Catalytic selective cleavage of a strong C–C single bond by rhodium in solution

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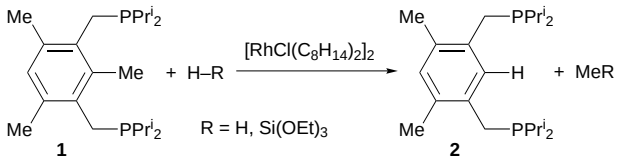
Reaction of $[RhCl(C_8H_{14})_2]_2$ with an excess of the diphosphine 1,3-bis(diisopropylphosphinomethylene)mesitylene 1 in dioxane under mild H_2 pressure (25 psi) or with an excess of $HSi(OEt)_3$ results in catalytic selective cleavage of a strong C–C single bond.

Activation and functionalization of strong C–C single bonds by soluble transition metal complexes is of considerable current interest.[1–6] Most challenging is the search for the underlying mechanisms and homogeneous catalysis based on such relatively inert bonds. While several examples of homogeneous catalytic activation of C–H bonds of hydrocarbons are known,[2] the few reports of catalytic C–C bond activation in solution are limited to weak C–C bonds α to a carbonyl group,[3] strained systems,[4] or a combination of both.[5] Selective transition metal insertion into a strong, unstrained C–C single bond in solution and details related to the mechanism were reported by us only recently.[6] We report here on the catalytic hydrogenolysis and hydrosilylation of a strong sp^2–sp^3 C–C bond. This rhodium catalyzed process is unprecedented, occurs under homogeneous reaction conditions and is highly selective.

Reaction of $[RhCl(C_8H_{14})_2]_2$ (C_8H_{14} = cyclooctene) with 50 equiv. of the phosphine substrate **1** under mild H_2 pressure (25 psi; 1 psi ≈ 6.894757×10^3 Pa) in dioxane at 180 °C for one day leads to catalytic formation of the demethylated phosphine **2** and CH_4 (Scheme 1; 16 turnovers based on rhodium and 32% yield). The CH_4 was collected by standard vacuum line techniques and was identified and quantified by GC. Compound **2** was identified spectroscopically by various NMR and MS techniques and by comparison with an added authentic sample.[6b] Reactions were also performed in [$^2H_8$]dioxane to record ^1H, $^{13}C\{^1H\}$, ^{13}C-DEPT-135 and $^{31}P\{^1H\}$ NMR spectra. Formation of product **2** is highly selective, the other two arylmethyl groups remaining unaffected and no other organic products were formed. Addition of another 50 equiv. of **1** to the reaction mixture and applying the same reaction conditions resulted in another 15 turnovers, demonstrating that the catalyst remains active. Similar results were obtained by performing the reaction for two days with 100 equiv. of **1** (31 turnovers and 31% yield). Using 500 equiv. of substrate **1** leads to 106 turnovers after three days. The hydrogenolysis proceeds also at lower temperatures (150 °C), but it is much slower, leading to only 15 turnovers after one week.

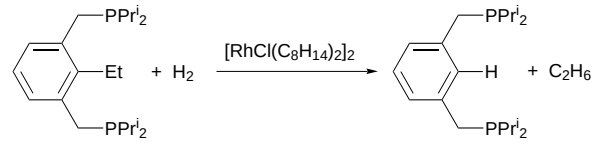


1 **2**

Scheme 1

To probe the possibility of catalytic hydrosilylation of a C–C single bond, we used an excess of $HSi(OEt)_3$ instead of H_2. Reaction of $[RhCl(C_8H_{14})_2]_2$ with 50 equiv. of **1** and an excess of $HSi(OEt)_3$ in dioxane (or toluene) at 150 °C for two days resulted in 10 turnovers to form **2** and $MeSi(OEt)_3$ (Scheme 1), which were unambiguously characterized by ^1H, $^{13}C\{^1H\}$, ^{13}C-DEPT, $^{29}Si\{^1H\}$ NMR and by GC–MS.[6b] Thus, catalytic transfer of a CH_2 group from an arene to a silane was observed. Again the reaction is completely selective.

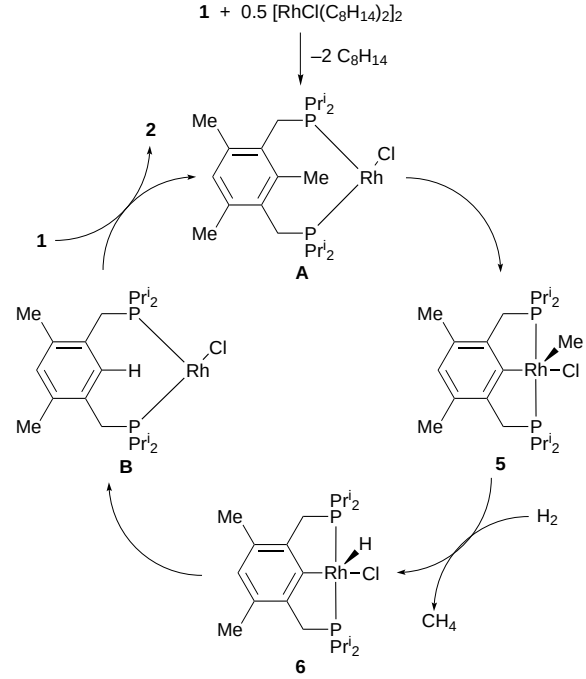
Reaction of 50 equiv. of the ethyl aromatic phosphine **3** with $[RhCl(C_8H_{14})_2]_2$ at 180 °C under mild H_2 pressure in dioxane for 3 days resulted in formation of compound **4** and C_2H_6, although only 4 turnovers were obtained (Scheme 2). Compound **4** was fully identified by comparison with an authentic sample. The expected amount of C_2H_6 was observed by GC analysis of the gas phase. Control reactions showed that **1** and **3** were stable under the same reaction conditions in the absence of rhodium.



3 **4**

Scheme 2

A postulated catalytic cycle is outlined in Scheme 3. The high selectivity of the catalytic processes, only one alkyl group being affected, provides strong evidence that both phosphines are coordinated to the metal centre prior to the C–C bond activation. Intermediates such as **A** have been observed with platinum and ruthenium.[7] At this stage competitive C–H and C–C oxidative addition might occur.[6f] C–H activation would result in the reversible formation of a benzylic rhodium species.[6] Metal insertion into the strong Ar–C bond was observed in a stoichiometric reaction of **1** (0.031 mmol) with 0.5 equiv. of $[RhCl(C_8H_{14})_2]_2$ in [$^2H_6$]benzene (2 ml) in a sealed tube for 2 h



Scheme 3 Proposed catalytic hydrogenolysis cycle for **1** with rhodium

at room temperature. ^{1}H, ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR analysis of the reaction solution showed the formation of **5** in 75% yield. The Rh–Me group is clearly observed in the ^{13}C{^{1}H} NMR at δ −4.3 [dt, ^1J(RhC) 30.2, ^2J(PC) 6.4 Hz] and the *ipso* carbon at δ 166.7 [dt, ^1J(Rh, C) 33.6, ^2J(PC) ≈ 1.0 Hz]. An isostructural rhodium(III) complex was recently fully characterized by X-ray analysis.[6f]

Subsequently, complex **5** reacts with H_2 to yield complex **6**. Indeed, reaction of **5** with H_2 (25 psi) at 80 °C for 1 day and analysis by ^{1}H, ^{31}P{^{1}H}, ^{13}C{^{1}H} NMR, IR and GC analysis showed the quantitative formation of complex **6** and CH_4.§ This reaction may proceed through a rhodium(V) intermediate or *via* σ-bond metathesis. Complex **6** can also be used as catalyst under the same reaction conditions. Release of the aryl phosphine **2** from **6** probably proceeds *via* **B**, which undergoes phosphine exchange with substrate **1** giving back **A**. This is likely to be the rate-determining step. Such a process was demonstrated by treating a dioxane solution of complex **6** with 20 equiv. of PEt_3 at 80 °C overnight, which resulted in formation of the PCP ligand **2** and $RhCl(PEt_3)_3$ by phosphine exchange. Replacement of a cyclometalated terdentate diamino ligand of a ruthenium(II) complex by a phosphorus analogue was reported very recently.[7b] The liberated arene **2** most probably strongly competes with substrate **1**, slowing down the catalytic process. It is well known that α,α′-diphosphine-*m*-xylenes such as **2** and **4** undergo readily Ar–H oxidative addition with rhodium forming thermally stable, isolable complexes such as **6**.[6c,8]

In summary, a novel catalytic process has been presented using simple diphosphine substrates. For the first time, an unstrained, strong Ar–C bond is selectively activated by a metal centre in solution in a catalytic fashion. Moreover, catalytic transfer of a methylene group to a primary silane has been observed using a rhodium complex. Stoichiometric reactions involved in the catalysis were directly demonstrated. Although the catalytic reactions were not optimized and the reactions are at present slow, more than one hundred turnovers were observed.

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Notes and References

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‡ Catalytic hydrogenolysis of an unstrained C–C single bond. A [$^2H_8$]dioxane solution (1.5 ml) of substrate **1** (106 mg, 0.278 mmol) was added dropwise to a [$^2H_8$]dioxane solution (1.5 ml) of $[RhCl(C_8H_{14})_2]_2$ (2 mg, 0.00278 mmol), loaded into a 90 ml Fischer porter pressure bottle equipped with a stirring bar and pressurized with H_2 (20–25 psi) (toluene can be used as well). After heating the reaction solution at 180 °C for 1 day, the gas phase was collected by standard vacuum line techniques and analyzed by GC using a molecular sieve column. The formed CH_4 was identified and quantified using authentic samples (13.6 turnovers). ^{31}P{^{1}H} NMR of the reaction mixture shows two signals at δ 5.6 (s, 2 P, **1**) and 3.20 (s, 2 P, **2**). The ratio of the signals (100 : 54) indicated 17.5 turnovers and a yield of 35%. Addition of trioctylphosphine oxide to the reaction mixture as an internal standard indicated 15.3 turnovers and a yield of 31%. The addition of authentic samples **1**, **2** to the reaction mixture resulted in overlap of resonances in ^{31}P{^{1}H} and ^{13}C{^{1}H} NMR.[6b] The same reaction conditions and analysis of the reaction mixture were used for substrate **3**. Similar reaction conditions were applied for the catalytic hydrosilylation, only an excess of $HSi(OEt)_3$ (91 mg, 0.556 mmol) was used instead of H_2.

§ *Spectral data* for **6**. ^{1}H NMR (C_6D_6, 400.1 MHz): δ 6.56 (s, 1 H, *p*-H of C_6HRh), 3.24 [m, ^3J(HH) 7.2 Hz, 2 H, C*H*Me$_2$], 3.14 [dvt, left part of ABq, ^2J(HH) 15.7 Hz, ^2J(HP) not resolved, 2 H, CH_2P], 2.95 [dvt, right part of ABq, ^2J(HH) 15.7 Hz, ^2J(HP) not resolved, 2 H, CH_2P], 2.28 [m, ^3J(HH) 7.1 Hz, 2 H, C*H*Me$_2$], 2.14 (s, 6 H, *Me*$_2$C$_6$HRh), 1.89, 1.72, 1.38, 1.24 [all q, ^3J(HH) ≈ 7.0 Hz, 6 H, CH*Me*$_2$], −19.36 [dt, ^1J(RhH) 31.1, ^2J(PH) 12.3 Hz, 1 H, HRh]. ^{31}P{^{1}H} NMR (C_6D_6, 161.9 MHz): δ 65.7 [d, ^1J(RhP) 113.6 Hz]. ^{13}C NMR (C_6D_6, 100.1 MHz): δ 161.1 [dm, ^1J(RhC) 31.9, ^2J(PC) ≈ 1.0 Hz, C_{ispo}], 142.8 [t, *J*(PC) 12.3 Hz, Ar], 129.7 [dt, *J*(PC) 7.4, *J*(RhC) 1.4 Hz, Ar], 126.5 (s, Ar), 32.8 [dt, *J*(PC) 12.6 Hz, CH_2P], 26.6 [t, *J*(PC) 10.0 Hz, CHMe$_2$], 23.2 [t, *J*(PC) 10.2 Hz, *C*HMe$_2$], 22.6 (s, *Me*$_2$Ar), 22.1, 19.7, 19.5 (all s, CH*Me*$_2$). IR (neat): ν 2071 cm^{-1}.

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