Carbon−Carbon vs Carbon−Hydrogen Bond Activation by Ruthenium(II) and Platinum(II) in Solution

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Reaction of $RuCl_2(PPh_3)_3$ with the bisphosphine {1,3,5-$(CH_3)_3$-2,6-($^iPr_2PCH_2)_2C_6H$} (**1**) under 30 psi H_2 results in quantitative C−C activation of an Ar−CH_3 bond to afford Ru(Cl)-(PPh_3){2,6-($^iPr_2PCH_2)_2$-3,5-$(CH_3)_2C_6H$} (**2**) and CH_4, whereas reaction of $RuCl_2(PPh_3)_3$ with **1** in the presence of NaO^{t}Bu results in selective $ArCH_2$−H bond activation to afford the benzylic complex Ru(Cl)(PPh_3){1-CH_2-2,6-($^iPr_2PCH_2)_2$-3,5-$(CH_3)_2C_6H$} (**7**). The identity of the 16-electron complex **2** was confirmed by reaction of the bisphosphine {2,6-($^iPr_2PCH_2)_2$-3,5-$(CH_3)_2C_6H_2$} (**3**), lacking the Ar−CH_3 group between the phosphine arms, with $RuCl_2(PPh_3)_3$. Metal insertion into an Ar−Et bond was observed as well. Follow-up of the reaction of RuHCl-(PPh_3)$_3$ with **1** by NMR and deuterium labeling studies reveal that the kinetic products of $ArCH_2$−H bond activation (**7** and H_2) are irreversibly converted into the thermodynamically more stable products of Ar−C bond activation (**2** and CH_4) via reversal of the C−H activation process. Reaction of (COD)$PtCl_2$ (COD = cycloocta-1,5-diene) with a stoichiometric amount of **1** at room temperature results in the exclusive formation of the benzylic Pt(II) complex Pt(Cl){1-CH_2-2,6-($^iPr_2PCH_2)_2$-3,5-$(CH_3)_2C_6H$} (**8**) and HCl. The iodide analogue of **8** has been characterized by X-ray analysis. Reaction of **8** with a 10-fold excess of HCl results in selective C−C bond activation to afford Pt(Cl){2,6-($^iPr_2PCH_2)_2$-3,5-$(CH_3)_2C_6H$} (**10**) and MeCl. The activation parameters for the overall process are $\Delta H^{\ddagger} = 10.6$ kcal/mol, $\Delta S^{\ddagger} = -40.1$ eu, and $\Delta G^{\ddagger}_{(298)} = 23.1$ kcal/mol in a benzene/dioxane solution (5.5:1 v/v) and $\Delta H^{\ddagger} = 2.1$ kcal/mol, $\Delta S^{\ddagger} = -65.4$ eu, and $\Delta G^{\ddagger}_{(298)} = 21.6$ kcal/mol in dioxane.

Introduction

Transition metal insertion into strong C−C single bonds in solution is rare, and mechanistic information about this process is scarce.[1] We have reported on C−C bond activation using phosphine-based substrates and various d^8 transition metals of group 9 and 10 in stoichiometric and even catalytic amounts.[2−13] Fluorinated substrates were used as well.[11,12] We report here on $ArCH_2$–H vs Ar−CH_3 bond activation with Ru(II) and Pt(II) in solution using aryl PCP-type ligands (PCP = [1,3,5-$(CH_3)_3$-2,6-($^iPr_2PCH_2)_2C_6R$], R = H, OMe, C(O)-OMe) and show that C−C bond activation in these systems is thermodynamically more favorable than the competing kinetically preferred C−H bond activation process. We have also observed de-ethylation of an aromatic system. A benzylic PCP−Pt(II) complex was fully characterized by X-ray analysis. Part of this work related to the Pt(II) chemistry has been communicated.[6] Activation of an Ar−Si bond by Pd(II) and Pt(II) was published recently.[14−16] To unambiguously identify the products of C−C bond activation, the PCP-type Ru(II) and Pt(II) complexes were independently prepared. Various aryl PCP-type complexes are known,[2−12,17−36]

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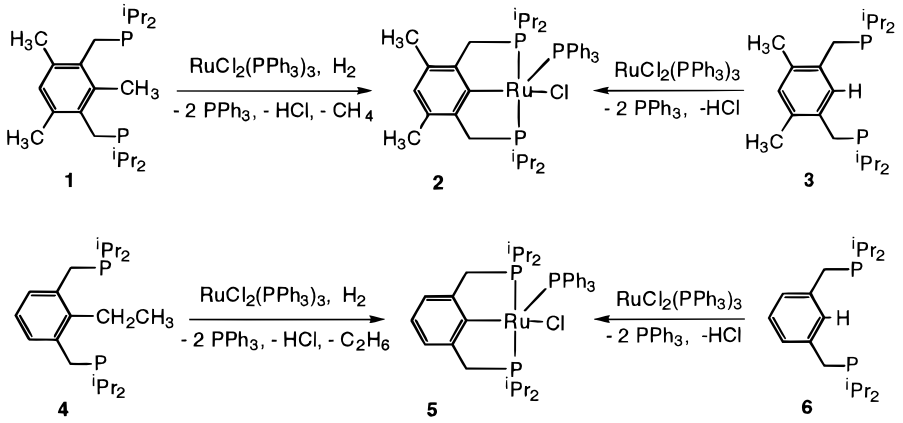
Scheme 1



and the formation and reactivity of related Ru(II) complexes is of current interest.[16,37−44] For instance, reactions of Ru(Cl)(PPh_3){2,6-(Ph_2PCH_2)$_2C_6H_3$} with various terminal alkynes resulted in their insertion into the Ru−C(aryl) bond.[38,45] An agostic interaction of an Ar−H bond of an aryl PCP ligand at a Ru(II) center was recently reported.[37]

Results and Discussion

Ar−CH_3 and Ar−CH_2CH_3 Bond Activation with Ru(II) under H_2. Reaction of a THF solution of $RuCl_2(PPh_3)_3$ with a stoichiometric amount of **1** under H_2 (30−35 psi) at 100 °C in a Fischer Porter pressure vessel resulted in quantitative formation of the air-sensitive, thermally stable complex **2** (Scheme 1). No other complexes were detected by ^{1}H and ^{31}P{^{1}H} NMR analysis of the green product solution. The gas phase was collected by standard vacuum line techniques and was analyzed by GC, showing formation of CH_4 in a nearly quantitative amount (>85%). Similar results were obtained using the phenylphosphine analogue of **1** {1,3,5-(CH_3)$_3$-2,6-(Ph_2PCH_2)$_2C_6H$}. Only the methyl group located between the two phosphine arms undergoes C−C bond activation. The fact that the other two Ar−CH_3 groups remain unaffected suggests that the C−C bond activation takes place in an intermediate in which the two phosphines are coordinated to the metal center, as observed for similar PCP substrates with Pt(II).[27] Phosphorus chelation precedes Ar−H bond activation in a PCP system with Ru(II).[37] Complex **2** was unambiguously identified by various NMR techniques, by MS, and by comparison to an authentic sample. It was obtained independently by reaction of a THF solution of $RuCl_2(PPh_3)_3$ with **3**, lacking one methyl substituent at the aromatic ring, at 100 °C in a sealed pressure vessel (Scheme 1). The mass spectrum of **2** contains the molecular ion (M^+ 763), having a correct isotope pattern, and a signal at *m*/*z* 728 corresponding to the elimination of Cl. Analogous square-pyramidal Ru(II) complexes having a meridional PCP-type ligand and PPh_3 occupying the apical position were reported.[38,40,45] The NMR data of **2** are fully consistent with such a geometry,[38,40,45−48] which is theoretically favored over a trigonal bipyramidal structure for d^6 metal complexes in the absence of steric effects.[49,50] For instance, the ^{13}C{^{1}H} NMR spectrum of **2** contains two characteristic resonances at δ 172.74 (dt, cis-$^2J_{PC}$ = 18.3 and 4.7 Hz), and at δ 33.28 (vt, $^{(2+4)}J_{PC}$ = 24.4 Hz), which may be interpreted (using ^{13}C-DEPT-135 NMR) as the ipso carbon σ bound to the metal center in cis position to the phosphine ligands and the magnetically equivalent carbons of the ArCH_2P moieties, receptively.

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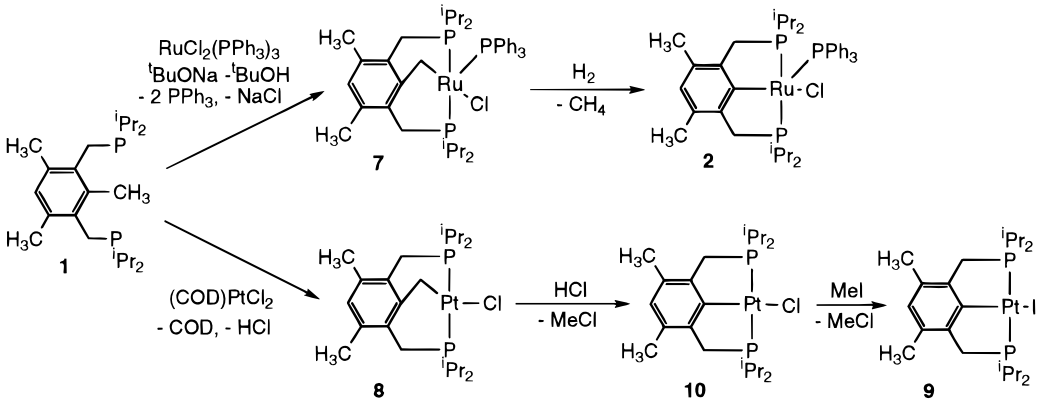
Scheme 2



The $^{31}P\{^1H\}$ spectrum displays two signals at δ 76.47 (t, PPh_3) and δ 45.83 (d, PCP) with cis-$^2J_{PP}$ = 31.5 Hz in the expected 1:2 ratio. The large downfield shift of the η^1-bound PPh_3 ligand ($\Delta\delta \sim 77$ ppm) is characteristic for square-pyramidal Ru(II) complexes with apical phosphine ligands.[38,39,44,46−48] The ^1H NMR shows a typically ABq pattern at δ 2.32 with ΔAB = 460 Hz and $^2J_{HH}$ = 16.9 Hz coupled by two magnetically equivalent phosphorus atoms of the PCP ligand ($^{(2+4)}J_{PH}$ = 9.9 Hz) for the diastereotopic Ar*CH*$_2$P groups.

De-ethylation was observed upon treatment of a THF solution of the phosphine 1-Et-2,6-(^{i}Pr$_2$PCH$_2$)$_2$C$_6$H$_3$ (**4**) and $RuCl_2(PPh_3)_3$ with H_2 (30−35 psi) at 100 °C in a Fischer Porter pressure vessel, resulting in formation of complex **5** and C_2H_6 in a low yield (∼15% by $^{31}P\{^1H\}$ NMR and GC; mainly starting material remained). Although **5** was not isolated, it was readily identified by comparison to an authentic sample, which was prepared by reaction of a THF solution of $RuCl_2(PPh_3)_3$ with **6** at 100 °C in a sealed pressure vessel (Scheme 1). Complexes **2** and **5** have almost identical spectroscopic properties in the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR. Similar results were obtained using the Ph analogue of **4** (with phenyl groups replacing isopropyl substituents on P), affording C_2H_6 and the known complex Ru(Cl)(PPh$_3$){2,6-(Ph$_2$PCH$_2$)$_2$C$_6$H$_3$} also in ∼15% yield.[37−39] The latter and the related square-pyramidal complex RuCl(PPh$_3$)(2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$) were recently fully characterized by X-ray analysis.[39,40] The low yield with **4** in comparison to the Ar−H and Ar−CH_3 PCP systems (**1**, **3**, and **6**) is most probably a result of a significantly increased steric hindrance imposed by the ethyl group. The Ar−CH_3 bond is slightly stronger than the Ar−CH_2-CH_3 bond (compare bond dissociation energy (BDE) of Ph−CH_3 = 102 kcal/mol vs Ph−CH_2CH_3 = 96.3 kcal/mol).[51,52] Although a consecutive sp^3−sp^3, sp^2−sp^3 C−C bond activation process forming **5** and 2 equiv of CH_4 would have been thermodynamically more favorable (by about 28 kcal/mol),[5,52] CH_4 was not observed by GC analysis. Direct Ar−Et bond activation was also observed upon reaction of Rh(I) with **4** and with its Ph or ^{t}Bu analogues (containing Ph and ^{t}Bu groups instead of isopropyl substituents on P) in quantitative yield,[9,10] indicating that sp^2−sp^3 C−C bond activation is kinetically preferable to sp^3−sp^3 C−C bond activation in these Ar−Et PCP systems, regardless of the higher bond strength (ΔBDE{Ph−CH_2CH_3 − PhCH$_2$−CH_3} = ∼24.5 kcal/mol)[33,34] and of the electron density and the bulk at the d^6 Ru(II) or d^8 Rh(I) transition metal center.[5,10]

It is noteworthy that Bergman reported C−C bond cleavage in hexafluoroacetone with (Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$-Ru(H)(OH) to afford (Me$_2$PCH$_2$CH$_2$PMe$_2$)$_2$Ru(H)(OC(O)-CF_3) and CF_3H and the stepwise degradation of a neopentyl ligand to a trimethylene−methane ligand by Ru(II) via a β-alkyl migration process.[53−56] Chaudret et al. demonstrated that reaction of the electrophilic [Cp*Ru$^+$] species with the A-rings of steroids resulted in cleavage of various C−X bonds including C−C and C−C bonds driven by an aromatization process.[57,58] Electrochemically induced two-electron oxidative cleavage of a C−C single bond of cyclooctatetraene with [Cp$_2$-Ru$_2$(μ-cyclo-C_8H_8)] is also known.[59]

ArCH$_2$−H Bond Activation with Ru(II). Reaction of $RuCl_2(PPh_3)_3$ with a stoichiometric amount of **1** and ^{t}BuONa in THF at 80 °C (∼30 min in a sealed tube) resulted in the formation of the benzylic Ru(II) complex **7** by a selective sp^3 C−H bond activation process (Scheme 2). Products resulting from metal insertion into the stronger Ar−CH_3 bond were not observed by ^1H and $^{31}P\{^1H\}$ NMR (ΔBDE = Ar−CH_3 − ArCH_2−H = 14 kcal/mol).[51] PPh_3 is readily displaced by the bisphosphine ligand **1,** but its removal from the product solutions is difficult. The reaction proceeds also in the absence of base but rather sluggishly. Complex **7** was characterized by various NMR techniques, MS, and elemental analysis. The $^{31}P\{^1H\}$ NMR spectrum of **7** showed a doublet resonance at δ 24.1 for the magnetically equivalent phosphorus atoms of the meridional bisphosphine ligand and a triplet resonance at δ 73.6 with cis-$^2J_{PP}$ = 29.6 Hz for the apical PPh_3 ligand. The structure is fully supported by ^1H and ^{13}C NMR spectroscopy. For instance, the Ar*CH*$_2$Ru moiety appears in the $^{13}C\{^1H\}$ NMR spectrum at δ 13.56 as a virtual quartet with $^2J_{PC} \approx 5.5$ Hz, respectively, and in the ^{13}C-DEPT-135 NMR a negative signal is observed indicative of an even number of protons. In the ^1H NMR spectrum of **7**, the Ar*CH*$_2$Ru group appears as a triplet at δ 3.28 with $^2J_{PH}$

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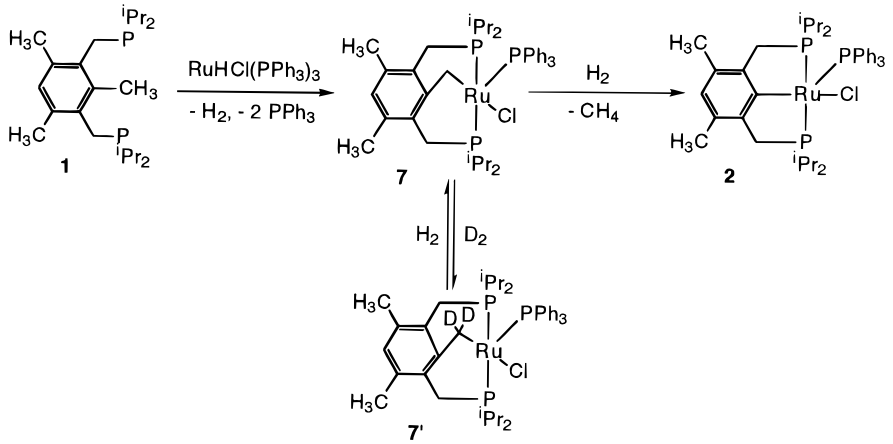
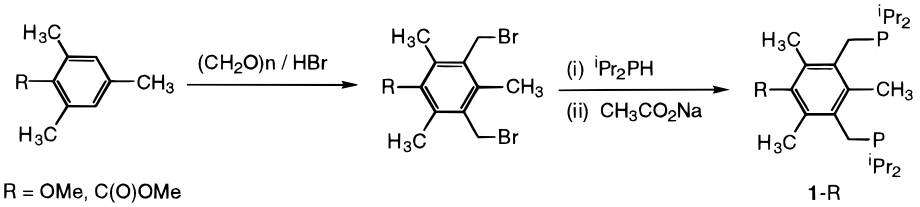
Scheme 3



Scheme 4



= 15.0 Hz, which collapses into a singlet resonance in the $^1H\{^{31}P\}$ NMR spectrum. The ipso carbon of the aromatic ring is probably close to the metal center,[38] but no evidence for any bonding interaction nor distortion of aromaticity is observed. For instance, the two magnetically equivalent Ar−CH_3 groups appear in the ^1H NMR spectrum as a sharp singlet at δ 2.20, while in the free ligand **1** and in the Ar−Ru complex **2** these groups are observed at δ 2.38 and δ 2.21, respectively. The mass spectrum of **7** shows the molecular ion (M^+ 777) having a correct isotope pattern. Complex **7** is thermally stable under the applied reaction conditions for at least 24 h, even in the presence of 1 equiv of HCl. However, addition of excess HCl (3−10 equiv) afforded mixtures of unknown products at 80 °C. No products indicative of C−C bond activation were observed either by ^1H or $^{31}P\{^1H\}$ NMR.

$ArCH_2$−H vs Ar−CH_3 Bond Activation with Ru(II). Reacting the hydrido complex $RhHCl(PPh_3)_3$ with a stoichiometric amount of **1** in THF at 100 °C in a sealed vessel resulted in quantitative formation of complex **2** and CH_4, as judged by NMR analysis of the product solution and the GC analysis of the gas phase, using authentic samples. Notably, no additional reagent is necessary in this system in order to the drive the C−C bond activation process. Monitoring the reaction at 60 °C in THF and at 110 °C in dioxane by $^{31}P\{^1H\}$ NMR reveals the initial formation of the benzylic Ru(II) complex **7**, which converts in time irreversibly to **2** and CH_4 (by GC). This shows that the C−C bond activation process generating an Ar−Ru(II) species **2** and CH_4 is thermodynamically more favorable than the competing C−H bond activation process generating an $ArCH_2$−Ru(II) complex **7** and presumably H_2. Formation of H_2 was not detected directly. In support of this, reaction of **7** with 1 equiv of H_2 in THF-d_8 at 80 °C in a sealed tube resulted in the formation of complex **2** and CH_4 (∼90% conversion) after 24 h, as observed by ^1H and $^{31}P\{^1H\}$ NMR. In the absence of H_2, complex **7** is stable under these reaction conditions (Scheme 3).

Deuterium incorporation into the Ar−CH_2−Ru group of **7** and C−C bond activation were observed by ^1H and $^{31}P\{^1H\}$ NMR upon treatment of a C_6D_6 solution of **7** with 2 equiv of D_2 at 60 °C (∼30% H/D exchange and ∼10% C−C bond activation after 2 h in a sealed tube), indicating that the sp^3 C−H bond activation is reversible and fast in comparison with the competing C−C bond activation process. In the case of Ir(I) and Rh(I) and the ^{t}Bu analogue of **1**, C−C activation is kinetically (and thermodynamically) more favorable than C−H activation, with $\Delta\Delta G^{\#}_{(CH-CC)} = 0.342$ kcal/mol for Ir(I) and 0.501 kcal/mol for Rh(I) in benzene at 293 K.[7]

While the Ar−CH_3 bond is substantially stronger than the $ArCH_2$−H bond, this is apparently more than compensated by the formed CH_3−H and Ar−M bonds. The chelate ring size may also play a role, although for related Rh(I) complexes electronic factors play a dominant role in controlling the relative stability of the products of C−H and C−C bond activation.[4]

$ArCH_2$−H vs Ar−CH_3 Bond Activation Using Para-Substituted Methoxy and Carbomethoxy PCP Substrates. To evaluate the role of the aromatic ring in the C−H and C−C bond activation processes, we prepared the new substrates **1**−R (R = OMe, C(O)OMe) by bromomethylation of mesitylene derivatives,[7,60] followed by phosphination (Scheme 4).[7]

Reactions of $RuHCl(PPh_3)_3$ with 1 equiv of the ligands **1**, **1**−OMe and **1**−C(O)OMe, respectively, in THF at 58 °C were monitored by $^{31}P\{^1H\}$ NMR at room temperature in a sealed NMR tube, showing the initial formation of the product of C−H bond activation (**7**, **7**−R, Figure 1). Formation of **7**, **7**−R is reversible (see below), and they are gradually transformed into the C−C

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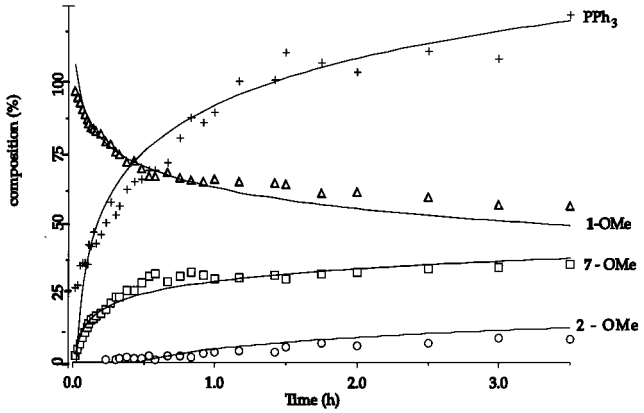

Figure 1. $^{31}P\{^1H\}$ NMR follow-up of the reaction of **1**−OMe (10 mg, 0.024 mmol) with 1 equiv of $RuHCl(PPh_3)_3$ (25 mg, 0.025 mmol) in 1 mL of THF at 58 °C in a sealed tube.

activation products (**2**, **2**−R). Interestingly, the rate of conversion of the products of C−H bond activation into the products of C−C bond activation is dependent on the substituent para to the cleaved C−C bond, following the order C(O)OMe > H > OMe. For instance, after 10 h the ratios of the products of C−H and C−C bond activation are distinctively different: C−H:C−C = 1:1.4 for R = C(O)OMe, 1:1 for R = H, and 1:0.4 for R = OMe. Thus, it seems possible to influence the overall $ArCH_2$−H vs Ar−CH_3 bond activation processes by altering the electron density on the aromatic ring of the PCP ligand **1**. Identification of the methoxy- and carboxy-substituted products of C−H and C−C bond activation was done by independent preparation of authentic compounds. As shown for ligand **1** (Schemes 1 and 2), treatment of **1**−OMe and **1**−C(O)OMe with $RuCl_2(PPh_3)_3$ under H_2 afforded the products of C−C bond activation (**2**−R and CH_4), whereas reaction of **1**−R with $RuCl_2(PPh_3)_3$ in the presence of ^{t}BuONa yielded the products of C−H bond activation (**7**−R). The benzylic (**7**−R) and aryl (**2**−R) compounds exhibit almost identical spectroscopic properties in the ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR, except for the presence of the methoxy or carboxy groups. The electronic difference is quite pronounced in ^{13}C NMR, which is an excellent tool for analyzing electronic trends in σ aryl-bound metal complexes.[28,61,62] For instance, in complex **2** the ipso carbon σ bound to the metal center is observed at δ 172.74, while in **2**−OMe this characteristic carbon is observed at δ 165.03, shifted upfield due to the higher electron density on the aromatic ring.

To ensure identical reaction conditions, we performed a competition experiment by reacting 1 equiv of $RuHCl(PPh_3)_3$ with an equimolar amount of ligands **1**−OMe and **1**−C(O)OMe at 65 °C in THF in one sealed tube (Figure 2). Monitoring this reaction by $^{31}P\{^1H]$ NMR at room temperature unambiguously showed that in the case of the electron-withdrawing carboxy substituent **1**−C(O)OMe the product of C−C bond activation **2**−C(O)-OMe is dominant (after 10 h, ratio C−H:C−C = 1:1.9), whereas the C−H activation product prevails with the electron-donating methoxy group (after 10 h, ratio C−H:C−C = 1:0.47). No intermediate compounds were observed and the ratio between **1**−OMe and **1**−C(O)OMe did not change during the experiment, indicating that chelation of the PCP ligands occurs with the same rate and is relatively slow.

Deuterium incorporation into the Ar−CH_2−Ru group of **7**−R was observed by $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR upon treatment of a C_6D_6 solution of an equimolar amount of **7**−OMe and **7**−C(O)OMe with 1 equiv of D_2 at room temperature. After 22 h, approximately 40% H/D exchange was observed for **7**−C(O)OMe and only 10% for **7**−OMe by $^1H\{^{31}P\}$ and $^{31}P\{^1H\}$ NMR, unambiguously showing that the rate of the H/D exchange process is significantly dependent on R: C(O)OMe > OMe regardless of the rate-determining step. The process was readily reversed upon treatment of the reaction mixture with H_2 at room temperature. No C−C bond activation took place and no intermediates were observed under these conditions. As is well documented, cyclometalation can be a highly reversible process.[2,3,63−67] A rare case of catalytic benzylic C−H bond activation involving a Ru(II)/Ru(0) mechanism was reported.[68,69]

Mechanistically, oxidative addition of H_2 affording a Ru(IV) intermediate such as **A** is possible (Scheme 5). Six-coordinated dihydrido-Ru(IV) phosphine complexes are known.[70] No C−C bond activation was observed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy during the H/D exchange with **7**−OMe and **7**−C(O)OMe at room temperature, clearly demonstrating that the reversible $ArCH_2$−H reductive elimination/oxidative addition process (**A** ↔ **B**) occurs prior to the slower C−C bond activation step. The rate of H/D exchange between D_2 and the benzylic protons (Ar−CH_2−Ru) of a 1:1 mixture of **7**−OMe and **7**−C(O)OMe follows the same trend as observed for the conversion of the products of C−H bond activation (**7**, **7**−R, and H_2) into the products of C−C bond activation (**2**, **2**−R, and CH_4), indicating that the observed substituent effect on the overall process primarily originates from the reversible C−H bond activation step. The net substituent effect on the C−C bond activation step, if any, seems insignificant. This might point toward a concerted oxidative addition process **C** with little, if any, participation of the aromatic π system. Formation of an arenium species **D** in the rate-determining step would have expected to show an opposite substituent effect. van Koten et al. postulated the formation of an arenium species in the activation of an Ar−H bond in a PCP ligand by a Ru(II) dichloride complex.[40] The postulated methyl−hydrido−Ru(IV) species **E** is expected to undergo rapid and irreversible C−H reductive elimination, yielding complex **2** and CH_4. A three-center nonpolar transition state was recently elucidated for the direct Ar−CH_3 bond activation with

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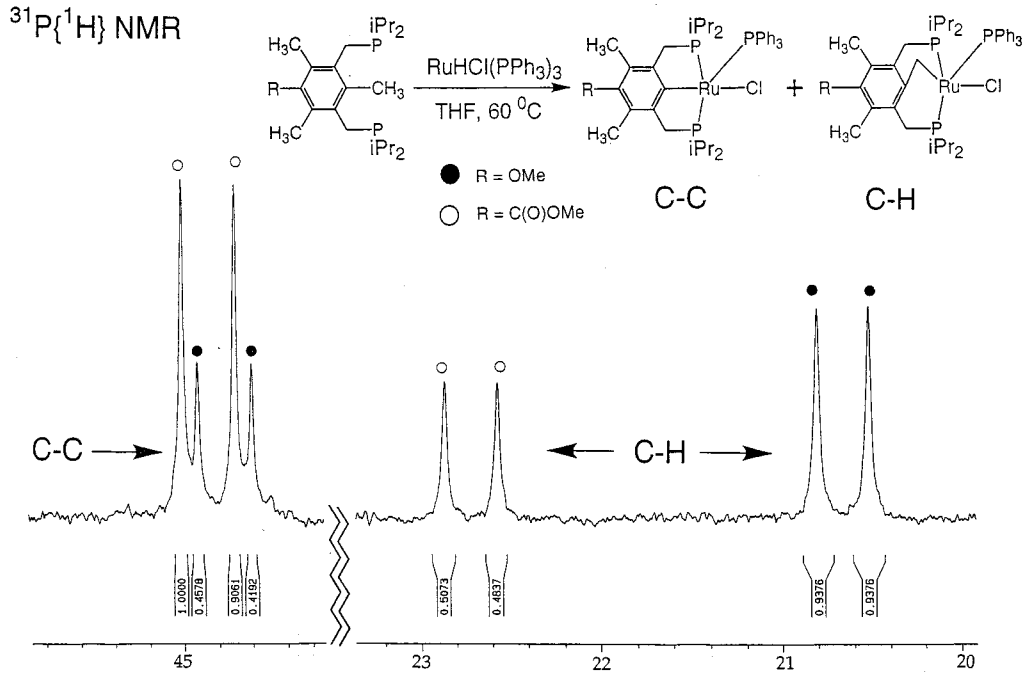
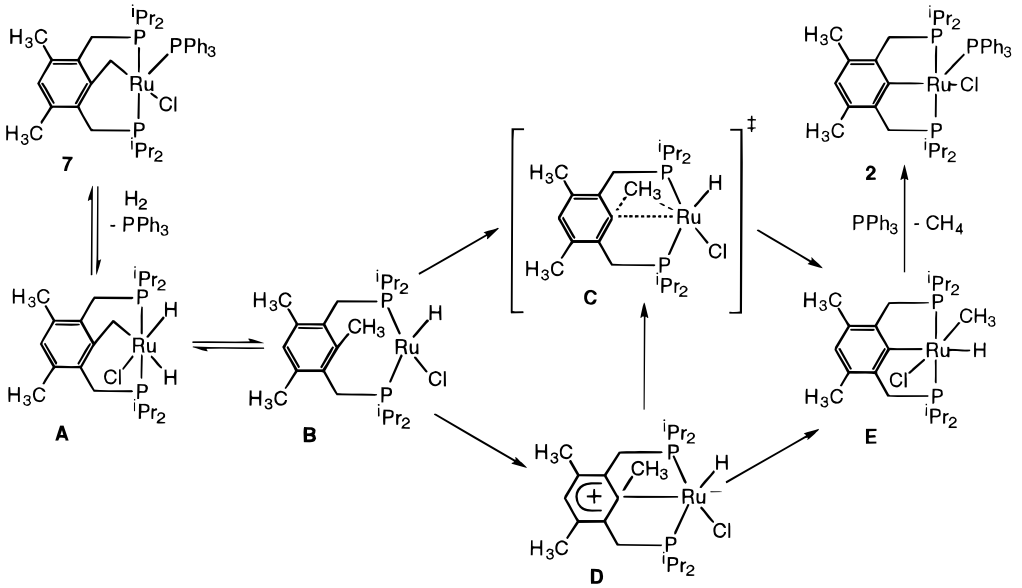


Figure 2. $^{31}P\{^1H\}$ NMR spectrum of a competition experiment with ligands **1**−OMe, **1**−C(O)OMe (5 mg, 0.012 mmol, each), and $RuHCl(PPh_3)_3$ (25 mg, 0.025 mmol) in 1 mL of THF at 65 °C after ∼10 h. Only the $PiPr_2$ groups are shown.

Scheme 5



the ^{t}Bu analogue of **1** and Rh(I) and Ir(I), which takes place even at room temperature.[7] However, other pathways cannot be rigorously excluded in this system.[71] Regardless of the exact mechanism, selective sp^2-sp^3 Ar−C bond cleavage with Ru(II) takes place under mild reaction conditions with significantly different electron densities at the aryl moiety of the PCP ligands, and the *overall* process (**7** + H_2 → **2** + CH_4) is clearly promoted by an electron-withdrawing carboxy substituent para to the cleaved C−C bond of **7**.

$ArCH_2$−H vs Ar−CH_3 Bond Activation with Pt(II). Treatment of a THF solution of **1** with $(COD)PtCl_2$ (COD = cycloocta-1,5-diene) at room temperature results in C−H bond activation to form HCl and **8** quantitatively by $^{31}P\{^1H\}$ NMR (Scheme 2). A lower yield (∼50%) of **8** is obtained with $(MeCN)_2PtCl_2$ and **1** in CH_2Cl_2.[6] Activation of benzylic C−H bonds by Pt(II) has been reported.[8,63,72,73] Displacement of COD from $(COD)PtCl_2$ by the analogue of **1** in THF at room temperature results in the quantitative formation of a compound with two coordinated phosphines to one metal center $Pt(Cl_2)\{1,3,5\text{-}(CH_3)_3\text{-}2,6\text{-}(Ph_2PCH_2)_2C_6H\}$.[27] Such a species is likely to be an intermediate in the reaction of **1** as well. The benzylic Pt(II) complex **8** has been identified by ^1H, ^{31}P, and ^{13}C NMR spectroscopy, FD−

(71) We were not able to observe the formation of Ru(II)−H or Ru(O) species by ^1H and $^{31}P\{^1H\}$ NMR when the H/D exchange was performed in the presence of ∼1 equiv of triethylamine. Therefore a σ-bond metathesis mechanism involving release of HCl and formation of a Ru(0) complex by $ArCH_2$−H reductive elimination from a benzylic Ru(II)−H species seems less likely.

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MS, and elemental analysis. The methylene group (Ar*CH*$_2$Pt) of **8** appears in the $^{13}C\{^1H\}$ NMR spectrum as a triplet at δ 1.12 (cis $^2J_{PC}$ = 4.8 Hz) clearly flanked by ^{195}Pt satellites ($^1J_{PtC}$ = 432.0 Hz), and the ^{13}C-DEPT-135 NMR indicated an even number of protons. In the ^{1}H NMR spectrum this alkyl group appears as a triplet at δ 2.32 ($^3J_{PH}$ = 9.9 Hz) flanked by ^{195}Pt satellites ($^2J_{PtH}$ = 92.0 Hz), which collapses into a singlet upon ^{31}P decoupling. The geometry renders the protons of the Ar*CH*$_2$P groups (AB quartet) and the four ^{i}Pr substituents magnetically nonequivalent. Importantly, the two Ar−CH$_3$ groups and the para proton appear as singlets at δ 2.18 and 6.51, respectively, clearly demonstrating that there is no distortion of aromaticity due to an Ar···M interaction, as recently proposed for PCP−Ru(II) complexes.[38] The FD−MS of **8** shows the molecular ion (M^+ 610) having the expected isotopic pattern. The $^{31}P\{^1H\}$ NMR spectrum of **8** shows a sharp resonance at δ 69.05 flanked by ^{195}Pt satellites ($^1J_{PtP}$ = 3539 Hz), indicating that both phosphorus atoms are mutually trans and magnetically equivalent. The low-field chemical shift reflects a deshielding effect of the phosphorus atoms due to the formation of two six-membered chelated rings. The iodide analogue of **8** was obtained by its reaction with MeI at 100 °C in toluene-d_8.[74] The X-ray analysis of this complex **9** reveals that the ipso-carbon is close to the metal center (Pt(1)···C(1) = 2.726 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 1.382(1)···1.403(10) Å) and by the ring planarity. Least-squares planar analysis through the aromatic ring shows a mean deviation from planarity of 0.0314 Å. The sp^2−sp^3 C−C bond (C(1)−C(10) = 1.476(10) Å) is not weakened by bonding of C(10) to the metal center, and the C(1)−C(10)−Pt(1) angle (98.9(4)°) is indicative of an approximate tetrahedral geometry around C(10).

In contrast to the reactivity of the benzylic Ru(II) complex **7** with H_2 (Scheme 3), complex **8** was recovered unchanged after treatment with H_2 (30 psi) at temperatures up to 150 °C in various solvents. However, mild heating of the thermally stable **8** in a dioxane solution with a 10-fold excess of HCl results in the selective formation of methyl chloride and the Ar−Pt complex **10** (Scheme 2), whereas treatment of the analogous Ru(II) complex **7** with a slight excess of HCl resulted in decomposition. The C−C bond activation proceeds even at *room temperature* (~20% conversion in 2 days by $^{31}P\{^1H\}$ NMR, starting material remained). Apparently, the choice of the methylene scavenger and the transition metal is crucial for reversing the kinetically preferred C−H bond cleavage and enabling a thermodynamically favorable C−C bond activation process.[75] Metal-selective bond activation has been demonstrated in C−H vs C−C,[8] C−H vs C−Si,[14−16] and alkyl vs aryl−O bond activation.[17,18] Characterization of complex **10** is unambiguous and is based on ^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analysis, and FD−MS. In addition, complex **10** was prepared independently by reaction of ligand **3**, lacking the Ar−CH$_3$ group between the phosphine arms, with (COD)PtCl$_2$ in toluene at 120 °C for 2 h (in a sealed vessel). The spectroscopic features of **10** are similar to analogous d^8 transition metal PCP complexes of group 10.[18−20,23,26] The ^{t}Bu analogue of **10** was first reported by Shaw et al.[19] The ^{1}H spectrum of **10** shows one sharp triplet resonance at δ 2.72 with J_{PH} = 4.2 Hz for the four protons of the two equivalent CH$_2$P groups. The signal collapses to a singlet flanked by platinum satellites with J_{PtH} = 8.5 Hz upon phosphorus decoupling in the $^1H\{^{31}P\}$ NMR. The $^{31}P\{^1H\}$ NMR exhibits one sharp singlet resonance at δ 56.4 ac-

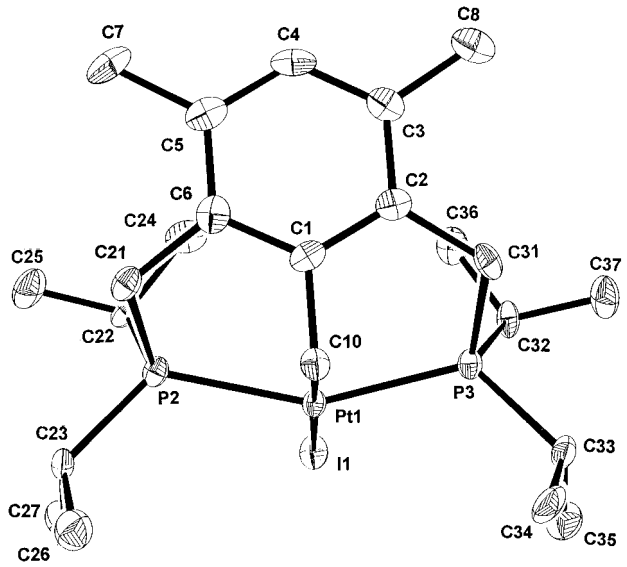


Figure 3. ORTEP view of Pt(I){1-CH$_2$-2,6-(^{i}Pr$_2$PCH$_2$)$_2$-3,5-(CH$_3$)$_2$C$_6$H}, **9**. Selected bond lengths (Å): Pt(1)−C(10) = 2.075(6); Pt(1)−P(3) = 2.296(2); Pt(1)−P(2) = 2.307(2); Pt(1)−I(1) = 2.6864(6); C(1)−C(10) = 1.476(10); C(3)−C(8) = 1.519(11); C(5)−C(7) = 1.509(10). Selected bond angles (deg): C(1)−C(10)−Pt(1) = 98.9(4); C(10)−Pt(1)−P(3) = 81.4(2); C(10)−Pt(1)−P(2) = 83.9(2); P(3)−Pt(1)−P(2) = 153.08(7); C(10)−Pt(1)−I(1) = 177.5(2); P(3)−Pt(1)−I(1) = 98.89(5); P(2)−Pt(1)−I(1) = 96.75(5).

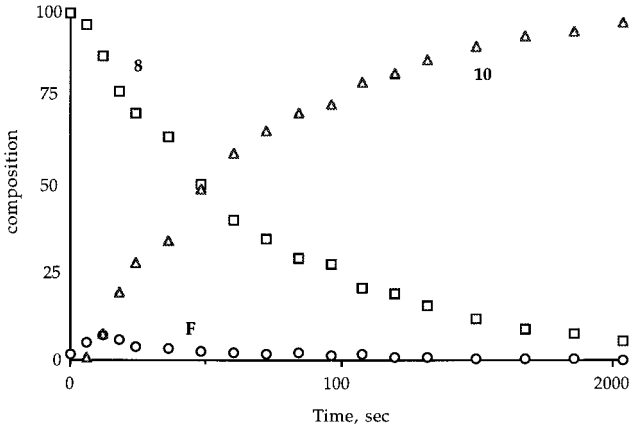
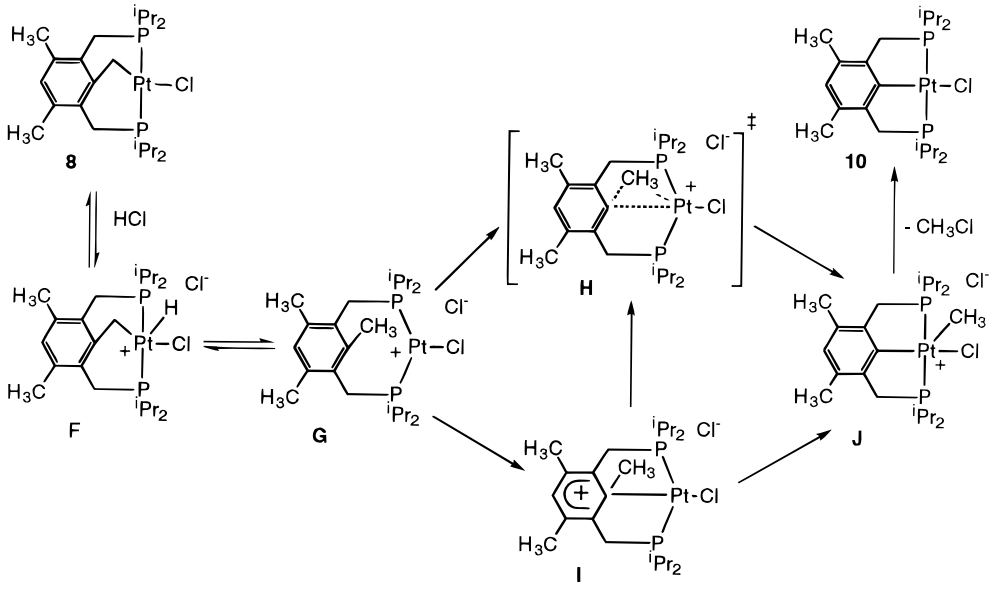


Figure 4. $^{31}P\{^1H\}$ NMR follow-up of the reaction of **8** (24 mg, 0.041 mmol) in benzene (550 μL) with HCl (4 M dioxane solution; 100 μL) to **10** and MeCl at 82 °C.

(74) Treatment of **8** with a 10-fold excess of $^{13}CH_3I$ in toluene-d_8 at 100 °C in a sealed tube resulted in halide exchange to afford $^{13}CH_3Cl$ and Pt(I){1-CH$_2$-2, 6-(^{i}Pr$_2$PCH$_2$)$_2$-3,5-(CH$_3$)$_2$C$_6$H} (**9**). Formation of $^{13}CH_3Cl$ was observed by ^{1}H and $^{13}C\{^1H\}$ NMR of the product solution. The reaction was monitored by $^{31}P\{^1H\}$ NMR at room temperature showing that the overall process (**8** → **9**) is first order in **8** with k_{obs} = 1.33 × 10^{-3} s^{-1} at 100 °C, corresponding to $\Delta G^{\ddagger}_{(373K)}$ = 20.5 kcal/mol. No intermediate species were observed.

(75) Reacting a THF solution of **7** with a 9-fold excess of HSi(OEt)$_3$ at 80 °C overnight in a sealed tube resulted in the formation of **2** and CH$_3$Si(OEt)$_3$ in a low yield (~20%; no starting material **7** remained), as judged by $^{31}P\{^1H\}$ NMR and GC−MS analysis of the product solution. No C−C bond activation was observed upon treatment of **8** with HSi(OEt$_3$).

Scheme 6



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companied by platinum satellites ($^1J_{PPt}$ = 2857 Hz), rendering both phosphorus atoms magnetically equivalent. The $^1J_{PtP}$ coupling is typical for two trans phosphorus atoms coordinated to Pt(II). The FD−MS spectrum shows the molecular ion (M^+ 596) and a logical isotope pattern. Formation of methyl chloride was confirmed by NMR and GC analysis of the product solution and by comparison with an authentic sample.

$^{31}P\{^1H\}$ NMR follow-up of the reaction of complex **8** with a 10-fold excess of HCl in a benzene/dioxane solution (5.5:1 v/v) reveals the formation of a new species (presumably **F**, Figure 4; Scheme 6), giving rise to a small singlet at δ 35.23 ppm flanked by platinum satellites ($^1J_{PtP}$ = 1919.3 Hz). Addition of the base $H_2N(CH_2)_3OH$ to the reaction mixture resulted in disappearance of **F** and an increase of **8**. The relatively small platinum−phosphorus coupling constant might suggest a Pt(IV) complex,[76] although further identification is hampered by the low concentration and instability of the intermediate. Formation of **F** was not observed in dioxane or at temperatures above 100 °C. Regardless of the exact nature of this adduct, the addition of HCl to the Pt(II) complexes is not the rate-determining step. HCl oxidative addition to Pt(II) complexes is known to be reversible and relatively fast. Bercaw et al. observed that *trans*-$(PEt_3)_2Pt(II)(CH_3)Cl$ reacts with HCl in CD_2Cl_2 at low temperatures to give $(PEt_3)_2Pt(IV)(CH_3)(H)Cl_2$ prior to C−H reductive elimination to afford CH_4 and $(PEt_3)_2Pt(II)Cl_2$.[77] The process **8** → **10** slows down upon addition of 2.5 equiv of $^tBu_4NCl$ to the dioxane solution, which has been shown to bring about deprotonation of alkylhydrido-Pt(IV) species.[77] The activation parameters for the conversion of **8** with a 10-fold excess of HCl to **10** and MeCl in dioxane and in benzene/dioxane (5.5:1 v/v) solutions were determined by $^{31}P\{^1H\}$ NMR. The overall process (**8** → **10**) is first order in **8** with $\Delta H^‡$ = 10.6 kcal/mol, $\Delta S^‡$ = −40.1 eu, and $\Delta G^‡_{(298)}$ = 23.1 kcal/mol in a benzene/dioxane (5.5:1 v/v) solution. In dioxane the values of $\Delta H^‡$ and $\Delta S^‡$ are 2.1 kcal/mol and −65.4 eu, respectively, and $\Delta G^‡_{(298)}$ = 21.6 kcal/mol. An inverse isotope effect of $k_D/k_H \approx 1.5$ was observed at 130 °C (by $^{31}P\{^1H\}$ NMR) when the reaction of **8** and HCl was compared in dioxane/H_2O vs dioxane/D_2O solutions (Figure 5). Both normal and inverse isotope effects have been reported for C−H reductive elimination from alkylhydrido-Pt(IV) species, and the values differ widely. It is likely that C−C bond activation becomes more competitive with C−H bond cleavage upon deuterium incorporation in the $ArCH_3$ group.

Complex **10** was recovered unchanged when treated with excess CH_3Cl at elevated temperatures. This indicates that the C−C bond activation process generating CH_3Cl is thermodynamically more favorable than the competing C−H bond activation process which generates HCl, while the latter process is kinetically preferred. Although the CH_3−Cl bond is weaker than the H−Cl bond (BDE 84 vs 103 kcal/mol, respectively)[78] and the Ar−CH_3 bond is stronger than the $ArCH_2$−H bond by about 14 kcal/mol,[51] the C−C bond activation process thermodynamics are compensated by the formed strong Ar−Pt and H−CH_2Cl bonds (BDE H−CH_2Cl = 100.9 kcal/mol). Moreover, the Ar−M σ bond is expected to be much stronger than the benzylic $ArCH_2$−M bonds.[79,80] Thus, the kinetic products of C−H bond activation of **1** by Pt(II) (**8** + HCl) can be readily converted into the thermodynamically more favored ones (**10** + MeCl) by an irreversible C−C bond activation process using a 10-fold excess of HCl. Reaction of **8** with H_2 to afford **10** and CH_4 would have been even more favorable thermodynamically, suggesting that the lack of reactivity of **8** with H_2 is for kinetic reasons.

Mechanistically, protonation of the kinetically favored C−H activation product **8** with excess HCl probably results in formation of **F**, which can form complex **G** by reductive elimination. **G** is likely to be a common intermediate for both the C−H and C−C bond activation

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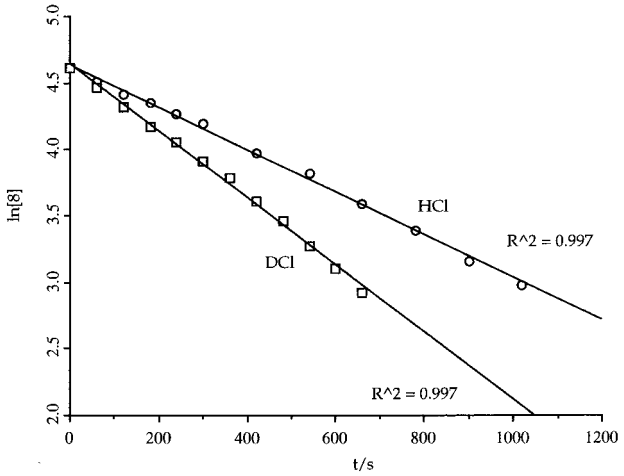
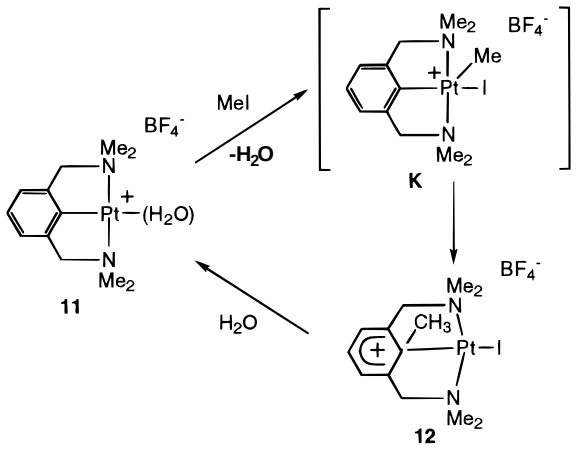


Figure 5. $^{31}P\{^1H\}$ NMR follow-up of the reaction of **8** (24 mg, 0.041 mmol) with HCl (4 M dioxane solution; 100 μL) in H_2O (20 μL)/dioxane (550 μL) and D_2O (20 μL)/dioxane (550 μL), respectively.

(Scheme 6). It is known that six-coordinated alkylhydrido-Pt(IV) complexes are relatively stable,[81] whereas analogous unsaturated Pt(IV) complexes undergo facile C−H reductive elimination.[82,83] Unsaturation seems also to play an important role in C−C bond activation.[1,7,13] The observation of **F**, which can be deprotonated, shows that the rate-determining step is not protonation of the metal center, but probably involves a later step such as the formation of a 14-electron complex (**G**) or the C−C bond activation itself (**G** → **J**). Complex **J** can be formed directly from **G** by a concerted oxidative addition process (**H**). Oxidative addition of strained C−C bonds to Pt(II) is well-known,[1,84−87] although here a nonstrained, strong C−C bond is involved. Oxidative addition of cyclopropane to Zeise's dimer is limited to substrates bearing electron-donating groups, suggesting that the C−C bond breaking process proceeds by an electrophilic attack of the Pt(II) center.[88] Alternatively, compound **G** might undergo an electrophilic attack by the metal on the ipso carbon of the aromatic ring, resulting in an arenium complex **I**, which can undergo a reversible 1,2 methyl shift, affording the Pt(IV) complex **J**, regenerating the aromatic π system. Reductive elimination from **J** can give **10** and CH_3Cl. CH_3X reductive elimination from Pt(IV) is known.[89]

The postulated mechanism involving an arenium intermediate is well precedented by the work of van Koten et al.,[14,90−93] in which it was shown that a NCN-type Pt(II) complex **11** (NCN = 1,3-$(Me_2NCH_2)_2$−C_6H_3), similar to **10**, reacts reversibly with MeI to yield a stable arenium complex **12** analogous to **I** (Scheme 7). This process was proven to proceed via an unobserved Pt(IV) intermediate **K**, akin to **J**. A theoretical study predicted that a 1,2 methyl shift between the ipso carbon of the aromatic group and the Pt center of **11** is an allowed process.[94] The reported C−C bond cleavage of the arenium cation is driven by the generation of the aromatic system and, interestingly, can be triggered with H_2O. It is noteworthy that no C−C bond activation was observed upon reacting the Pd(II) analogue of complex **8** with HCl.[20] This observation is consistent with the mechanism postulated here involving a Pt(II)/Pt(IV) oxidative addition process. Reacting Pd(X){1-CH_2-2,6-$(R_2PCH_2)_2$-3,5-$(CH_3)_2$−C_6H_3} (R = Ph, Me; X = Cl, CF_3CO_2) with HCl resulted in the formation of 16-membered macrocycles.[54,86]

Scheme 7



Summary and Conclusions

In conclusion, this study demonstrates that it is possible, using a model system, to achieve selective activation of an unstrained C−C single bond with two metals, Ru(II) and Pt(II), under mild reaction conditions in solution *with an overall retention of the metal oxidation state*. An aromatic PCP system having three Ar−CH_3 groups is selectively dealkylated by sp^2−sp^3 C−C bond activation. The C−C bond activation process might be driven thermodynamically by reaction of the kinetic products of C−H bond activation with another substrate. Using a slight excess of HCl, it is possible to drive the reaction with Pt(II) toward a thermodynamically favorable C−C bond activation process. Remarkably, this process proceeds even at *room temperature*. Methylene transfer from benzylic PCP−Rh(I) complexes to nonpolar H−C, H−Si, and even Si−Si bonds was reported.[3] Formally, the transformation from **8** to **10** can be viewed as another entry into this fascinating "methylene transfer" chemistry in which a methylene group is selectively transferred to HCl by activation of a strong C−C single bond. The balance between a C−H and C−C bond activation process with Ru(II) is readily

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tuned by addition of H_2 or utilizing a metal precursor, which generates H_2 upon the kinetically favorable C−H bond activation. Both C−H and C−C bond activation were observed with $RuHCl(PPh_3)_3$, the C−H activation product being ultimately converted into the C−C one, whereas with $RuCl_2(PPh_3)_3$ benzylic C−H bond activation is the only observed process. This indicates that Ru(II) phosphine complexes may be selected for either C−C or C−H bond activation.

Experimental Section

General Procedures. The procedures and spectroscopic analyses are similar to those previously reported.[10,18] Assignments of ^1H and $^{13}C\{^1H\}$ NMR signals were done with $^1H\{^{31}P\}$ and ^{13}C-DEPT-135 NMR, respectively. All reactions were carried out under an inert atmosphere. Solvents were dried, distilled, and degassed before use. $RuCl_2(PPh_3)_3$ and $RuHCl(PPh_3)_3$ were prepared by published procedures.[3,95] Reaction flasks were washed with deionized 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. Elemental analyses were carried out at the Hebrew University, Jerusalem. Field desorption (FD) mass spectra were measured at the Institute of Mass Spectrometry, the University of Amsterdam. The organometallic Ru(II) products containing ^{i}Pr substituents on the phosphorus atoms are difficult to separate from the liberated PPh_3 due to similar solubility properties.

Preparation of Ligands. The new ligands **1**−R (R = OMe, C(O)OMe) were prepared by bromomethylation of mesitylene derivatives followed by phosphination.

Preparation of 1−C(O)OMe: (a) Formation of 2,4,6-Trimethylbenzoic Acid. A solution of 2-bromomesitylene (38.9 g, 30.4 mL, 0.195 mol) in 100 mL of dry ether was added dropwise to Mg tunings (5.1 g, 0.21 mol) in dry ether (50 mL). Initiation of the reaction required the addition of I_2 and heating with a fan blower. The reaction mixture was refluxed for 1 h and stirred overnight at room temperature under argon. CO_2 was passed through H_2SO_4 and bubbled into the Grignard reaction for approximately 1 h. The reaction mixture was acidified with HCl and ice, and the resulting solid was extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4, filtered, and then concentrated under vacuum. The crude solid was suspended in pentane and filtered on a sintered funnel (16.6 g, 51%). ^1H NMR ($CDCl_3$) δ: 9.0 (br, CO_2H), 6.88 (s, 2H, ArH), 2.41 (s, 3H, *p*-Me) 2.28 (s, 6H, *o*-Me).

(b) Formation of Methyl 2,4,6-Trimethylbenzoate. A solution of CH_2N_2 in ether (under KOH) was added to an ether solution (150 mL) of 2,4,6-trimethylbenzoic acid (14.2 g, 0.0865 mol) until a yellow color persisted and TLC indicated full conversion of the acid to a new less polar product. The reaction mixture was concentrated under vacuum, and the residue was distilled under high vacuum (0.2 mm.) The fraction distilling at 83−85 °C contained the desired product (14.5 g, 94%). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H 7.92. Found: C, 73.78; H, 8.13. MS: *m*/*z* 179 ($M^+ + 1$, calc *m*/*z* 178). IR (neat): λ = 2953, 2924, 2560 (all m), 1732, 1268, 1087 (all s).

(c) Bromomethylation. A mixture of methyl 2,4,6-trimethyl benzoate (4.7 g, 0.026 mol), HBr (48%, 20 mL), glacial acetic acid (4.0 mL), trioxane (4.8 g, 0.053 mol), and $MeNEt_3$-Br (0.3 g, 1.5 mmol) was heated for 24 h and poured over H_2O/ice. The product was extracted with CH_2Cl_2, and the combined organic layers were washed twice with H_2O until neutral, dried with Na_2SO_4, filtered, and concentrated under vacuum. The product, 2,6−Bis(bromomethyl)-4-carbomethoxymesitylene, was purified by column chromatography (eluent hexane/ether, 9:1; yield 3.4 g, 35%). Mp = 122−123 °C. ^1H NMR ($CDCl_3$) δ: 4.51 (s, 4H, CH_2Br), 3.90 (s, 3H, CO_2CH_3), 2.43 (s, 3H, CH_3), 2.29 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 170.44 (C=O), 138.29, 134.58, 134.19, 133.03 (all s, Ar), 28.97 (s, CO_2CH_3), 28.93 (s, CH_2Br_2), 16.70 (s, $ArCH_3$), 15.03 (s, $ArCH_3$). IR (KBr): λ = 1732, 1218, 1208, 1178, 1041, 560.

(d) Phosphination. An acetone solution (25 mL) of 2,6−bis(bromomethyl)-4-carbomethoxymesitylene (3.8 g, 0.010 mol) was treated with an acetone solution (25 mL) of $^i Pr_2PH$ (2.4 g, 0.020 mol) at room temperature, resulting in the formation of white crystals. The phosphonium salt was decanted from the mother liquid and decomposed with H_2O (40 mL) followed by an aqueous solution (40 mL) of NaOAc (11 g, 7.5 mol). The product was obtained as an oil after extraction with ether (3.9 g, 85%). For **1**−C(O)OMe: $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 6.4 (s). ^1H NMR (C_6D_6) δ: 3.66 (s, 3H, CO_2Me), 2.83 (s, 4H, CH_2P), 2.72 (s, 3H, $ArCH_3$), 2.50 (s, 6H, $ArCH_3$), 1.76 (m, 4H, $CH(CH_3)_2$), 1.1 (dq, 24H, $CH(CH_3)_2$). ^{13}C NMR (C_6D_6) δ: 171.63 (s, CO_2-Me), 136.29, 135.35, 129.66 (all s, Ar), 51.27 (s, CO_2Me), 24.6 (d, $^1J_{PC}$ = 16.9 Hz, CH_2P), 23.60 (d, J_{PC} = 17.2 Hz, $CH(CH_3)_2$), 19.70 (t, $J_{PC} \approx$ 14.0 Hz, $CH(CH_3)_2$), 18.97 (t, $ArCH_3$), 18.51 (d, $ArCH_3$). IR (neat) λ: 1728 cm^{-1}. Compound **1**−OMe was obtained in a similar manner by phosphination of α,α′-dibromo-2-methoxymesitylene.[7] For **1**−OMe: $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ: 8.0 (s). ^1H NMR ($CDCl_3$) δ: 3.59 (s, 3H, OMe), 2.87 (d, $^2J_{PH}$ = 2.2 Hz, 4H, CH_2P), 2.43 (s, 3H, $ArCH_3$), 2.31 (s, 6H, $ArCH_3$), 1.81 (m, $^3J_{HH}$ = 7.0 Hz, 4H, $CH(CH_3)_2$), 1.10 (dd, $^3J_{HH}$ = 7.1 Hz, $^3J_{PH}$ = 12.2 Hz, 12H, $CH(CH_3)_2$), 0.98 (dd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 12.0 Hz, 12H, $CH(CH_3)_2$). ^{13}C NMR ($CDCl_3$) δ: 155.15 (s, Ar), 135.29 (m, Ar), 130.50 (m, Ar), 129.59 (t, J_{PC} = 5.0 Hz, Ar), 59.91 (s, OMe), 24.4 (d, $^1J_{PC}$ = 22.1 Hz, CH_2P), 23.60 (d, J_{PC} = 12.7 Hz, $CH(CH_3)_2$), 19.56 (t, $J_{PC} \approx$ 14.0 Hz, $CH(CH_3)_2$), 18.20 (t, J_{PC} = 7.3 Hz, $ArCH_3$), 13.66 (d, $J_{PC} \sim$ 5.2 Hz, $ArCH_3$). Anal. Calcd for $C_{24}H_{44}O_1P_2$: C, 70.21; H, 10.80. Found: C, 69.99; H, 10.36

Hydrogenolysis of the Ar−CH_3 Bond. A THF solution (2 mL) of **1** (30 mg, 0.078 mmol) was added dropwise to a stirred THF suspension (2 mL) of $RuCl_2(PPh_3)_3$ (75 mg, 0.078 mmol). The reaction mixture was stirred under H_2 (30−35 psi) at 110 °C for 17 h in a 90 cm^3 Fischer Porter pressure vessel. Quantitative analysis of the gas phase by GC showed the formation of CH_4 (>85%). $^{31}P\{^1H\}$ NMR analysis of the green reaction solution indicated the selective formation of complex **2** and PPh_3, with no starting materials remaining. Removal of the volatiles under vacuum resulted in the quantitative formation of a green powder. It is possible to remove the liberated PPh_3 only partly by multiple washings of the solid with cold (−30 °C) pentane. Ligands **1**−OMe and **1**−C(O)OMe can be used as well, affording CH_4 and **2**−OMe and **2**−C(O)-OMe, respectively. For **2**: ^1H NMR (C_6D_6) δ: 7.6−6.9 (ArH), 2.89 (dvt, left part of ABq, $^2J_{HH}$ = 16.9 Hz, $^{(2+4)}J_{PH}$ = 9.9 Hz, 2H, CH_2P), 2.61 (m, 2H, CH), 2.21 (s, 6H, $ArCH_3$), 1.74 (dvt, right part of ABq, $^2J_{HH}$ = 16.8 Hz, $^{(2+4)}J_{PH}$ is not resolved, 2H, CH_2P), 1.52 (m {d upon ^{31}P decoupling}, $^3J_{HH\ =\ 7.1\ Hz}$, $^3J_{PH}$ = Hz, CH_3), 1.35 (m, 2H, CH), 1.16 (m {d upon ^{31}P decoupling}, $^3J_{HH}$ = 7.0 Hz, CH_3), 1.06 (m {d upon ^{31}P decoupling}, $^3J_{HH}$ = 7.1 Hz, CH_3), 0.78 (m {d upon ^{31}P decoupling}, $^3J_{HH\ =\ 7.0\ Hz}$, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 172.74 (dt, $^2J_{PC,\ PC}$ = 18.3, 4.7 Hz, C_{ipso}), 149−125 (C_{Ar}), 33.28 (vt, $^{(2+4)}J_{PC}$ = 24.4 Hz, CH_2P), 26.64 (vt, $^{(1+3)}J_{PC}$ = 18.3 Hz, CH), 26.28 (vt, $^{(1+3)}J_{PC}$ = 17.1 Hz, CH), 22.62 (s, $ArCH_3$), 20.73 (s, CH_3) 20.03 (CH_3), 19.65 (vt, $^{(2+4)}J_{PC}$ = 4.5 Hz, CH_3), 17.63 (vt, $^{(2+4)}J_{PC}$ = 4.4 Hz, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 76.47 (t, $^2J_{PP}$ = 62.9 Hz, 1P), 45.83 (d, $^2J_{PP}$ = 31.5 Hz, 2P). Anal. Calcd for $C_{40}H_{54}Cl_1P_3Ru\cdot PPh_3$: C, 67.86; H, 6.77. Found: C, 67.28; H, 6.37. MS: *m*/*z* 763 (M^+, calc *m*/*z* 764), 728 (M^+ − Cl, calc *m*/*z* 729); correct isotope patterns. Similar results were obtained using the analogue of **1** with phenyl groups replacing isopropyl substituents on P, affording $Ru[2,6\text{-}(Ph_2PCH_2)_2\text{-}3,5\text{-}(CH_3)_2C_6H](PPh_3)Cl$ and CH_4. ^1H NMR (C_6D_6): δ 8.1−6.7 (ArH), 3.57 (dvt, left part of ABq, left part of ABq, $^2J_{HH}$ = 16.5 Hz, $^{(2+4)}J_{PH}$ is not resolved, 2H,

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CH_2P), 2.30 (s, 6H, $ArCH_3$), 2.12 (dvt, right part of ABq, right part of ABq, $^2J_{HH}$ = 16.5 Hz, $^{(2+4)}J_{PH}$ = 12.0 Hz, 2H, CH_2P). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 80.81 (t, $^2J_{PP}$ = 63.0 Hz, 1P), 39.84 (d, $^2J_{PP}$ = 32.4 Hz, 2P). MS: *m*/*z* 899; correct isotope patterns.

Formation of Complexes 2 and 5 by Ar−H Activation. A THF solution (2 mL) of **3** or **6** (40 mg or 37 mg, 0.11 mmol) was added dropwise to a stirred THF suspension (2 mL) of $RuCl_2(PPh_3)_3$ (105 mg, 0.11 mmol). The solution was stirred for 10 h at 110 °C in a sealed pressure vessel. $^{31}P\{^1H\}$ analysis of a green aliquot showed complex **2** or **5** and PPh_3 as the only products. Consequently, the reaction mixture was filtered through a cotton pad, pumped to dryness, washed with cold pentane (−30 °C, 3 × 5 mL), and dried in vacuo, affording a green powder (68%). Complex **2** and the analogous complex **5**, having two methyl substituents in the 3 and 5 positions of the aromatic ring, exhibit similar spectroscopic features. For **5**: Anal. Calcd for $C_{38}H_{50}Cl_1P_3Ru\cdot H_2O$: C, 60.51; H, 6.95. Found: C, 60.67; H, 7.17. ^1H NMR (C_6D_6) δ: 7.65 (m, 6H, ortho-H of PPh_3), 7.0−6.8 (m, 12H, Ar), 2.86 (dvt, left part of ABq, $^2J_{HH}$ = 16.5 Hz, $^{(2+4)}J_{PH}$ = 10.2 Hz, 2H, CH_2P), 2.57 (m, 2H, CH), 2.03 (dvt, right part of ABq, $^2J_{HH}$ = 16.5 Hz, $^{(2+4)}J_{PH}$ = 7.4 Hz, 2H, CH_2P), 1.50 (vq, 6H, $^3J_{HH}$ = 7.2 Hz, $^{(3+5)}J_{PH}$ = 7.4 Hz, CH_3), 1.34 (m, 2H, $^3J_{HH}$ = 7.2 Hz, CH), 1.1 (m, 12H, $^3J_{HH} \approx$ 6.9 Hz, CH_3), 0.75 (dvt, 6H, J_{HH} = 7.1 Hz, $^{(3+5)}J_{PH}$ = 5.4 Hz, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 174.1 (dt, $^2J_{PC,\ PC}$ = 18.2, ≈ 4 Hz, C_{ipso}), 153−121 (C_{Ar}), 36.29 (vt, $^{(2+4)}J_{PC}$ = 23.6 Hz, CH_2P), 26.15 (vt, $^{(1+3)}J_{PC}$ = 16.4 Hz, CH), 26.12 (vt, $^{(1+3)}J_{PC}$ = 16.4 Hz, CH), 20.84, 20.08, 19.57, 17.86 (all s, CH_3). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 79.11 (t, $^2J_{PP}$ = 62.8 Hz, 1P), 43.91 (d, $^2J_{PP}$ = 31.9 Hz, 2P).

Hydrogenolysis of the Ar−CH_2CH_3 Bond. A THF solution (2 mL) of **4** (29 mg, 0.079 mmol) was added dropwise to a stirred THF suspension (2 mL) of $RuCl_2(PPh_3)_3$ (75 mg, 0.078 mmol). The resulting solution was stirred for 5 days under H_2 (30−35 psi) at 110 °C in a 90 mL Fischer Porter pressure vessel. The resulting green solution was analyzed by $^{31}P\{^1H\}$ NMR, showing the formation of **5** in ∼15% yield and unreacted starting materials. Quantitative analysis of the gas phase by GC showed the formation of 1 equiv of C_2H_6 (∼15% yield). No CH_4 formation was observed. Similar results were obtained using the Ph analogue of **4**, affording the known Ru[2,6-$(Ph_2PCH_2)_2C_6H_3$](PPh_3)Cl and C_2H_6 in a low yield (∼15% yield based on $^{31}P\{^1H\}$ and GC).[38,39] The Ar−Ru complexes were identified by $^{31}P\{^1H\}$ NMR using authentic samples.

$ArCH_2$−H Bond Activation with $RuCl_2(PPh_3)_3$ and ^{t}BuONa; Formation of 7. A THF solution (1 mL) of **1** (30 mg, 0.078 mmol) and ^{t}BuONa (10 mg, 0.104 mmol) was added to a THF suspension (1 mL) of $RuCl_2(PPh_3)_3$ (75 mg, 0.078 mmol) and heated at 80 °C for 30 min in a sealed tube. $^{31}P\{^1H\}$ analysis of the reaction solution showed the selective formation of complex **7**. Subsequently, the volatiles were evaporated and the residue was dissolved in benzene (5 mL), filtered through a cotton pad, and dried in vacuo. It is possible to remove the liberated PPh_3 by multiple washings of the solid with cold (−30 °C) pentane. Ligands **1**−OMe and **1**−C(O)OMe can be used as well, affording **7**−OMe and **7**−C(O)OMe, respectively. For **7**: Anal. Calcd for $C_{41}H_{56}Cl_1P_3Ru$: C, 63.27; H, 7.25. Found: C, 64.01; H, 7.83. MS: *m*/*z* 777 (M^+, calc 778), 742 (M^+ − Cl, calc *m*/*z* 743), correct isotope patterns. ^1H NMR (C_6D_6) δ: 8.3−6.6 (ArH), 3.28 (t, {s upon ^{31}P decoupling}, $^3J_{PH}$ = 15.0 Hz, 2H, $ArCH_2Ru$), 3.01 (dvt, left part of ABq, $^2J_{HH}$ = 14.6 Hz, $^{(2+4)}J_{PH}$ is not resolved, 2H, CH_2P), 2.38 (m, 2H, CH), 2.20 (s, 6H, $ArCH_3$), 1.72 (m, 2H, CH), 1.45 (m {d upon ^{31}P decoupling}, $^3J_{HH}$ = 6.9 Hz, CH_3), 1.40 (m {d upon ^{31}P decoupling}, $^3J_{HH}$ = 7.0 Hz, CH_3), 0.87 (m {d upon ^{31}P decoupling}, $^3J_{HH}$ = 6.8 Hz, CH_3), 0.66 (m {d upon ^{31}P decoupling}, $^3J_{HH}$ = 6.8 Hz, CH_3). $^{13}C\{^1H\}$ NMR (C_6D_6) δ: 140−126 (C_{Ar}), 33.03 (vt, $^{(1+3)}J_{PC}$ = 16.8 Hz, CH), 22.17 (vt, $^{(2+4)}J_{PC}$ = 18.8 Hz, CH_2P), 20.10, 19.67, 19.41, 17.67 (s, CH_3), 16.83 (vt, $^{(2+4)}J_{PC}$ = 4.7 Hz, CH_3), 13.56 (vq, $^2J_{PC}$ = 5.3, 11.0 Hz, $ArCH_2Ru$). $^{31}P\{^1H\}$ NMR (C_6D_6) δ: 73.58 (t, $^2J_{PP}$ = 59.4 Hz, 1P), 24.1 (d, $^2J_{PP}$ = 29.6 Hz, 2P).

Reaction of $RuHCl(PPh_3)_3$ with 1. A dioxane solution (1 mL) of **1** (10 mg, 0.025 mmol) was added to $RuHCl(PPh_3)_3$ (23 mg, 0.025 mmol). The violet suspension was heated for 5 min in a sealed tube at 110 °C. $^{31}P\{^1H\}$ analysis of the green reaction solution showed the presence of complexes **2** and **7** in a 2.7:1 ratio. Continuous heating for another 10 min shows **2** and **7** in a 3.8:1 ratio. After 75 min only traces of **7** remained (<5%). Analysis of the gas phase by GC showed the formation of CH_4. Monitoring the reaction at 60 °C by $^{31}P\{^1H\}$ NMR reveals also the formation of **2** and **7**. Heating a THF solution (2 mL) of **1** (10 mg, 0.025 mmol) and $RuHCl(PPh_3)_3$ (23 mg, 0.025 mmol) for 17 h in a sealed vessel results in exclusive formation of **2** and CH_4 (85% by GC).

Ar−C Bond Cleavage with Ru(II); Reaction of 7 with H_2. Reaction of a THF-d_8 (1 mL) solution of **7** (37 mg, 0.048 mmol) with 1 equiv of H_2 (1 mL, 0.045 mmol) at 80 °C in a sealed tube resulted in the selective formation of complex **2** and CH_4 (∼90% conversion after 24 h by ^1H and $^{31}P\{^1H\}$ NMR). Complex **7** is stable under those reaction conditions in the absence of H_2.

H/D Exchange with 7 and 7−R. A C_6D_6 solution (1 mL) of **7**−OMe (19 mg, 0.024 mmol) and **7**−CO(OMe) (20 mg, 0.023 mmol) was treated with D_2 (1 mL, 0.045 mmol) at room temperature in a sealed tube (total volume = 2.5 mL). The exchange progress was monitored by ^1H and $^{31}P\{^1H\}$ NMR showing ∼40% H/D exchange for R = C(O)OMe and only ∼10% H/D exchange for R = OMe after 22 h. Flushing the tube with N_2 and treatment of the reaction mixture with H_2 reversed this labeling process. No other formation of Ru(0) or Ru(II)−H was observed when the reaction was performed in the presence of 1 equiv of triethylamine (8 μL, 0.058 mmol). Deuterium incorporation into the ArCH_2Ru group of **7** and C−C bond activation were observed upon treatment of a C_6D_6 solution (1 mL) of **7** (19 mg, 0.024 mmol) with excess of D_2 (2 mL, 0.090 mmol) at 60 °C in a sealed tube (total volume = 2.5 mL, ∼30% H/D exchange after 2h).

Follow-Up Experiments. (a) Three THF solutions (1 mL each) of **1**, **1**−OMe, **1**−C(O)OMe (10 mg, each), and $RuHCl(PPh_3)_3$ (25 mg, 0.025 mmol) were heated simultaneously in sealed tubes in an oil bath at 58 °C and monitored by $^{31}P\{^1H\}$ NMR at room temperature. In all three cases formation of the products of C−H bond activation (**7**, **7**−R) was observed first. After 10 h the ratios of the products of C−H and C−C bond activation are distinctively different: C−H:C−C = 1:1.4 for R = C(O)OMe, 1:1 for R = H, and 1:0.4 for R = OMe. The results for **1**−OMe are presented in Figure 1. Formation of CH_4 was observed by GC analysis of the gas phase. (b) A THF solution (1 mL) of **1**−OMe, **1**−C(O)OMe (5 mg each), and $RuHCl(PPh_3)_3$ (25 mg, 0.025 mmol) was heated in a sealed tube in an oil bath at 65 °C and monitored by $^{31}P\{^1H\}$ NMR at room temperature. The ratio between the ligands remained constant during the reaction. After 10 h, C−H:C−C = 1:1.9 for R = C(O)OMe and C−H:C−C = 1:0.47 for R = C(O)OMe (Figure 2). No intermediate compounds were observed, and during the experiment the ratio between **1**−OMe and **1**−C(O)OMe did not change. Formation of CH_4 was observed by GC analysis of the gas phase.

$ArCH_2$−H Bond Activation with $(COD)PtCl_2$; Formation of 8. To a stirred slurry of $(COD)PtCl_2$ (105 mg, 0.281 mmol) in THF (10 mL), a solution of **1** (110 mg, 0.289 mmol) in THF (10 mL) was added dropwise over a period of 5 min at room temperature. The clear yellow solution was stirred for 12 h, then filtered through a cotton pad, and reduced in volume to about 1 mL. Addition of cold pentane (10 mL, − 30 °C) caused precipitation of the slightly yellow product, which was washed twice with cold pentane (−30 °C, 2 × 10 mL) and then dried in vacuo to give an off-white powder **8** in nearly quantitative yield (171 mg, 0.28 mmol). Anal. Calcd for $C_{23}H_{41}Cl_1P_2Pt\cdot 0.5$ THF: C, 46.47; H, 7.02. Found: C, 46.52; H, 6.81.

Table 1. Crystal Data for 9

formula	$C_{23}H_{41}P_2PtI$
fw	701.49
space group	*P*2(1)/*c* (no. 14)
crystal system	monoclinic
a, Å	9.042(2)
b, Å	17.059(3)
c, Å	16.703(3)
β, deg	104.450(3)
V, Å^3	2494.9(8)
D_{calcd}, g cm^{-3}	1.868
Z	4
μ(Mo Kα), mm^{-1}	6.997
crystal size, mm^3	0.2 × 0.2 × 0.4
T, K	110
no. of reflns collected	11633
no. of indep reflns	5730[R(int)=0.0533]
final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0448, R2 = 0.0821
R indices (all data)	R1 = 0.0614, R2 = 0.0927

FD-MS: M^+ 610 (correct isotope pattern). ^{1}H (C_6D_6) δ: 6.51 (s, 1H, ArH), 2.91 (dt, left part of AB quartet, $^2J_{HH}$ = 14.9 Hz, $^{(2+4)}J_{PH}$ = 6.8 Hz, $^3J_{PtH}$ = 54.6 Hz, 2H, CH_2P), 2.27 (m, 2H, CH), 2.53 (d, left part of AB quartet, $^2J_{HH}$ = 14.9 Hz, 2H, CH_2P), 2.32 (t, $^3J_{PH}$ = 9.9 Hz, $^2J_{PtP}$ = 92.0 Hz, 3H, $ArCH_2Pt$), 2.18 (s, 6H, $ArCH_3$), 1.89 (m, 2H, CH), 1.20 (m, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 7.6 Hz, $^3J_{PH}$ = 14.9 Hz, $^3J_{PH}$ = 15.5 Hz, 12H, CH_3), 1.05 (m, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 15.0 Hz, 6H, CH_3), 0.84 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 13.3 Hz, 6H, CH_3). $^{31}P\{^1H\}$ (C_6D_6) δ: 69.05 (s, $^1J_{PtP}$ = 3599 Hz). $^{13}C\{^1H\}$ (C_6D_6) δ: 145.34 (t, $^3J_{PC}$ = 6.0 Hz, $^2J_{PtC}$ = 41.0 Hz, C_{ipso}), 132.51 (vt, J_{PC} = 2.9 Hz, $^3J_{PtC}$ = 9.3 Hz, C_{ortho}), 128.00 (vt, J_{PC} = 1.5 Hz, $^4J_{PtC}$ = 19.3 Hz, C_{meta}), 124.93 (s, J_{PtC} = 9.6 Hz, C_{para}), 26.77 (vt, J_{PC} = 9.9 Hz, CH), 24.44 (vt, J_{PC} = 12.6 Hz, CH), 21.17 (vt, J_{PC} = 13.0 Hz, J_{PtC} = 22.0 Hz, CH_2P), 19.43 (vt, J_{PC} = 1.9 Hz, $^3J_{PtC}$ = 7.8 Hz, CH_3), 18.82 (vt, J_{PC} = 2.4 Hz, CH_3), 18.35 (s, CH_3), 17.41 (s, $^3J_{PtC}$ = 9.6 Hz, CH_3), 1.12 (t, $^2J_{PC}$ = 4.8 Hz, $^1J_{PtC}$ = 432.0 Hz, $ArCH_2Pt$).

X-ray Crystal Structure Determination of 9. Yellow crystals suitable for X-ray diffraction studies were obtained by slow evaporation of the benzene solvent. A prismatic crystal (0.2 × 0.2 × 0.4 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 (λ = 0.71073 Å) and a graphite monochromator. Accurate unit-cell dimensions were obtained from a least-squares fit to setting angles of 25 reflections in the range 1.73° ≤ θ ≤ 27.50°. The SHELXS-92 and SHELXL-93 program packages installed on a Silicon Graphics workstation were used for structure solution and refinement. The structure 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 for **9** gave an agreement factor R = 0.0448 (based on F^2) for all data with $I > 2\sigma I$ and R = 0.0614 for all data based on 5711 reflections. Hydrogens were calculated from difference Fourier maps and refined in a riding mode with individual temperature factors. ORTEP views of the molecular structures and the adopted numbering schemes are shown in Figure 3. Table 1 gives details of the crystal structure determination.

Attempted Reaction of 8 and H_2. A yellowish C_6D_6 solution (2 mL) of **8** (25 mg) was loaded into a 90 mL Fischer Porter pressure vessel, charged with H_2 (30 psi), and heated at 120 °C for 24 h. ^{1}H and $^{31}P\{^1H\}$ NMR analysis showed only the presence of unreacted **8**. No methane formation was observed by GC analysis of the gas phase. Similar results were obtained using THF or toluene at 150 °C.

Ar−C Bond Activation with Pt(II); Formation of Complex 10. In a typical experiment complex **8** (24 mg, 0.041 mmol) was dissolved in C_6D_6 (0.55 mL) and loaded into a 5 mm screw-cap NMR tube (5 mm high-pressure NMR tubes were used as well). A solution of HCl in dioxane (4 M; 100 μL, 0.40 mmol) was added. The tube was sealed and heated to 82 °C. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR at room temperature. After 35 min the reaction was complete, as judged by $^{31}P\{^1H\}$ NMR spectroscopy. The reaction solution was evaporated and the solid washed with cold pentane (2 × 5 mL; −30 °C) and then dried in vacuo (20 mg; 80% yield). The formation of MeCl was unambiguous based on GC experiments and NMR spectroscopy of the reaction solution and by comparison to an authentic sample of MeCl in ^{t}BuOMe. The follow-up measurements were performed at 58, 82, 101, and 125 °C in C_6D_6/dioxane and at 90, 115, and 150 °C in dioxane. For each set of experiments, samples were prepared from the same batch of **8**. For **10**; Anal. Calcd for $C_{22}H_{39}Cl_1P_2Pt$: C, 44.33; H, 6.60. Found: C, 43.89; H, 6.37. FD-MS: M^+ 596 (correct isotope pattern). $^{31}P\{^1H\}$ (161.9 MHz, C_6D_6): δ 56.37 (s, $^1J_{PtP}$ = 2857 Hz). ^{1}H (C_6D_6): δ 6.75 (s, 1 H; ArH), 2.72 (vt, J_{PH} = 4.2 Hz, J_{PtH} = 18.5 Hz, 4H, CH_2P), 2.26 (m, 4H, CH), 2.19 (s, 6H; $ArCH_3$), 1.39 (dd, J_{HH} = 7.2 Hz, J_{PH} = 16.4 Hz, 12H, CH_3), 0.91 (dd, J_{HH} = 7.1 Hz, J_{PH} = 14.7 Hz, 12H, CH_3). $^{13}C\{^1H\}$ (C_6D_6): δ 150.19 (s, C_{ipso}), 145.42 (vt, J_{PC} = 9.5 Hz, $^2J_{PtC}$ = 95.4 Hz, C_{ortho}), 131.34 (vt, J_{PC} = 8.3 Hz, C_{meta}), 127.44 (s, $^4J_{PtC}$ = 6.4 Hz, C_{para}), 31.72 (vt, J_{PC}= 5.3 Hz, $^3J_{PtC}$ = 108.0 Hz, CH_2P), 24.34 (vt, J_{PC} = 14.6 Hz, $^2J_{PtC}$ = 54.7 Hz CH), 18.47 (s, $J_{PtC} \approx$ 14 Hz, CH_3), 17.76 (s, $^2J_{PtC}$ = 26.1 Hz, CH_3).

Ar−C Bond Activation with Pt(II); Kinetic Isotope Effect. Complex **8** (24 mg, 0.041 mmol) was dissolved in dioxane (0.55 mL) and loaded into a 5 mm screw-cap NMR tube. A solution of HCl in dioxane (4 M; 100 μL, 0.040 mmol) and H_2O or D_2O (20 μL, 1.1 mmol) was added. The tube was sealed and heated to 130 °C. The progress of the reaction was monitored by $^{31}P\{^1H\}$ NMR at room temperature. The results are presented in Figure 5.

Preparation of Complex 10. A toluene solution (10 mL) of **3** (76 mg, 0.20 mmol) was added to a stirred toluene suspension (10 mL) of (COD)$PtCl_2$ (75 mg, 0.20 mmol). The reaction mixture was heated for 2 h at 150 °C in a pressure flask. All volatiles were removed in vacuo, and the product was extracted with excess pentane (∼30 mL) and obtained as a waxy solid in 80% yield (91 mg).

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Supporting Information Available: Tables of crystallographic data and structure refinement, atomic coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atomic coordinates for **9**. This material is available free of charge via the Internet at http://pubs.acs.org.

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