) in H_2O (200 mL). After 24 h of stirring at room temperature, it was filtered and washed with an aqueous saturated NaCl solution (1 L). The resulting salt was dissolved in water (4 L) and neutralized with acetic acid to afford light-pink crystals, which were filtered and washed with H_2O. The product was dissolved in hot ethyl acetate (400 mL), dried over Na_2SO_4, filtered hot, concentrated to 270 mL, and recrystallized overnight. The formed crystals of oxyuvitin alcohol were filtered and washed with cold ethyl acetate. ^{1}H NMR (CD_3COCD_3): δ 6.92 (s, 2H, *m*-C_6H_2), 4.70 (s, 4H, CH_2OH), 3.19 (br, 3H, O*H*), 2.19 (s, 3H, CH_3). **(b) Synthesis of α,α′-Dibromo-2-hydroxymesitylene.** Oxyuvitin alcohol (7.8 g) was dissolved in a HBr/acetic acid solution (33% HBr, 41 mL) and stirred overnight under argon. The reaction mixture was diluted with excess H_2O, and the formed solid was filtered and dried in high vacuum to afford the dibromide (10.2 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.06 (s, 2H, *m*-C_6H_2), 5.5 (br, 1H, O*H*), 4.50 (s, 4H, CH_2Br), 2.24 (s, 3H, ArCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.94, 131.82, 130.50, 124.98 (s, Ar), 29.52 (CH_2-Br) 20.23 (s, ArCH_3). **(c) Phosphination.** The procedure is analogous to the one used for **1**. White crystals were obtained from cold pentane (−30 °C), and the product was further purified by column chromatography (hexane/THF = 95:5) to afford pure **3** (5.7 g, 75%). ^{1}H NMR ($CDCl_3$): δ 7.58 (br, 1H, O*H*), 6.97 (s, 2H, *m*-C_6H_2), 2.95 (d, 4H, $^2J_{PH}$ = 2.8 Hz, CH_2P), 2.26 (s, 3H, CH_3), 1.19 (d, 36H, $^3J_{PH}$ = 11.2 Hz, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 150.22 (t, J_{PC} = 2.0 Hz, C_{ipso}), 129.15 (dd, J_{PC} = 1.8 Hz, J_{PC} = 8.5 Hz, C_{ortho}), ∼129 (s, partly overlapped, C_{para}), 127.20 (d, J_{PC} = 7.5 Hz, C_{meta}), 31.72 (d, J_{PC} = 19.3 Hz, C(CH_3)$_3$), 29.60 (d, J_{PC} = 12.1 Hz, C(CH_3)$_3$), 23.24 (d, J_{PC} = 19.3 Hz, CH_2P), 20.56 (s, CH_3). MS (M + H) = 425. Anal. Calcd for $C_{25}H_{45}O_1P_2$: C, 70.7; H, 10.9. Found: C, 70.3; H 10.7.

Synthesis of 4. (a) Synthesis of 2-Ethoxy-*m*-xylene. Ethyl iodide (18.3 mL, 0.2 mol), NaH (6.0 g), and DMF (50 mL) were added to a THF solution (500 mL) of 2,6-dimethylphenol (12.2 g, 0.1 mol) and refluxed for 36 h at 85 °C. Upon cooling, a white percipitate was formed. The reaction mixture was poured over H_2O (1 L), saturated with NaCl, dried over Na_2SO_4, filtered and concentrated in vacuo, and dried under high vacuum to give a white powder (12.6 g, 85%).[36] **(b) Synthesis of α,α′-Dibromo-2-ethoxy-*m*-xylene.** The bromination was performed analogously to the synthesis of α,α′-dibromo-2-methoxy-*m*-xylene. ^{1}H NMR ($CDCl_3$): δ 7.35 (d, 2H, J_{HH} = 7.6 Hz, *m*-C_6H_3), 7.08 (t, 1H, J_{HH} = 7.6 Hz, *p*-C_6H_3), 4.54 (s, 4H, CH_2Br), 4.16 (q, 3H, J_{HH} = 7.0 Hz, OCH_2CH$_3$), 1.50 (t, 3H, J_{HH} = 7.0 Hz, CH$_2$CH_3). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 155.68, 132.14, 131.93, 124.84 (s, Ar), 70.49 (s, OCH_2CH$_3$), 27.72 (s, CH_2Br), 15.17 (s, OCH$_2$CH_3). **(c) Phosphination.** The procedure is analogous to the one used for the preparation of **1**. White crystals of pure **4** (75%) were obtained from cold pentane (−30 °C). ^{1}H NMR ($CDCl_3$): δ 7.28 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-C_6H_3), 6.91 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 3.84 (q, 2H, $^3J_{HH}$ = 7.0 Hz, OCH_2-CH$_3$), 2.77 (d, 4H, $^2J_{PH}$ = 3.2 Hz, CH_2P), 1.40 (t, 3H, $^3J_{HH}$ = 7.0 Hz, OCH$_2$CH_3), 1.05 (d, 36H, $^3J_{PH}$ = 10.8 Hz, C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 154.15 (t, J_{PC} = 3.6 Hz, C_{ipso}), 134.15 (d, J_{PC} = 25.8 Hz, C_{meta}), 128.50 (d, J_{PC} = 30.6 Hz, C_{ortho}), 123.56 (s, C_{para}), 69.04 (s, OCH_2CH$_3$), 31.56 (d, J_{PC} = 18.7 Hz, C(CH_3)$_3$), 29.47 (d, J_{PC} = 13.2 Hz, C(CH_3)$_3$), 20.77 (d, J_{PC} = 19.2 Hz, CH_2P), 15.71 (s, OCH$_2$CH_3). ^{31}P{^{1}H} ($CDCl_3$): δ 35.95 (s). Anal. Calcd for $C_{26}H_{48}O_1P_2$: C, 71.20; H, 11.03. Found: C, 71.31; H 11.06.

Ar−O Activation by Rh(I). Formation of Complexes 5 and 7. [(RhCl(C_8H_{14})$_2$)$_2$] (19 mg; 0.027 mmol) and 2 equiv of **1** (23 mg; 0.054 mmol) were dissolved in benzene (2.5 mL). The resulting red solution was stirred for 24 h at room temperature. ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR analysis of the reaction mixure showed the formation of complex **5** (20% conversion by ^{31}P{^{1}H}).[6] The reaction was completed after approximately 3 h at 85 °C in a sealed pressure vessel (quantitative conversion). No Rh(III)−D formation was observed by ^{2}H NMR when

C_6D_6 was used. Addition of an authentic sample of **5** to the reaction mixture resulted in overlap of signals in ^{1}H and ^{31}P{^{1}H} NMR. Free cyclooctene was observed by ^{1}H NMR and GC-MS analysis of the reaction mixture. Performing the reaction at 140 °C in a sealed vessel results also in the formation of complex **7** (14% conversion by ^{31}P-{^{1}H} NMR after 4 h). Addition of paraformaldehyde (16 mg, 0.53 mmol) to the reaction mixture (or reacting the isolated **5**) result, upon heating to 140 °C, in quantitave formation of **7**.[6]

Formation of Complexes 8 and 12. A THF solution (5 mL) of **3** (21 mg; 0.050 mmol) was treated with an excess of KH or NaH (30 equiv) and stirred at room temperature for 45 min. The suspension was filtered and added dropwise to a stirred solution of $[RhCl(C_8H_{14})_2]_2$ (18 mg; 0.025 mmol) in THF (5 mL). The resulting yellowish solution was stirred overnight and filtered, and the solvent was removed in vacuo to afford **8** quantitatively as a yellow-green powder. A loosely sealed vial containing a THF solution (5 mL) of **8** was left under a dinitrogen atmosphere in a drybox for a week at room-temperature resulting in the formation of **12** as orange prismatic X-ray quality crystals. Data for **8**. IR: 2095 cm^{-1} (film). ^{1}H NMR (C_6D_6): δ 6.83 (s, 2H, *m*-C_6H_2), 3.20 (d, 2H, J_{HH} = 13.3 Hz, CH_2P, left part of ABq), 2.58 (dvt, 2H, J_{HH} = 13.4 Hz, J_{PH} = 4.0 Hz, CH_2P, right part of ABq), 2.31 (s, 3H, ArCH_3), 1.16 (vt, 18H, J_{PH} = 12.3 Hz, C(CH_3)$_3$). (vt, 18H, J_{PH} = 11.6 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 91.4 (d, J_{RhP} = 163.1 Hz). FD-MS M$^+$ 554 (correct isotope pattern). Data for **12**. ^{31}P{^{1}H} NMR (C_6D_6; 161.9 MHz): δ 88.2 (dd, $^1J_{RhP}$ = 168.0 Hz, $^4J_{RhP}$ = 24.5 Hz).

Reaction of Complex 8 with Methyl Iodide. Formation of Complex 9. Complex **8** (17 mg; 0.021 mmol) was dissolved in C_6D_6 (0.6 mL) and transferred to a 5 mm screwcap NMR tube, treated with 1 or 2 equiv of CH_3I or $^{13}CH_3I$ (1−2 μL; 0.020−0.040 mmol, respectively), and heated for 10 min at 80 °C. The progress of the reaction was monitored at room temperature by NMR in short time intervals. No intermediates were observed by ^{1}H, ^{31}P{^{1}H}, or ^{13}C-{^{1}H} NMR. After completion, all volatiles were removed in vacuo to afford **9** quantitatively as a yellow-green powder. ^{1}H NMR (C_6D_6; 400.19 MHz): δ 6.85 (s, 2H, *m*-C_6H_2), 3.65 (ddt, J_{CH} = 142.0 Hz, J_{RhH} = 3.0 Hz, J_{PH} = 3.9 Hz, 3H, RhCH_3), 3.52 (dvt, 2H, J_{HH} = 12.8 Hz, J_{PH} = 4.2 Hz, CH_2P, left part of ABq), 2.57 (dvt, 2H, J_{HH} = 12.8 Hz, J_{PH} = 3.7 Hz, CH_2P, right part of ABq), 2.20 (s, 3H, ArCH_3), 1.26 (m, 36H, J_{PH} = 11.4 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 58.0 (d, J_{RhP} = 118.7 Hz). ^{13}C{^{1}H} NMR (C_6D_6): δ 10.0 (dt, $^1J_{RhC}$ = 27.4 Hz, $^2J_{PC}$ = 2.7 Hz, Rh*C*H$_3$). FD-MS M$^+$ 668 (correct isotope pattern).

Methoxy Transfer. Formation of Complex 16. $[RhCl(C_8H_{14})_2]_2$ (15 mg; 0.021 mmol) and PPh_3 (11 mg; 0.042 mmol) were dissolved in C_6D_6 or dioxane (1 mL) and added to **2** (20 mg; 0.040 mmol). The resulting dark red solution was stirred for 30 min, loaded into a 5 mm screwcap NMR tube, treated with 50 μL of $HSiR_3$ (R = OCH_2CH_3, CH_2CH_3), and heated for approximately 30 min at 130 °C. ^{1}H, ^{1}H-{^{31}P}, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR analysis of the reaction solution showed the formation of **16** as major organometallic product (∼95%). FD-MS showed the molecular ion (M$^+$ 838) and a correct isotope pattern. GC-MS (CI and EI) and ^{29}Si NMR analysis of the product solution shows the presence of (MeO)SiR_3 (R = OCH_2CH_3, CH_2CH_3).[57−59] Formation of $ClSi(CH_2CH_3)_3$ was observed by GC-MS. The gas phase was collected by a standard vacuum line technique and analyzed by GC, showing only traces of methane (<3%). Formation of (Me)SiR_3 (R = OCH_2CH_3, CH_2CH_3) is not observed either by ^{1}H NMR, ^{29}Si NMR, or GC-MS analysis of the product solution.

Me−O Activation by Pd(II). Formation of Complex 18. Pd-$(CF_3CO_2)_2$ (12 mg, 0.036 mmol) and **1** (16 mg; 0.033 mmol) were dissolved in C_6D_6 (3 mL). The resulting yellow solution was transferred to a pressure vessel and heated for 6 h at 110 °C resulting in quantitave formation of **18** as jugded by ^{1}H, ^{1}H{^{31}P}, and ^{31}P{^{1}H} NMR. The reaction proceeds also at room temperature. NMR analysis of the reaction mixture shows the presence of unreacted **1** (60%) and complex **18** (40%) after 24 h. Heating the reaction mixture for 3 h at 85 °C drives the reaction to completion. $CF_3CO_2CH_3$ formation was observed by ^{1}H NMR analysis of the product solution and by comparison with an authentic added sample. A loosely sealed vial containing a benzene solution (5 mL) of **18** was left under a nitrogen atmosphere for 1 week at room-temperature resulting in formation of orange X-ray suitable crystals. ^{1}H NMR (C_6D_6): δ 6.90 (d, 2H, J_{HH} = 7.2 Hz, *m*-C_6H_3), 6.69 (t, 1H, J_{HH} = 7.5 Hz, *p*-C_6H_3), 2.96 (d, 2H, J_{HH} = 13.5 Hz, CH_2P, left part of ABq), 2.39 (dvt, 2H, J_{HH} = 13.5 Hz, J_{PH} = 4.0 Hz, CH_2P, right part of ABq), 1.35 (vt, 18H, J_{PH} = 6.8 Hz, C(CH_3)$_3$), 1.04 (vt, 18H, J_{PH} = 6.6 Hz, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (C_6D_6): δ 101.1 (s). FD-MS M$^+$ 628 (correct isotope pattern). Anal. Calcd for $C_{26}H_{43}O_3F_3P_2Pd_1$: C, 49.65; H, 6.89. Found: C, 49.74; H 6.82.

Formation of Complex 19. A solution of **20** (23 mg, 0.058 mmol) in 2 mL of toluene was added dropwise to a stirred suspension of Pd-$(CF_3CO_2)_2$ (20 mg, 0.057 mol) in 2 mL of toluene. The resulting colorless solution was loaded into a high-pressure vessel equipped with a stirring bar and heated to 130 °C for 1 h. The solution was filtered over a cotton pad and pumped to dryness, resulting in quantitave formation of complex **19** as a white powder. ^{1}H NMR (C_6D_6): δ 6.98 (t, 1H, J_{HH} = 7.3 Hz, *p*-C_6H_3), 6.84 (d, 2H, J_{HH} = 7.3, Hz, *m*-C_6H_3), 2.83 (vt, 4H, J_{PH} = 4.1 Hz, CH_2P), 1.18 (vt, 36H, J_{PH} = 6.9 Hz, C(CH_3)$_3$). ^{13}C-DEPT-135 NMR (C_6D_6): δ 125.40 (s, C_{para}), 122.74 (vt, J_{PC} = 10.2 Hz, C_{meta}), 33.09 (vt, J_{PC} = 10.7 Hz, *C*H$_2$P), 29.00 (vt, J_{PC} = 3.1 Hz, C(*C*H$_3$)$_3$). ^{31}P{^{1}H} (C_6D_6): δ 77.85 (s). FD-MS M$^+$ 612 (correct isotope pattern).

Me−O Activation by Ni(II). Formation of Complexes 21 and 22. A solution of **3** (59 mg, 0.14 mmol) in 5 mL of ethanol was added dropwise to a stirred solution of NiI_2 (44 mg, 0.14 mmol) in 5 mL of ethanol. The resulting green solution was heated overnight to 130 °C in a pressure flask and was pumped to dryness. After addition of toluene (20 mL), the reaction mixture was filtered through a cotton pad and was pumped to dryness, yielding 52 mg (61%) of **22** as a green powder. Use of compound **1** (instead of **3**) gave **21** in 67% yield. Data for **22**. ^{1}H NMR (C_6D_6): δ 6.88 (s, 2H, *m*-C_6H_2), 2.60 (br dvt, 2H, $^2J_{HH}$ = 13.0 Hz, left part of ABq, CH_2P), 2.56 (m, 2H, $^2J_{HH}$ = 13.0 Hz, right part of ABq, CH_2P), 2.30 (s, 3H, ArCH_3), 1.60 (vt, 18H, J_{PH} = 6.2 Hz, C(CH_3)$_3$), 1.37 (vt, 18H, J_{PH} = 6.0 Hz, C(CH_3)$_3$). ^{31}P-{^{1}H} NMR (C_6D_6): δ 81.01 (s). FD-MS M$^+$ 609 (correct isotope pattern). Anal. Calcd for $C_{25}H_{45}O_1P_2Ni_1I_1$: C, 49.29; H, 7.45. Found: C, 50.61; H 7.64. Data for **21**. ^{1}H NMR (C_6D_6): δ 7.04 (d, 2H, J_{HH} = 7.5 Hz, *m*-C_6H_3), 6.86 (t, 1H, J_{HH} = 7.6 Hz, *p*-C_6H_3), 2.58 (br dvt, 2H, J_{HH} = 13.2 Hz, left part of ABq, CH_2P), 2.39 (dvt, 2H, J_{HH} = 13.2 Hz, J_{PH} = 4.9 Hz, right part of ABq, CH_2P), 1.58 (vt, 18H, J_{PH} = 6.2 Hz, C(CH_3)$_3$), 1.34 (vt, 18H, J_{PH} = 6.0 Hz, C(CH_3)$_3$). ^{31}P-{^{1}H} NMR (C_6D_6): δ 77.69 (s). FD-MS M$^+$ 595 (correct isotope pattern).

Formation of Complex 23. A solution of **3** (40 mg, 0.094 mmol) in 2 mL of toluene was added dropwise to a stirred suspension of Pd-$(CF_3CO_2)_2$ (31 mg, 0.093 mmol) in 2 mL of toluene. The resulting red solution was stirred overnight at room temperature. ^{31}P{^{1}H} analysis of an aliquid showed **23** as the only product. Consequently, the reaction mixture was filtered through a cotton pad and pumped to dryness, resulting in quantitave formation of **23** as an orange powder. The complex can be recrystallized by slowly concentration a benzene solution to give orange X-ray suitable crystals. ^{1}H NMR (C_6D_6): δ 6.73 (s, 2H, *m*-C_6H_2), 3.03 (d, 2H, left part of ABq, $^2J_{HH}$ = 13.5 Hz, CH_2P), 2.41 (dvt, 2H, right part of ABq, $^2J_{HH}$ = 13.5 Hz, J_{PH} = 4.0 Hz, CH_2P), 2.17 (s, 3H, ArCH_3), 1.35 (vt, 18H, J_{PH} = 6.7 Hz, C(CH_3)$_3$), 1.05 (vt, 18H, J_{PH} = 6.4 Hz, C(CH_3)$_3$). ^{13}C-DEPT-135 NMR (C_6D_6): δ 127.89 (vt, J_{PC} = 2.0 Hz Hz, C_{meta}), 28.74 (vt, J_{PC} = 3.1 Hz, C(CH_3)$_3$), 28.40 (vt, J_{PC} = 2.4 Hz, C(CH_3)$_3$), 25.13 (vt, J_{PC} = 6.7 Hz, *C*H$_2$P), 21.22 (s, Ar*C*H$_3$). ^{31}P{^{1}H} (C_6D_6): δ 100.14 (s). FD-MS M$^+$ 643 (correct isotope pattern).

Competitive sp^2−sp^3 and sp^3−sp^3 C−O Bond Activation by Pd(II). Reaction of 4 with $Pd(CF_3CO_2)_2$. A solution of **4** (20 mg, 0.046 mmol) in 2 mL of toluene was added dropwise to a stirred suspension of $Pd(CF_3CO_2)_2$ (15 mg, 0.045 mmol) in 2 mL of toluene. The resulting yellow solution was loaded into a high-pressure vessel equipped with a stirring bar and heated for 3 h at 130 °C. Analysis of the gas phase by GC showed traces of methane (<3%). The red reaction mixture was filtered through a cotton pad and pumped to dryness, yielding an orange powder. ^{1}H, ^{1}H−^{1}H COSY, ^{1}H{^{31}P}, ^{31}P{^{1}H}, ^{13}C{^{1}H}, and ^{13}C-DEPT-135 NMR analysis of the powder showed the presence of **18** and **19** (9:1). CF_3CO_2Et was observed by NMR and GC-MS analysis.[72] Performing the same reaction for 16 h does not change the

product distribution. Complex **18** can be crystallized from the product solution at room temperature to give orange crystals.

Ar−O Hydrodeoxygenation (HDO) by Pd(II). Formation of Complexes 19 and 24. A red toluene solution (3 mL) of **18** or **23** (15 mg) was loaded into a Fischer−Porter pressure tube, charged with H_2 (30 psi), and heated at 180 °C for 8 h. $^{31}P\{^1H\}$ analysis of the colorless reaction mixture indicated the formation of complexes **19** or **24** in ∼55% yield, some decomposition products, and the consumption of the starting material (**18** or **23**). Subsequently, the reaction mixture was filtered through a cotton pad and pumped to dryness to yield a white powder. Complexes **19** and **24** were not further purified and have been identified in situ. Addition of an authentic sample of **19** to the reaction mixture of **18** resulted in overlap of signals in ^1H and $^{31}P\{^1H\}$ NMR. Data for **24**. ^1H NMR (C_6D_6): δ 6.63 (s, 2H, *m*-C_6H_2), 2.81 (vt, 4H, J_{PH} = 4.0 Hz, CH_2P), 2.18 (s, 3H, $ArCH_3$), 1.19 (vt, 36H, J_{PH} = 6.9 Hz, $C(CH_3)_3$). ^{13}C-DEPT-135 NMR (C_6D_6): δ 123.71 (vt, J_{PC} = 10.4 Hz, C_{meta}), 32.97 (vt, J_{PC} = 10.8 Hz, CH_2P), 29.03 (vt, J_{PC} = 3.5 Hz, $C(CH_3)_3$), 26.69 (s, $ArCH_3$). $^{31}P\{^1H\}$ (C_6D_6): δ 77.60 (s). FD-MS M^+ 627 (correct isotope pattern).

X-ray Crystal Structure Determination of Complex 12. An orange prismatic crystal (0.25 × 0.25 × 0.3 mm^3) was mounted on a glass fiber and flash frozen in a cold nitrogen stream (at 110 K) on a Rigaku AFC5R four-circle diffractometer mounted on a rotating anode with Mo Kα radiation and a graphite monochromator (λ = 0.710 73 Å). Accurate unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range 1.39° ≤ θ ≤ 27.52°, −32 ≤ h ≤ 33, −1≤ k ≤ 23, −15 ≤ l ≤ 3; ω scan method, scan speed 8°/min, typical half-height peak width = 0.45°, three standards were collected 40 times each with an 3% change in intensity, 6056 independent reflections. Structure **12** was solved using direct methods (SHELXS-92) and refined by full-matrix least-squares techniques based on F^2 (SHELXL-93). The final cycle of the least-squares refinement gave an agreement factor R_1 of 0.0330 for data $I > 2\sigma$ and R_1 = 0.0450 for all data based on 6056 reflections, goodness-of-fit on F^2 = 1.054, largest electron density = 0.928 e/Å. Hydrogens were calculated in idealized positions and refined in a riding mode. The molecule is a dimer with one-half a molecule per asymmetric unit, i.e., the full dimer is also the crystallographic dimer. The N(2)−N(2a) distance is 1.129 Å. An ORTEP view of the molecular structure and the adopted numbering scheme are shown in Figure 1. Table 1 gives details of the crystal structure determination.

X-ray Crystal Structure Determination of Complex 18. An orange plate crystal (0.1 × 0.1 × 0.05 mm^3) was mounted on a glass fiber and flash frozen in a cold nitrogen stream (at 110 K) on a Rigaku AFC5R four-circle diffractometer mounted on a rotating anode with Mo Kα radiation and a graphite monochromator (λ = 0.710 73 Å). Accurate unit cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range 1.14° ≤ θ ≤ 23.02°, −11 ≤ h ≤ 11, −17≤ k ≤ 17, −21 ≤ l ≤ 21; ω scan method, scan width = 1.2°, scan speed 8°/min, typical half-height peak width = 0.40°, three standards were collected 84 times each with an 4% change in intensity, 16 284 reflections collected, 8020 independent reflections. Structure **18** was solved using direct methods (SHELXS-92) and refined by full-matrix least-squares techniques based on F^2 (SHELXL-93). The space group is $P\bar{1}$ with two independent molecules per asymmetric unit. The final cycle of the least-squares refinement gave an agreement factor R_1 of 0.0630 (based on F^2) for data $I > 2\sigma I$ and R_1 = 0.1301 for all data based on 6408 reflections, goodness-of-fit on F^2 = 1.159, largest electron density = 0.701 e/Å. Hydrogens were calculated in idealized positions and refined in a riding mode.

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Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates for complexes **12** and **18** (16 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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