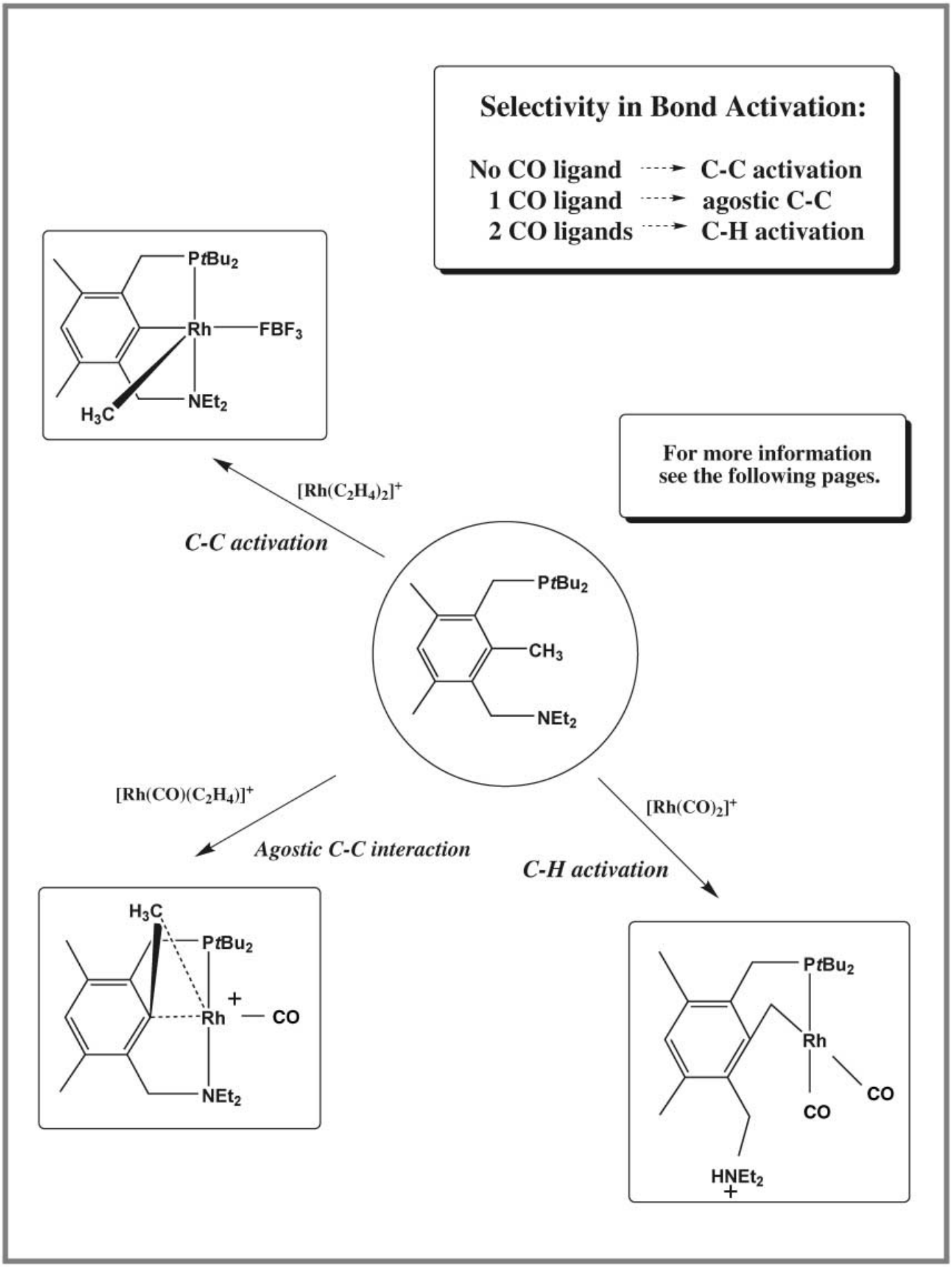

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C–C versus C–H Activation and versus Agostic C–C Interaction Controlled by Electron Density at the Metal Center

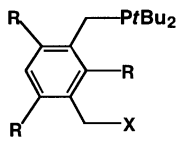
Mark Gandelman,[a] Linda J. W. Shimon,[b] and David Milstein*[a]

Abstract: Based on the PCN ligand **2**, a remarkable degree of control over C–C versus C–H bond activation and versus formation of an agostic C–C complex was demonstrated by choice of cationic $[Rh(CO)_n(C_2H_4)_{2-n}]$ ($n = 0, 1, 2$) precursors. Whereas reaction of **2** with $[Rh(C_2H_4)_2(solv)_n]BF_4$ results in exclusive C–C bond activation to yield product **5**, reaction with the dicarbonyl precursor $[Rh(CO)_2(solv)_n]BF_4$ leads to formation of the C–H activated complex **9**. The latter process is promoted by intramolecular deprotonation of the C–H bond by the hemilabile amine arm of the PCN ligand. The mixed monocarbonyl monoethylene Rh species $[Rh(CO)(C_2H_4)]BF_4$ reacts with the PCN ligand **2** to give an agostic complex **7**. The C–C activated complex **5** is easily converted to the C–H activated one (**9**) by reaction with CO; the reaction proceeds by a unique sequence of 1,2-metal-to-carbon methyl shift, agostic interaction, and C–H activation processes. Similarly, the C–C agostic complex **7** is converted to the same C–H activated product **9** by treatment with CO.

Keywords: agostic interactions · carbonyl ligands · C–C activation · C–H activation · dearomatization · tridentate ligands

Introduction

While C–H activation[1] is generally both thermodynamically and kinetically favored over C–C activation,[2] an appropriate choice of the reaction system can change the reaction profile in favor of insertion into the C–C bond. Thus, we have demonstrated that upon coordination to bischelating PCX (X = P,[3] N,[4] O[5]) ligand systems (Scheme 1) a metal center can be directed to the proximity of an unstrained, "hidden" C–C bond, resulting in thermodynamically and kinetically favored C–C bond activation.[6] Moreover, utilizing these PCX systems, a remarkable degree of control over metal insertion into strong C–H versus C–C bonds can be achieved by choice of solvent,[7] metal, or ligand set.[2a] In addition, PCP-type complexes containing an agostic interaction of a C–C bond with the metal center were isolated.[8]



Scheme 1. Bischelating PCX ligand systems: **1a**: R = CH_3, X = P*t*Bu_2, (PCP(CH_3)); **1b**: R = H, X = P*t*Bu_2, (PCP(H)). **2**: R = CH_3, X = NEt_2, (PCN). **3**: R = CH_3, X = OCH_3, (PCO).

We report herein that by using a PCN-type cationic rhodium system it is possible to achieve a remarkable degree of control over the activation processes, leading selectively to a) C–H activation, b) C–C activation and c) an agostic (σ-arenium) C–C interaction, simply by changing the number of CO molecules coordinated to the rhodium center. An interesting cascade of C–C coupling and C–H activation via C–C agostic interaction, caused by reaction of the rhodium complex with CO, is demonstrated.

Results and Discussion

While studying the activation of strong bonds, we found that cationic unsaturated Rh^I precursors can undergo carbon–carbon bond activation upon coordination to PCP,[7] PCN,[9] or PCO[5] ligands. Thus, the PCN ligand **2** reacted with the cationic complex $[Rh(C_2H_4)_2(solv)_n]BF_4$ (**4**)[10] to quantitatively yield the C–C activation product **5** as the only product under very mild conditions (Scheme 2)

No C–H-activated product was observed even at low temperatures. The same exclusive selectivity towards carbon–carbon bond activation was found in the reaction of the PCN ligand with neutral Rh^I precursors.[11] Addressing the question of the effect of electron density on the metal center

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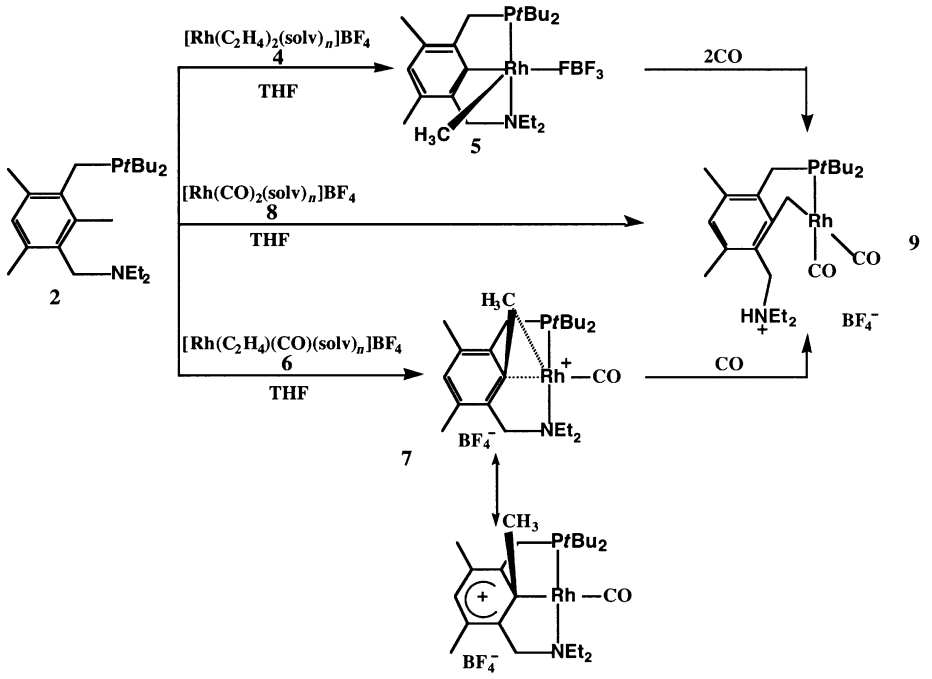


Scheme 2. C–C (**5**) or C–H (**9**) bond activation or C–C agostic interaction (**7**) tuned by the number of carbonyl ligands on the Rh precursor. Conversion of complexes **5** and **7** to compound **9** by treatment with CO.

on its ability to insert into C–C bonds, we examined the reactivity of relatively electron-poor rhodium(I) precursors bearing carbonyl ligands. Interestingly, contrary to the reaction of precursor **4**, no C–C activation was observed when ligand **2** was treated with an equimolar amount of the monocarbonyl complex $[Rh(C_2H_4)(CO)(solv)_n]BF_4$ (**6**) in THF. Rather, the reaction smoothly produced complex **7** in quantitative yield (Scheme 2). Compound **7** was unequivocally characterized by multinuclear NMR techniques. The $^{31}P\{^1H\}$ NMR spectrum of complex **7** exhibits a doublet at $\delta =$ 38.6 ppm ($J_{P,Rh} = 113.9$ Hz). The methyl group bound to the *ipso*-carbon gives rise to a broad singlet in the ^1H NMR spectrum at $\delta = 3.05$ ppm. The proton bound to the ring appears as a singlet at $\delta = 7.2$ ppm, only about 0.5 ppm downfield from the corresponding proton in other known PCN-based complexes with an intact aromatic ring.[4, 12] This proton is shifted significantly upfield relative to the same proton in the PCN–Rh methylene arenium complex[9] ($\Delta\delta =$ 1.3 ppm), in which the dearomatized ring bears a positive charge. In the ^{13}C NMR spectrum of **7** the *ipso*-carbon atom exhibits a signal at $\delta = 108.8$ ppm, which represents a large upfield shift relative to the *ipso*-carbon atom of cyclometalated, PCN-based, rhodium complexes. Noteworthy, there is no observable coupling between the Rh atom and the *ipso*-carbon atom, which can be as large as 30 Hz in other PCN-type Rh complexes,[4, 12] indicating that the interaction between the two atoms is weak. Based on the NMR characteristics of compound **7** and on previous experimental and theoretical studies of similar isoelectronic PCP(CH_3)-based[8] (**1a**) and PCP(H)-based[13] (**1b**) rhodium complexes, we conclude that **7** is best viewed as an arene complex stabilized by an agostic interaction of the C–C bond with the Rh center, with a minor contribution of the σ-arenium form. Thus, we refer to it in this paper as an agostic C–C (σ-arenium) complex. While agostic interactions of C–H bonds,[14] particularly those stabilizing cationic metal centers,[15] are well documented, examples of C–C agostic interactions are extremely rare.[8, 16] C–H agostic metal complexes are normally viewed as intermediates in C–H oxidative addition.[14] Since, as we have shown, C–H and C–C bond activation processes by Rh^I have similar electronic requirements,[5] complex **7** can be viewed as a 'frozen' intermediate toward C–C bond activation. Interestingly, the neutral [RhCl] complex undergoes very facile oxidative addition of the C–C bond in the PCN-type ligand (even at $-70\,^\circ C$) to give the corresponding Rh^{III} methyl chloride complex, and the fully characterized P,N-coordinated 14-electron intermediate in this reaction is very unstable.[11] Here, despite the fact that the cationic $[RhCO]^+$ fragment is sterically unhindered and can easily approach the Ar–CH_3 bond, it is not sufficiently electron rich to undergo the C–C oxidative addition, probably because of thermodynamic rather than kinetic reasons (see also the discussion below regarding reaction of **5** with CO).

In view of the major influence of the carbonyl ligand on the activation process, we next examined the reactivity of the PCN ligand with a Rh–biscarbonyl cationic species. Surprisingly, reaction of ligand **2** with $[Rh(CO)_2(solv)_n]BF_4$ (**8**)[10] in THF at room temperature resulted in the formation of the benzylic complex **9** in quantitative yield (Scheme 2). The air-stable complex **9** was fully characterized spectroscopically and its structure was confirmed by a single-crystal X-ray analysis.

The $^{31}P\{^1H\}$ NMR spectrum of **9** exhibits a doublet at $\delta =$ 114.9 ppm ($J_{P,Rh} = 154.2$ Hz). The broad singlet at $\delta = 9.5$ ppm in the ^1H NMR spectrum is characteristic of a R_3N–H^+ proton. The benzylic carbon atom bound to Rh (ArCH_2Rh) gives rise to a doublet of doublets signal at $\delta = 11.8$ ppm ($J_{Rh,C} = 13.5$ Hz, $J_{P,C} = 4.8$ Hz) in the ^{13}C NMR spectrum. In this spectrum, two carbonyl ligands exhibit two different signals at $\delta = 186.5$ and 185.8 ppm, indicating their magnetic inequivalence. In the IR spectrum the CO ligands give rise to bands at 1969 cm^{-1} and 2038 cm^{-1} in equal intensity, indicating an OC-Rh-CO angle of 90°.

Colorless needles suitable for X-ray analysis were obtained by crystallization of **9** from THF at $-78\,^\circ C$.[17] The rhodium atom is located in the center of a distorted square plane with the two carbonyl ligands located in *cis* positions (Figure 1). In agreement with the NMR data, the N-arm of the PCN frame is protonated and not coordinated to the metal center. Selected bond lengths and bond angles are given in Table 1.

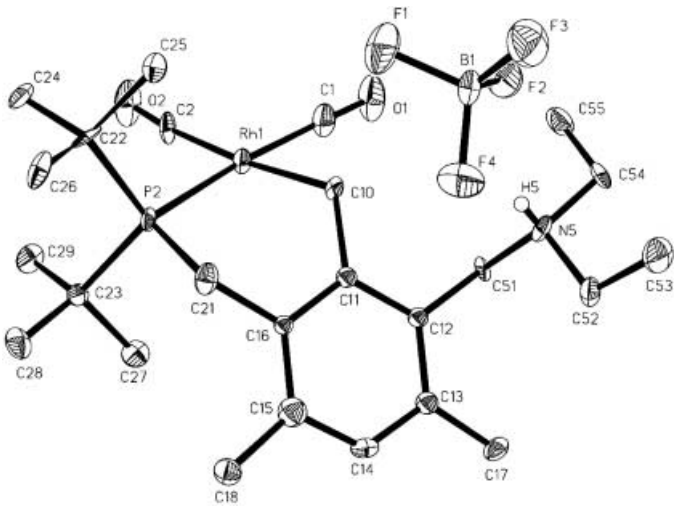


Figure 1. Structure of **9** (ORTEP drawing; 50 % of probability; hydrogen atoms (except N-*H*) are omitted for clarity).

Table 1. Selected bond lengths [Å] and angles [°] for **9**.

Rh1−C1	1.892(10)	Rh1−P2	2.361(2)
Rh1−C2	1.896(10)	O1−C1	1.129(10)
Rh1−C10	2.168(8)	O2−C2	1.131(10)
C1-Rh1-C2	93.5(4)	C10-Rh1-P2	84.5(2)
C1-Rh1-C10	85.6(3)	C2-Rh1-P2	96.2(3)
C2-Rh1-C10	173.5(4)	C1-Rh1-P2	170.0(3)

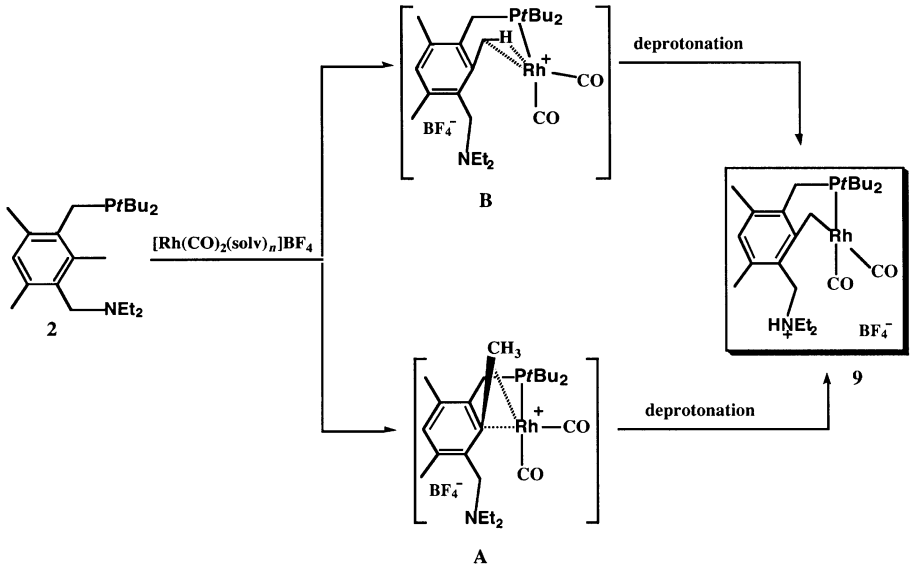
As described above, the monocarbonyl complex **6** is not electron-rich enough to activate C−H or C−C bonds in the reaction with the PCN ligand and leads to formation of the agostic C−C (σ-arenium) compound **7**. Also, it was reported that the methyl group bound to the *ipso*-carbon atom in the PCP – Rh(CO) C−C agostic complex, analogous to **7**, is acidic and can easily be deprotonated by triethylamine to give the corresponding benzylic complex.[8] On the basis of these considerations we believe that a probable mechanism for the formation of complex **9** includes formation of a square-planar $Rh(CO)_2$-C−C agostic intermediate **A** with a non-coordinated amine arm (Scheme 3). The relatively acidic protons of the methyl group bound to the *ipso*-carbon atom undergo intramolecular deprotonation by the amine base, resulting in the benzylic product **9**. An alternative scenario, involving an agostic C−H coordinated to a cationic phosphine $Rh(CO)_2$ species (intermediate **B**) followed by deprotonation by the noncoordinated amine ligand, is also possible. A cationic Rh^I benzylic intermediate which exhibited an agostic C−H bond was recently reported.[18]

Significantly, only the methyl group located between the two ligand arms underwent C−H activation, the other two arylmethyl groups remaining unaffected. This result underlines the important role of the amine, as an internal base, in the selective C−H activation of a specific methyl group.

The overall result of this reaction is the exclusive formation of a C−H-activated product, in contrast to the reaction of the PCN ligand with other cationic[9] and neutral[11] Rh precursors, which yielded exclusively C−C activation products. Thus, it is possible to direct the reaction toward C−C or C−H activation or toward a complex with a C−C agostic (σ-arenium) interaction by simple choice of the cationic $Rh(CO)_n$-based ($n = 0, 1, 2$) precursor.

Complex **9** can be obtained independently by reaction of compound **5** with CO. Thus, reaction of **5** in THF with two equivalents of CO at room temperature yielded complex **9** quantitatively. Interestingly, reaction with an equimolar amount of CO led to 50 % conversion of the starting material to complex **9**, while the monocarbonyl complex **7** was not observed (Scheme 2). Most likely, the first molecule of CO coordinates to the cationic Rh^{III} center, replacing the BF_4 ion, which was shown to be coordinated at room temperature.[8] This causes a direct 1,2-metal-to-carbon methyl shift[8, 19] and leads to the formation of the agostic C−C (σ-arenium) complex **7**. A 1,2-alkyl shift, caused by reduction of electron density on the cationic Rh^{III} center upon CO coordination, was observed in the analogous PCP system.[8] Apparently, reaction of the Rh^I complex **7** with a second molecule of CO is faster than that of the Rh^{III} complex **5**. This reaction probably involves replacement of the hemilabile N-donor arm by a CO ligand, leading to the reactive species **A** (or **B**), which undergoes the C−H activation process as described above.

To examine the possible intermediacy of **7** in the reaction of **5** with CO, a solution of complex **7** in THF was treated with an equimolar amount of CO. An immediate reaction took place, cleanly producing complex **9** as the only product (Scheme 2). Thus, both the C−C-activated product **5** and the C−C agostic complex **7** are easily converted to the C−H activated complex **9** by simple reaction with CO.



Scheme 3. Possible mechanism of formation of C−H-activated complex **9**.

Conclusion

Using the PCN system, a remarkable degree of control over C–C versus C–H bond activation and versus formation of an agostic C–C complex can be achieved by choice of cationic $Rh(CO)_n$-based ($n = 0, 1, 2$) precursors. When $n = 0$, the C–C-activated product was smoothly obtained, whereas with the dicarbonylrhodium complex ($n = 2$) the C–H-activated compound was formed, a process promoted by protonation of the hemilabile amine arm. The monocarbonyl cationic Rh species ($n = 1$) afforded, upon reaction with the PCN ligand, an agostic C–C (σ-arenium) compound. Conversion of the C–C activated complex **5** to the C–H activated one (**9**) was easily achieved by reaction with CO, via an unprecedented sequence of 1,2-methyl shift, agostic interaction and C–H activation processes. In addition, the C–C agostic (σ-arenium) complex **7** was similarly converted to the same C–H-activated product **9** by treatment with CO. These observations clearly demonstrate the crucial influence of π-accepting ligands on the selectivity of C–C versus C–H activation. Whereas an agostic (C–C or C–H) complex has acidic C–H bonds and can undergo deprotonation by base, leading to a C–H activation product, this direction is not available as a route towards C–C activation.

Experimental Section

General procedures: All experiments with metal complexes and phosphine ligands were carried out under an atmosphere of purified nitrogen in a Vacuum Atmospheres glove box equipped with a MO 40–2 inert gas purifier or using standard Schlenk techniques. All solvents were reagent grade or better. All nondeuterated solvents were refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere. Deuterated solvents were used as received. All the solvents were degassed with argon and kept in the glove box over 4 Å molecular sieves. Commercially available reagents were used as received. Complexes $[\{Rh(C_2H_4)_2Cl\}_2]$,[20] $[\{Rh(CO)(C_2H_4)Cl\}_2]$,[21] $[[Rh(CO)_2Cl\}_2]$[22] were prepared according to a literature procedure.

^1H, ^{13}C, ^{31}P, and ^{19}F NMR spectra were recorded at 400, 100, 162, and 376 MHz, respectively, using a Bruker AMX-400 NMR spectrometer. All spectra were recorded at 23 °C. ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^1H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvent ($\delta = 7.24$ ppm, chloroform). In $^{13}C\{^1H\}$ NMR measurements the signal of $CDCl_3$ ($\delta = 77.0$ ppm) was used as a reference. ^{31}P NMR chemical shifts are reported in parts per million downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. ^{19}F NMR chemical shifts were referenced to C_6F_6 ($\delta = -163$ ppm). Screw-cap 5 mm NMR tubes were used in the NMR follow-up experiments. Abbreviations used in the description of NMR data are as follows: b, broad; s, singlet; d, doublet; t, triplet; q, quartet, m, multiplet. Elemental analyses were performed by H. Kolbe, Mikroanalytisches Laboratorium, Germany.

Reaction of the PCN ligand 2 with $[Rh(CO)_2(solv)_n]BF_4$: formation of 9: A solution of $[\{Rh(CO)_2Cl\}_2]$ (30 mg, 0.077 mmol) in THF (2 mL) was mixed with a solution of $AgBF_4$ (30 mg, 0.154 mmol) in THF at room temperature, resulting in the formation of the cationic rhodium precursor $[Rh(CO)_2(solv)_n]BF_4$ and a precipitate of AgCl. The precipitate was removed by filtration and the filtrate containing the cationic rhodium monomer was added to a solution of the PCN ligand **2** (56 mg, 0.154 mmol) in THF. The color changed to yellow within 3 min and the $^{31}P\{^1H\}$ NMR spectrum showed quantitative formation of **2** as a single product. The solvent was evaporated and the resulting solid was washed with pentane (3 × 2 mL) and vacuum dried.

$^{31}P\{^1H\}$NMR ($CDCl_3$): $\delta = 114.81$ ppm (d, $J_{Rh,P} = 154.1$ Hz); ^1H NMR ($CDCl_3$): $\delta = 6.57$ (s, 1H; Ar), 3.77 (m, 1H; Ar-CH_2-N), 3.45 (m, 1H; Ar-CH_2-N), 2.99 (m, 1H; CH_3-CH_2-N), 2.81 (m, 1H; Ar-CH_2-P), 2.76 (m, 1H; Ar-CH_2-P), 2.67 (m, 1H; CH_3-CH_2-N), 2.48 (m, 1H; CH_3-CH_2-N), 2.22 (m, 1H; CH_3-CH_2-N), 2.16 (s, 3H; Ar-CH_3), 2.03 (s, 3H; Ar-CH_3), 1.75 (dd, $J_{Rh,H} = 2.9$ Hz, $J_{P,H} = 1.2$ Hz, doublet in $^1H\{^{31}P\}$ NMR, 3H; Rh-CH_3), 1.19 (d, $J_{P,H} = 13.5$ Hz, singlet in $^1H\{^{31}P\}$ NMR, 9H; $(CH_3)_3$C-P), 1.13 (d, $J_{P,H} = 13.4$ Hz, singlet in $^1H\{^{31}P\}$ NMR, 9H; $(CH_3)_3$C-P), 1.09 (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH_2-N), 0.81 ppm (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH_2-N); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 186.5$ (171.12 (dd, $J_{Rh,C} = 29.1$ Hz, $J_{P,C}$,*cis* = 3.6 Hz, C_{ipso}; Rh-Ar), 145.25 (dd, $J_{P,C} = 11.3$ Hz, $J_{Rh,C} = 2.9$ Hz; Ar), 140.07 (s; Ar), 138.56 (s; Ar), 131.91 (dd, $J_{P,C} = 15.7$ Hz, $J_{Rh,C} = 1.8$ Hz; Ar), 130.62 (s; Ar), 61.65 (bs; Ar-CH_2-N), 48.91 (bs; CH_3-CH_2-N), 48.00 (bd, $J_{Rh,C} = 1.8$ Hz; CH_3-CH_2-N), 36.11 (d, $J_{P,C} = 19.33$ Hz; Ar-CH_2-P), 35.07 (d, $J_{P,C} = 2.4$ Hz; $(CH_3)_3$C-P), 34.84 (d, $J_{P,C} = 2.3$ Hz; $(CH_3)_3$C-P), 30.70 (d, $J_{P,C} = 3.4$ Hz; $(CH_3)_3$C-P), 28.86 (d, $J_{P,C} = 2.6$ Hz; $(CH_3)_3$C-P), 20.57 (s; CH_3-Ar), 19.43 (s; CH_3-Ar), 11.16 (s; CH_3-CH_2-N), 6.40 (s; CH_3-CH_2-N), 0.08 ppm (dd, $J_{Rh,C} = 35.1$ Hz, $J_{P,C} = 7.2$ Hz; Rh-CH_3); (assignment of $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT); $^{19}F\{^1H\}$ NMR ([D_8]THF): $\delta = -164.40$ (s, BF_4); elemental analysis (%) calcd: C 49.92, H 7.67; found: C 50.93, H 8.02.

Reaction of the PCN ligand 2 with $[Rh(CO)(C_2H_4)(solv)_n]BF_4$: formation of 7: A solution of $[\{Rh(CO)(C_2H_4)Cl\}_2]$ (30 mg, 0.077 mmol) in THF (2 mL) was mixed with a solution of $AgBF_4$ (30 mg, 0.154 mmol) in THF at room temperature, resulting in formation of the cationic rhodium precursor $[Rh(CO)_2(solv)_n]BF_4$ and an AgCl precipitate. The precipitate was removed by filtration and the filtrate containing the cationic rhodium monomer was added to a solution of the PCN ligand **2** (56 mg, 0.154 mmol) in THF to give complex **7**. The solvent was evaporated and the resulting orange solid was washed concomitantly with pentane (3 × 2 mL) and diethyl ether (3 × 2 mL) and dried under vacuum, resulting in a pure complex **7** in 95% yield.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 38.56$ ppm (d, $J_{Rh,P} = 113.9$ Hz); ^1H NMR ($CDCl_3$): $\delta = 7.21$ (s, 1H; Ar), 4.37 (d, 1H; $J_{H,H} = 13.6$ Hz; Ar-CH_2-N), 3.93 (dd, $J_{H,H} = 13.6$ Hz, $J_{H,Rh} = 4.8$ Hz, 1H; Ar-CH_2-N), 3.74 (dd, $J_{H,H} = 15.4$ Hz, $J_{H,P} = 10.5$ Hz, doublet in $^1H\{^{31}P\}$ NMR, 1H; Ar-CH_2-P), 3.43 (dd, $J_{H,H} = 15.4$ Hz, $J_{H,Rh} = 12.1$ Hz, doublet in $^1H\{^{31}P\}$ NMR, 1H; Ar-CH_2-P), 3.25 (m, 1H; CH_3-CH_2-N), 3.10 (m, 1H; CH_3-CH_2-N), 3.07 (bs, 3H; C_{ipso}-CH_3) 3.00 (m, 1H; CH_3-CH_2-N), 2.91 (m, 1H; CH_3-CH_2-N), 2.49 (d, $J_{H,P} = 2.2$ Hz, 3H; Ar-CH_3), 2.41 (s, 3H; Ar-CH_3), 1.47 (t, $J_{H,H} = 7.2$ Hz, 3H; CH_3-CH_2-N) 1.40 (d, $J_{P,H} = 14.7$ Hz, singlet in $^1H\{^{31}P\}$ NMR, 9H; $(CH_3)_3$C-P), 1.19 (t, $J_{H,H} = 7.4$ Hz, 3H; CH_3-CH_2-N), 1.13 (d, $J_{P,H} = 14.5$ Hz, singlet in $^1H\{^{31}P\}$ NMR, 9H; $(CH_3)_3$C-P); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 182.5$ (dd, $J_{Rh,C} = 101.6$ Hz, $J_{P,C} = 18.6$ Hz; Rh-CO), 138.60 (s; Ar), 137.34 (s; Ar), 134.35 (dd, $J_{P,C} = 6.3$ Hz, $J_{Rh,C} = 2.1$ Hz; Ar), 132.46 (s; Ar), 125.11 (s; Ar), 108.81 (bs, C_{ipso}; Rh-Ar), 55.23 (bs; Ar-CH_2-N), 54.91 (bs; CH_3-CH_2-N), 54.25 (bs; CH_3-CH_2-N), 30.11 (d, $J_{P,C} = 3.1$ Hz; $(CH_3)_3$C-P), 29.60 (d, $J_{P,C} = 2.9$ Hz; $(CH_3)_3$C-P), 24.11 (d, $J_{P,C} = 17.33$ Hz; Ar-CH_2-P), 19.93 (s; CH_3-Ar), 19.24 (s; CH_3-Ar), 12.90 (s; CH_3-CH_2-N), 12.09 (s; CH_3-CH_2-N), 11.15 (s; C_{ipso}-CH_3); (assignment of $^{13}C\{^1H\}$NMR signals was confirmed by ^{13}C DEPT); $^{19}F\{^1H\}$ NMR ([D_8]THF): $\delta = -151.23$ (s, BF_4).

Reaction of complex 5 with CO: Complex **5** (30 mg, 0.054 mmol) was dissolved in THF (2 mL) and CO (2.5 mL, 0.11 mmol) was slowly bubbled through the solution, resulting in a color change to yellow. The solvent was evaporated and the residual solid was washed with pentane (3 × 2 mL) and dried under vacuum, resulting in quantitative formation of complex **9**.

Reaction of complex 7 with CO: Complex **7** (30 mg, 0.054 mmol) was treated with CO (1.5 mL, 0.066mmol) similarly to complex **5**. The solvent was evaporated and the resulting orange solid was washed with pentane (3 × 2 mL) and diethyl ether (3 × 2 mL) and dried under vacuum, resulting in the quantitative formation of complex **9**.

X-ray crystal structure determination of 9: Complex **9** was crystallized from a concentrated THF solution at −78 °C to give colorless crystals.

Crystal data: $C_{25}H_{42}NPO_2Rh \cdot BF_4$, colorless needles, 0.2 × 0.05 × 0.05 mm^3, triclinic, $P\bar{1}$ (no.2), $a = 8.088(2)$, $b = 12.677(3)$, $c = 14.075(3)$ Å, $T = 120$ K, $V = 1386.2(6)$ Å^3, $Z = 2$, $Fw = 609.29$, $\rho_{calcd} = 1.460$ Mg m^{-3}, $\mu = 0.723$ mm^{-1}.

Data collection and treatment. Nonius KappaCCD diffractometer, $Mo_{K\alpha}$, graphite monochromator ($\lambda = 0.71073$ Å), total of 9488 reflections collected, $0 \le h \le 8$, $-12 \le k \le 12$, $-14 \le l \le 13$, frame scan with 1.0°, scan speed 1° per 60 s, 2893 independent reflections ($R_{int} = 0.1105$).

Solution and refinement: The structure was solved by direct methods (SHELXS-97), full-matrix least-squares refinement based on F^2 (SHELXL-97), hydrogens calculated in idealized positions and refined in a rigid mode, with the exception of H5 on N5 and H10a and H10b on C10 which were located in the electron density map, 306 parameters with 0 restrains, final $R1 = 0.0555$ (based on F^2) for data with $I > 2\sigma I$ based on all 3393 reflections, $R1 = 0.0889$ for all data, goodness-of-fit on $F^2 = 1.059$, largest electron density = 0.583 e Å^{-3}.
CCDC-206717 contains the supplementary crystallographic data for **9**.

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