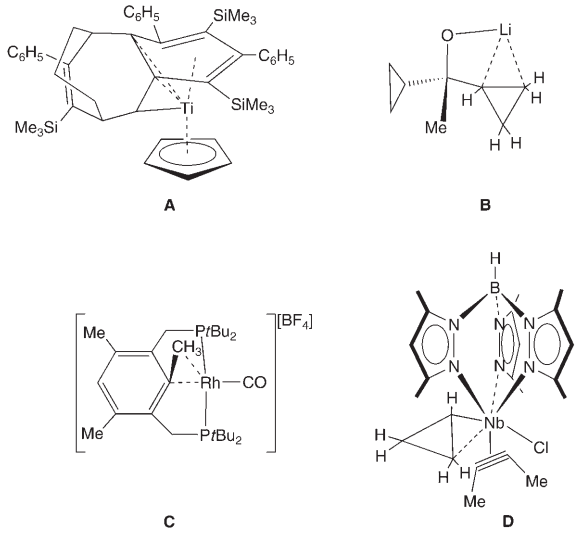

C–C Activation

DOI: 10.1002/ange.200503036

A Rhodium Complex with One Rh···C–C and One Rh···H–C Agostic Bond**

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The metal-mediated activation of carbon–carbon single bonds is the subject of significant contemporary interest,[1] with the putative intermediates in such processes being complexes in which the metal is bound through a C–C σ interaction.[2] Complexes showing such M···CC interactions are extremely rare, and are limited to intramolecular (agostic) interactions that have been reported for complexes **A**–**D**;[3–6] although in one case (**A**) the bonding mode has been queried.[7] The lack of well-characterized examples of such species is in contrast with M···HC agostic complexes that are well established;[2,8–10] and further examples of genuine, fully-characterized examples of M···C–C σ interactions are of clear importance regarding the fundamental study of C–C activation processes. We report here the facile synthesis of a complex that has such a Rh···CC interaction, its full characterization, and some preliminary reactivity studies.

Treatment of [RhCl(nbd)(P*i*Pr$_3$)] with Na[BAr$^F{}_4$] (nbd = norbornadiene, BAr$^F{}_4$ = B(C$_6$H$_3$(CF$_3$)$_2$)$_4$) and a tenfold excess of norbornadiene in fluorobenzene at room temperature results in the formation of [Rh(P*i*Pr$_3$)(C$_{14}$H$_{16}$)][BAr$^F{}_4$] (**1**) as the only organometallic product (Scheme 1). Complex **1** has been characterized by single-crystal X-ray diffraction, NMR spectroscopy, and DFT calculations. Also formed are the organic products of norbornadiene dimerization, which include Binor-S, consistent with the previously reported Rh^I-catalyzed dimerization of norbornadiene.[11]

The solid-state structure of **1** (Figure 1) has a cationic rhodium center coordinated with one P*i*Pr$_3$ ligand, which shows an additional weak γ-agostic C–H interaction from one of the isopropyl groups (Rh–C2 2.901(3), Rh–H2a 2.52(3) Å).[8,12] The other ligand is a saturated hydrocarbon derived from Binor-S (by dimerization of norbornadiene) in which one cyclopropane ring has opened and is now part of a rhodacyclobutane (C11–C15 2.204(4) Å). The Rh–C distances associated with this four-membered ring lie within the range of Rh–C single bonds (Rh–C11 2.032(3), Rh–C15 2.042(3) Å), and are similar to those reported in [Rh(η^5-C$_5$Me$_5$)(PMe$_3$)(CH$_2$)$_3$].[13] The coordination sphere of rhodium is completed by a close approach of the remaining Binor-S cyclopropane ring (C21-C25-C26) (Rh–C21 2.352(3), Rh–C25 2.369(3) Å). These distances are longer than expected for a Rh–C single bond but lie well within the combined van der Waals radii of Rh and C (3.7 Å), suggesting a significant interaction. With an overall cationic charge and metallacyclobutane ring, in the solid-state the rhodium center in **1** is best described as being Rh^{III}.

The question that immediately arises is as to the nature of this close contact with the cyclopropane ring: is it two agostic Rh···HC interactions or one Rh···CC interaction? In the solid state, the hydrogen atoms associated with the cyclopropane ring are certainly close enough to the Rh center to potentially engage in an agostic interaction (Rh–H25 2.30(5), Rh–H21 2.32(3) Å).[8] However, within the limits of the X-ray diffraction experiment the C–H bonds are not significantly length-

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[**] We thank the EPSRC, under grant GR/T10169, and the Royal Society for support.

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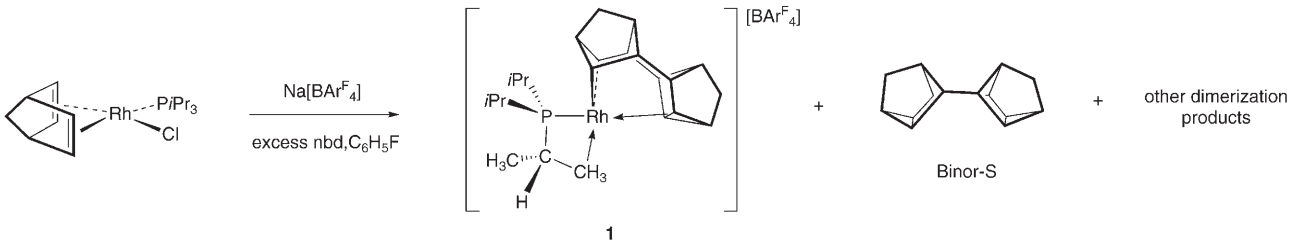


Scheme 1.

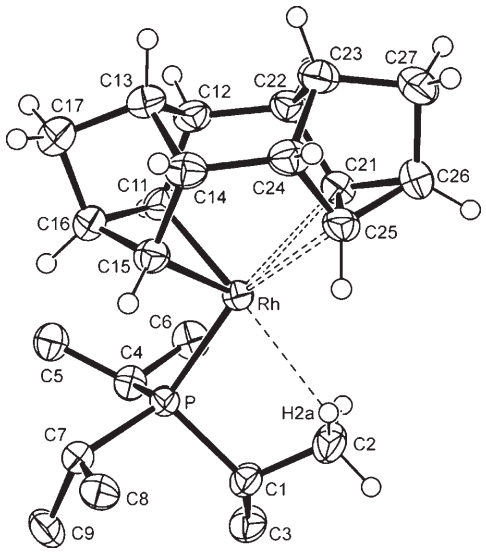
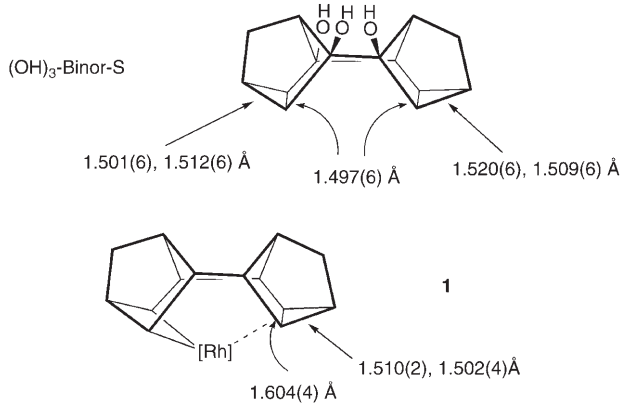


Figure 1. Solid-state structure of the cationic portion of **1**. Thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms on the phosphine ligand, apart from those associated with C2, are omitted for clarity. Selected bond lengths [Å] and angles [°]: Rh–P 2.2693(7), Rh–C11 2.032(3), Rh–C15 2.042(3), Rh–C21 2.352(3), Rh–C25 2.369(3), Rh–C2 2.901(3), Rh–H2a 2.52(3), C21–C25 1.604(4), C21–C26 1.510(4), C25–C26 1.502(4), C11–C15 2.204(4), C21–H21 0.97(3), C25–H25 0.95(3); P-C1-C2 109.7(2), P-C1-C3 117.1(2).



Scheme 2.

ened (C25–H25 0.97(3), C21–H21 0.95(3) Å), contrary to what would be expected for an agostic M···HC interaction. In contrast, compared with free Binor-S (as determined from the structure of the tris-hydroxylated derivative[14]), the C–C bond that is in close proximity with the metal is lengthened by ≈ 0.1 Å, whereas the two other C–C bonds in the cyclopropane unit remain unchanged (Scheme 2). A similar, but slightly smaller, increase in C–C bond length (0.049 Å) has been noted in **D**.[6] The DFT calculated structure of **1** (see below; see Supporting Information for full details) is in close agreement with the experimentally determined structure, showing a lengthening of the C21–C25 bond (1.620 Å), while the calculated C–H bond lengths (1.104/1.105 Å) are not significantly lengthened compared with the other calculated C–H distances (cf. C24–H24 1.104 Å). These observations all point towards a Rh···CC interaction rather than Rh···HC interactions, and are supported by the NMR data and DFT calculations presented below.

In solution at 298 K, the ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** show only five and four[15] resonances, respectively, for the Binor-S ligand, indicating C_s symmetry in solution (in contrast to the solid-state structure), which demonstrates that this ligand undergoes a fluxional process at room temperature. These resonances have been unequivocally assigned by using ^{1}H–^{1}H and ^{13}C–^{1}H correlation experiments. In particular, the signals associated with the four carbon atoms close to rhodium (C11, C15, C21, C25) are all equivalent ($\delta(^1\text{H}) = 3.23$, $\delta(^{13}\text{C}) = 25.5$ ppm) and show coupling to both ^{103}Rh and ^{31}P in the ^{13}C{^{1}H} NMR spectrum, suggesting a significant time-averaged Rh···C interaction in solution. Upon progressive cooling to 200 K the fluxional process is halted ($\Delta G^{\neq} = 48 \pm 2$ kJ mol^{-1}), and 10 signals are observed in both the ^{1}H and ^{13}C{^{1}H} NMR spectra for the Binor-S ligand, which is thus consistent with the solid-state structure. At 200 K the measured ^1J(C,H) value for the cyclopropane carbons (C21, C25) in **1** (170 Hz) is similar to that for the equivalent carbons in free Binor-S (174 Hz), suggesting that Rh···HC agostic interactions are not present, as these would be expected to result in a significant decrease in the observed J(C,H) coupling constant.[9] The contact carbons all show coupling to rhodium at low temperature, but consistent with a weaker agostic interaction, ^1J(Rh,C) for C21/C25 is smaller than for C11/C15 (9 versus 22 Hz respectively). Coupling to ^{103}Rh or ^{31}P is not observed in the ^{1}H NMR spectrum, although the signals are broadened somewhat (fwhm 13 Hz). Over all temperatures the Rh···H_3C interactions from the P*i*Pr$_3$ ligand (Rh···HC(2)) must be rapidly exchanging and this secondary agostic interaction is not observed in solution. A single doublet ($\delta = 49.2$ ppm, J(Rh,P) = 211 Hz) is observed in the ^{31}P{^{1}H} NMR spectrum at room temperature that is essentially invariant on cooling to 200 K.

Topological analysis of the electron density (ρ) in complex **1** has been performed (see Supporting Information for full

details), using DFT calculations in conjunction with Bader's "Atoms in Molecules" (AIM) approach,[16] to quantify the nature of the bonding interactions between Rh and the Binor-S fragment. Such calculations have previously been used to analyze the extent of bonding in situations where simple analysis of bond lengths (obtained from crystallographic studies) cannot provide a complete understanding of the interactions present. Indeed recent AIM analysis of the titanium complex **A**,[7] which contains a short Ti···CC contact in the solid state, indicates that there is no agostic interaction between the Ti and the C–C single bond. This result was contrary to that from previous DFT calculations,[5] for which a natural orbital analysis was used as evidence for an agostic interaction, and highlights the power of methods, such as AIM, which use criteria solely based on a topological analysis of the electron distribution to characterize bonding interactions. AIM analysis of **1** (see Figure 2 and Supporting Information) shows the expected (3, −1) bond critical points (BCPs) between C25–C21 (BCP 1), Rh–C15 (BCP 14), Rh–C11 (BCP 15), and furthermore, the manifestation of an agostic Rh···CC interaction is observed through the presence of (3, −1) BCPs between Rh–C25 (BCP 8) and Rh–C21 (BCP 9). Crucially, no BCP was located between Rh–H25 or Rh–H21, and in a self-consistent check a BCP *is* located between Rh and the isopropyl C2–H2a. Figure 3 shows the topology of the charge density in the plane defined by Rh, C25, and C21. The existence of an agostic CC bond is clearly proven by the presence of: a) BCPs 8 and 9, b) bond paths (BPs) between Rh and C25/C21, and c) an interatomic surface, which forms the boundary between two atoms sharing a BP.

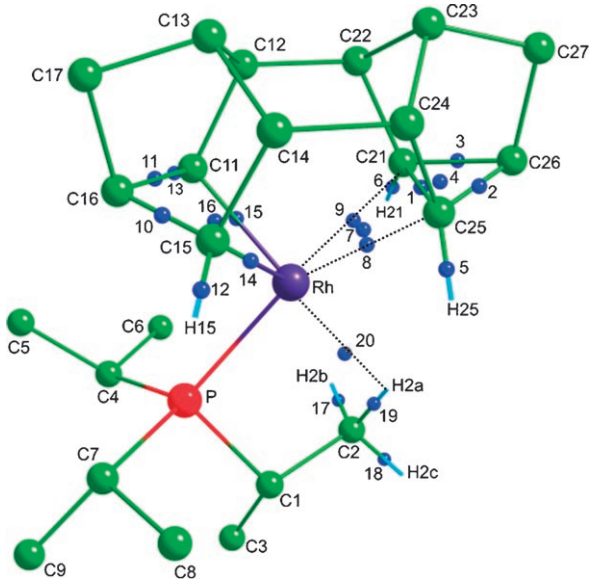


Figure 2. Calculated structure of complex **1** including selected protons (pale blue), BCPs and RCPs (plotted as dark blue spheres). Selected calculated bond lengths [Å]: C25–C21 1.620, Rh–C25 2.273, Rh–C21 2.273, C15–C11 2.185, Rh–C15 2.027, Rh–C11 2.031, C21–H21 1.105, C25–H25 1.104 Å. Broken lines (•••••) represent the agostic interactions present in **1**.

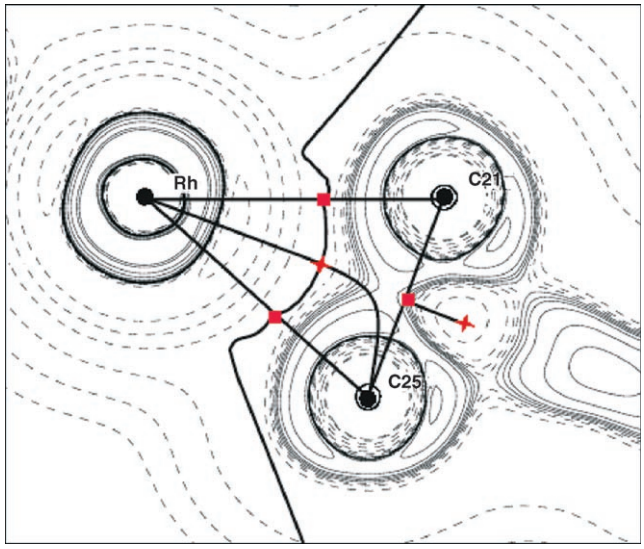
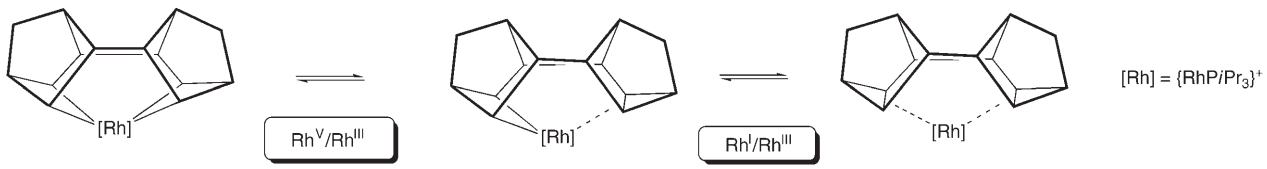


Figure 3. Theoretical bond paths, interatomic surfaces, and $\nabla^2\rho(\boldsymbol{r})$ contour map in the plane defined by Rh, C21, and C25 in complex **1**. Bond critical points are denoted by red squares, and ring critical points are denoted by red crosses.

The fluxional process occurring in **1** in solution at room temperature for the Binor-S fragment is one that equivalences the rhodacyclobutane and cyclopropane fragments observed in the solid state, presumably by concerted or stepwise C–C oxidative addition/reductive elimination. Two possible mechanisms for this invoke a rhodium(v) bis(rhodacyclobutane) intermediate, or a rhodium(i) bis(cyclopropane) (i.e. Binor-S) intermediate (Scheme 3). We favor the latter Rh^{III}/Rh^{I} couple on the basis of the scarcity of Rh^{V} complexes, and reactivity studies (see below) which show that complex **1** reacts more like a latent Rh^{I} rather than a Rh^{III} or Rh^{V} species. DFT calculations are presently being used to elucidate the mechanism and precise geometries of the transition state(s) or intermediates involved in the fluxional process and will be reported upon elsewhere. Further support for the Rh^{III}/Rh^{I} couple comes from cyclopropane activation by Rh^{I} complexes that has been reported previously. For example, experiments



Scheme 3.

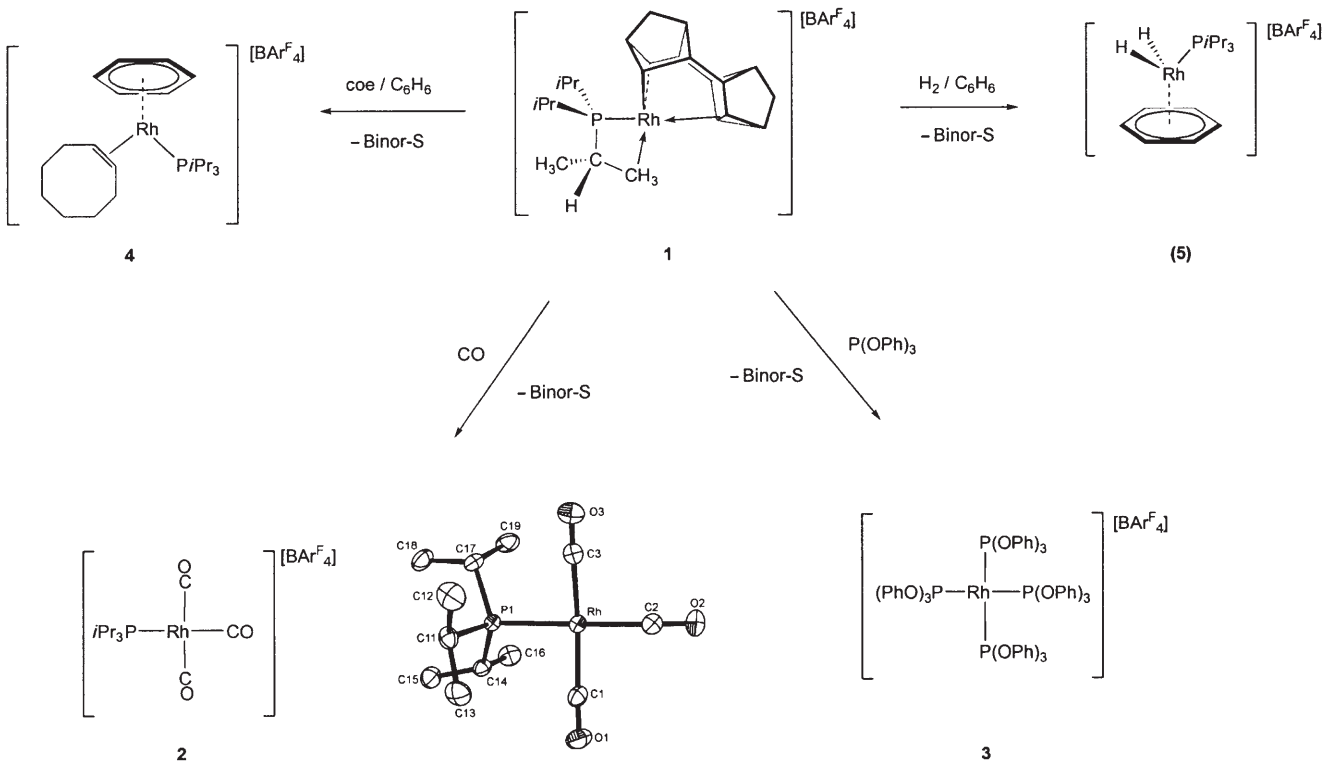
and calculations on the reaction of cyclopropane with a neutral {Cp*Rh(PMe_3)} fragment[13,17] to form a rhodacyclobutane product suggest intermediates with a Rh^I···CC interaction, similar to that experimentally observed for **1**; while complex **1** also has direct relevance to the recently reported catalytic carbon–carbon bond activation of cyclopropanes using [Rh(PPh_3)$_3$Cl],[18] which is suggested to proceed through intermediates with Rh^I···CC interactions.

Complex **1** decomposes in CH_2Cl_2 solution over a period of 24 h, but is relatively stable in fluorobenzene (days, argon atmosphere). In solution, **1** reacts as if it were a source of Rh^I coordinated with Binor-S (Scheme 4), suggesting that the cyclometalated Rh^{III} species observed at low temperature and in the solid state is a resting state for a reactive {Rh(P*i*Pr$_3$)}$^+$ fragment.[19] Thus, reaction with simple Lewis bases such as CO and P(OPh)$_3$ gives free Binor-S and the rhodium(I) complexes [Rh(P*i*Pr$_3$)(CO)$_3$][BAr^F_4] (**2**) or [Rh{P(OPh)$_3$}$_4$][BAr^F_4] (**3**),[20] respectively. The solid-state structure of **2** reveals the expected square-planar Rh^I species. Complex **1** does not react with benzene or exchange with free Binor-S (the latter by EXSY NMR experiments). However, addition of cyclooctene (coe) and benzene to a dichloromethane solution of **1** does result in the facile displacement of Binor-S to form the rhodium(I) complex [Rh(P*i*Pr$_3$)(η^2-C_8H_{14})(η^6-C_6H_6)][BAr^F_4] (**4**).[21] Addition of H_2 and benzene to **1** results in oxidative addition of H_2 and the elimination of Binor-S to afford the rhodium(III) complex [Rh(P*i*Pr$_3$)(H_2)(η^6-C_6H_6)][BAr^F_4] (**5**).[22] Finally, complex **1** is also an isolated resting state of a norbornadiene dimerization catalyst, as addition of excess of diene results in the rapid formation of Binor-S and related dimerization products.

In summary, a rare example of a coordinated C–C single bond with a transition metal has been synthesized and characterized structurally, spectroscopically, and by theoretical calculations. The stability of this complex is no doubt associated with the fact that C–C σ orbitals in the strained cyclopropane ring are sufficiently high in energy to engage in bonding with the metal center,[10] coupled with the chelating nature of the Binor-S derived ligand that brings the cyclopropane fragment into close proximity with the metal center. The facile synthesis of **1** and the rapid equilibrium at room temperature between cyclopropane and metallacyclobutane species suggests that such complexes may prove useful in the further study of C–C activation processes.

Experimental Section

Norbornadiene (100 μL, 930 μmol) was added to a mixture of Na[BAr^F_4] (93 mg, 105 μmol) and [Rh(P*i*Pr$_3$)(nbd)Cl] (40 mg, 102 μmol) in fluorobenzene (3 mL), and the solution was stirred for 2 h. The mixture was filtered, and the filtrate was layered with pentanes and held at 5 °C for 48 h to give **1** as yellow crystals (80 mg, 60 %). ^{1}H (400 MHz, CD_2Cl_2, 298 K): $\delta = 7.71$ (m, 8H; BAr^F_4), 7.55 (m, 4H; BAr^F_4), 3.23 (br, 4H; H11/15/21/25), 2.43 (virtual octet, J(H,H) ≈ J(P,H) = 7 Hz, 3H; PCH), 2.31 (br, 2H; H16/26), 2.13 (br, 2H; H13/23), 1.94 (br, 4H; H12/22/14/24), 1.37 (br, 4H; H17/27), 1.31 ppm (dd, J(P,H) = 14.2, J(H,H) = 7.2 Hz, 18H; CH_3); ^{31}P{^{1}H} (162 MHz): $\delta = 49.24$ ppm (d, J(Rh,P) = 211 Hz); ^{13}C{^{1}H} (101 MHz): $\delta = 162.08$ (q, J(B,C) = 50.0 Hz; B–C), 135.12 (BAr^F CH), 129.21 (m, *C*CF_3), 124.93 (q, J(F,C) = 273 Hz; CF_3), 117.79 (BAr^F CH), 43.63 (s, C12/22/14/24), 34.88 (C13/23), 33.08 (C17/27), 25.53 (dd, J(Rh,C) = 12.4 Hz, J(P,C) = 4.4; C11/15/21/25), 23.69 (dd, J(P,C) = 22.9, J(Rh,C) = 1.3 Hz; PCH), 19.69 ppm (CH_3); elemental analysis calcd (%) for $C_{55}H_{49}BF_{24}PRh$: C 50.40, H 3.76; found: C 50.62, H 3.76.



Scheme 4.

^{1}H NMR (400 MHz, CD_2Cl_2, 200 K): $\delta = 7.71$ (m, 8H; BAr^F_4), 7.52 (m, 4H; BAr^F_4), 3.41 (m, 2H; H11/15), 2.78 (d, J(H,H) = 6.2 Hz, 2H, H21/25), 2.65 (m, 1H; H16), 2.30 (m, 3H; PCH), 2.23 (d, J(H,H) = 9.4 Hz, 2H; H22/24), 2.02 (m, 1H; H23), 1.94 (m, 1H; H13), 1.64 (t, J(H,H) = 6.6 Hz, 1H; H26), 1.45 (s, 2H; H27), 1.42 (br m, 2H; H12/14), 1.16 (dd, J(P,H) = 14.0, J(H,H) = 7.1 Hz, 18H; CH_3), 1.01 ppm (s, 2H; H17). ^{13}C{^{1}H} NMR (101 MHz; J(C,H) values were determined from a coupled HMQC experiment): $\delta = 161.1$ (q, J(B,C) = 49.6 Hz; BC), 133.9 (s; BAr^F_4 CH), 127.9 (q, J(F,C) = 32.2 Hz; CF_3), 123.8 (q, J(F,C) = 237 Hz; CF_3), 116.9 (s; BArF CH), 58.3 (J(C,H) = 148 Hz; C16), 44.6 (J(C,H) = 135 Hz; C12/14), 40.3 (J(C,H) = 138 Hz; C22/24), 35.13 (J(C,H) = 144 Hz; C13), 33.74 (J(C,H) = 133 Hz; C17), 32.52 (J(C,H) = 152 Hz; C23], 30.73 (J(C,H) = 136 Hz; C27), 25.30 (d, J(Rh,C) = 22, J(CH) = 160 Hz; C11/15), 23.78 (d, J(Rh,C) = 9.2, J(C,H) = 170 Hz; C21/25), 22.29 (d, J(P,C) = 24, J(CH) = 124 Hz; PCH), 21.42 (J(C,H) = 185 Hz; C26), 18.68 ppm (J(C,H) = 126; CH_3); ^{31}P{^{1}H} (162 MHz): $\delta = 47.01$ ppm (d, J(Rh,P) = 209 Hz).

Crystallographic data: Crystals of **1** were grown from C_6H_5F/pentane. Intensity data were collected at 150 K on a Nonius Kappa CCD diffractometer, using graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). $C_{55}H_{49}BF_{24}PRh$, $M_r = 1310.63$, $P2_1/n$, $a = 14.8240(2)$, $b = 16.3870(3)$, $c = 22.3530(5)$ Å, $\beta = 99.5330(10)°$ $V = 5355.02(17)$ Å^3, $Z = 4$, $\mu = 0.471$ mm^{-1}, unique reflections = 12123 [R(int) = 0.0647], $R_1 = 0.0458$, $wR_2 = 0.1020$ [$I > 2\sigma(I)$]. The hydrogen atoms H21, H25, and H2A-C were located in the final difference map and freely refined. CCDC-280042 and CCDC-280043 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Received: August 25, 2005
Published online: December 2, 2005

Keywords: agostic interactions · C—C activation · fluxionality · rhodium · X-ray diffraction

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