Solvent-Stabilized Alkylrhodium(III) Hydride Complexes: A Special Mode of Reversible C–H Bond Elimination Involving an Agostic Intermediate

Boris Rybtchinski,[a] Leonid Konstantinovsky,[a] Linda J. W. Shimon,[b] Arkadi Vigalok,[a] and David Milstein*[a]

Abstract: Reaction of the complex $[Rh(coe)_2(solv)_n]BF_4$ (coe = cyclooctene) with the phosphane 1-di-*tert*-butylphosphinomethyl-2,4,6-trimethylbenzene (**1**) results in selective C–H bond activation, yielding the spectroscopically characterized solvento complexes $[(solv)_nRhH\{CH_2C_6H_2(CH_3)_2\text{-}[CH_2P(t\text{Bu})_2]\}]BF_4$ (solv = acetone, **2a**; THF, **2b**; methanol, **2c**). The stability of these complexes is solvent dependent, alcohols providing significant stabilization. Although *cis*-alkylrhodium hydride complexes containing labile ligands are generally unstable, **2a–c** are stable at room temperature. Complex [(acetone)-(ketol)$RhH\{CH_2C_6H_2(CH_3)_2[CH_2P(t\text{-}Bu)_2]\}]BF_4$ (**2d**, ketol = 4-hydroxy-4-methyl-2-pentanone, the product of acetone aldol condensation), crystallized from a solution of **2a** in acetone and was structurally characterized. Unusual solvent- and temperature-dependent selectivity in reversible C–H bond elimination of these complexes, most probably controlled by a special mode of strong agostic interactions, is observed by spin saturation transfer experiments.

Keywords: agostic interactions · C–H activation · eliminations · hydrido complexes · rhodium

Introduction

Cationic late transition metal complexes mediate a variety of important catalytic and stoichiometric reactions, such as alkane C–H bond activation[1] and efficient selective olefin polymerization.[2] Unsaturated cationic complexes are in many cases stabilized by agostic interactions involving C–H bonds and/or by coordinated solvent molecules. Cationic iridium complexes proved to be excellent models for studies of C–H agostic interactions[3] and advantageous systems for intermolecular alkane C–H bond activation.[1b] C–H–metal agostic bonding is an important mode of stabilization of unsaturated metal centers. The transition state of intramolecular C–H activation can be viewed as elongation of an agostic C–H bond,[4] and involvement of the agostic intermediate in C–H oxidative addition was implied in many cases, although identification of the agostic species on the reaction pathway was possible only in a few systems.[5] Intermolecular metal–alkane σ complexes were implicated as intermediates in oxidative addition and reductive elimination in several cases.[6] We have recently reported a cationic Rh–PCP system, which can be driven towards selective C–C or C–H activation by solvent choice; unsaturation of the metal center is of primary importance.[7]

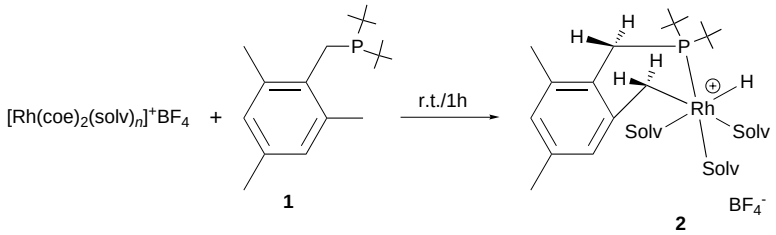
Here we report on stable cationic alkylrhodium(III) hydride complexes, stabilized by solvent coordination. These complexes exhibit unusual selectivity in reversible C–H bond elimination, which is most probably controlled by a special mode of strong agostic interactions. C–H reductive elimination from rhodium(III) phosphane complexes was reported to be promoted by unsaturation (ligand dissociation).[8] Therefore, stable *cis*-alkylrhodium hydride complexes, which are generally rare, are normally limited to saturated electron-rich complexes stabilized towards ligand dissociation.[9] The alkylrhodium(III) hydrides reported here, while containing labile coordinated solvent molecules, are the only observed species at various temperatures, although they undergo reversible C–H elimination.

[a] Prof. Dr. D. Milstein, B. Rybtchinski, Dr. L. Konstantinovsky, Dr. A. Vigalok
Department of Organic Chemistry
The Weizmann Institute of Science
Rehovot, 76100 (Israel)
Fax: (+972) 8-9344142
E-mail: david.milstein@weizmann.ac.il

[b] Dr. L. J. W. Shimon
Department of Chemical Services
The Weizmann Institute of Science
Rehovot, 76100 (Israel)

Results and Discussion

Synthesis and characterization of alkylrhodium(III) hydrides: Reaction of the complex $[Rh(coe)_2(solv)_n]BF_4$ (coe = cyclooctene)[10] in THF at room temperature with one equivalent of phosphane **1**[11] led to the quantitative formation of the C–H activation product **2** after 1 h (Scheme 1).[12] Complex **2** does not coordinate an additional molecule of the



Scheme 1. Synthesis of **2**. coe = cyclooctene. **a**: Solv = acetone; **b**: Solv = THF; **c**: Solv = methanol.

phosphane when excess of **1** is used. It is stable in polar coordinating solvents such as acetone, THF, and methanol, but decomposes when it is dissolved in benzene, dichloromethane, or chloroform. Complex **2** was characterized spectroscopically. Importantly, the solvent used for the NMR measurements greatly influences the spectra of the compound. In acetone, complex **2** gives rise to broad signals in the ^{1}H and ^{13}C {^{1}H} NMR spectra at room temperature, the signals becoming sharp at $-20\,^\circ$C. In THF the ^{1}H and ^{13}C NMR the signals are sharp at $-10\,^\circ$C, and in methanol the NMR spectra show sharp resolved signals even at room temperature. These observations are consistent with the stabilization of **2** by coordinated solvent molecules, reflecting the ability of the solvent to bind to the cationic metal center.[13] Thus, **2** binds solvent molecules forming **2a** in acetone, **2b** in THF, and **2c** in methanol. Complexes **2a**–**c** were characterized by NMR spectroscopy at -20, -10, and $22\,^\circ$C, respectively, showing very similar spectra (Table 1). For example, complex **2c** gives rise to a doublet centered at $\delta =$ 125.67 (^1J(Rh,P) = 197.0 Hz) in the ^{31}P{^{1}H} NMR spectrum, such a large downfield chemical shift being characteristic of six-membered phosphane chelates.[12b, 14]

The Rh-CH_2-aryl methylene protons of **2c** give rise to two resolved signals at $\delta = 2.82$ (doublet of doublets, $J = 9.0$ Hz, $J = 3.5$ Hz) and at $\delta = 2.70$ (multiplet) in the ^{1}H NMR spectrum. In the ^{13}C{^{1}H} NMR spectrum the Rh-CH$_2$-aryl methylene carbon atom appears as a broad doublet at $\delta =$ 15.25 (^1J(Rh,C) = 31.2 Hz). The ^{1}H NMR signal of the hydride ligand appears as a doublet of doublets at $\delta = -25.52$ (J(P,H) = 20.6 Hz, J(Rh,H) = 6.9 Hz), indicating that it is *trans* to a weak ligand or an empty coordination site. The assignment of the NMR signals was confirmed by the ^{13}C–^{1}H heteronuclear correlation (Figure 1). No signals due to coordinated cyclooctene were observed.

Interestingly, the coordinated acetone molecules in **2a** are relatively labile, even in neat acetone, and can be substituted by an equivalent amount of ethylene glycol. The ^{1}H NMR spectrum of the resulting complex shows coordination of one molecule of the diol, whereas IR spectroscopy reveals the presence of a coordinated carbonyl moiety. Thus, three solvent molecules appear to be coordinated to the metal center (as is also evident from X-ray structure analysis, vide infra).[13] Similarly, substitution of coordinated THF takes place upon addition of ethylene glycol to a solution of **2** in THF. Notably in acetone and THF solutions complexes **2a** and **2b** are stable for days at room temperature, while in methanol, complex **2c** is stable for weeks. Such stability of cationic *cis*-alkylrhodium hydride complexes is unexpected considering the lability of coordinated solvent molecules. The reversible reductive elimination which **2** undergoes and its stabilization effect are discussed below.

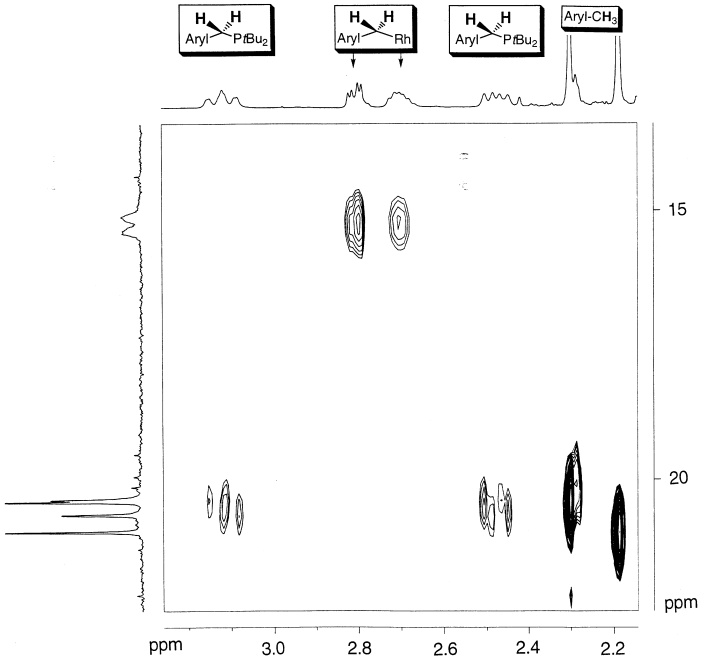


Figure 1. A ^{13}C-^{1}H heteronuclear correlation spectrum of **2c**, showing part of the aliphatic region.

X-ray structure analysis: Yellowish needles suitable for a single-crystal X-ray structure analysis were obtained by slow crystallization from a solution of **2** in acetone. The structure obtained (complex **2d**, Figure 2, Table 2) shows that the Rh atom is situated in the center of an octahedral ligand environment, in which alkyl, hydride, and phosphane ligands are facially coordinated. Three other coordination sites are occupied by an acetone molecule, and a ketol moiety (diacetone alcohol, 4-hydroxy-4-methyl-2-pentanone),[15] the product of aldol condensation of two acetone molecules, most probably

Table 1. Selected NMR data for complexes **2a**–**c**.

	2a	**2b**	**2c**
Rh–*P*	124.59 (d, ^1J(Rh,P) = 191.8 Hz)	127.17 (d, ^1J(Rh,P) = 200.0 Hz)	125.67 (d, ^1J(Rh,P) = 197.0 Hz)
Rh–*H*	−24.47 (dd, J(Rh,H) = 17.7 Hz, J(P,H) = 5.5 Hz)	−26.37 (br. dd, J(Rh,H) = 18.4 Hz)	−25.52 (dd, J(Rh,H) = 20.6 Hz, J(P,H) = 6.9 Hz)
Aryl-CH_2-Rh	13.80 (br. d, ^1J(Rh,C) = 25.9 Hz)	15.41 (br. d, ^1J(Rh,C) = 26.6 Hz)	15.25 (br. d, ^1J(Rh,C) = 31.2 Hz)

0947-6539/00/0617-3288 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

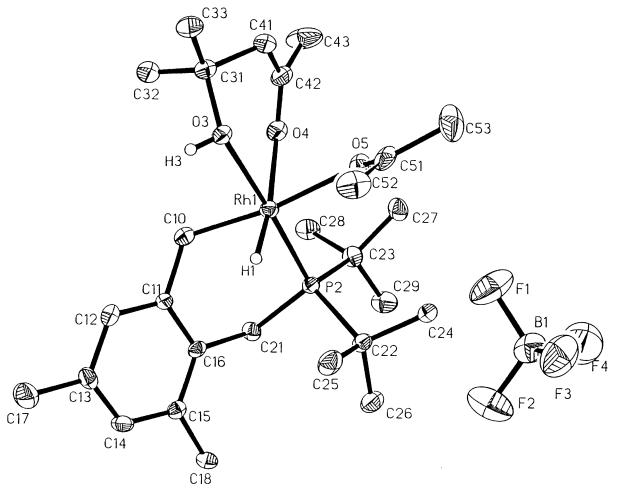


Figure 2. Structure of complex **2d** (ORTEP diagram). Hydrogen atoms, except for H1 and H3, are omitted for clarity.

Table 2. Selected bond lengths and bond angles for **2d**.

Rh1–H1 1.53(7)	Rh1–C10 2.045(5)	Rh1–O3 2.204(3)
Rh1–O4 2.246(3)	Rh1–O5 2.227(3)	Rh1–P2 2.226(1)
C10–C11 1.504(6)	C16–C21 1.513(6)	C31–O3 1.457(5)
C42-O4 1.224(6)	C51–O5 1.233(6)	C10-Rh1-P2 87.80(14)
O3-Rh1-P2 174.55(9)	C10-Rh1-O3 91.18(16)	C10-Rh1-O4 94.47(15)
C10-Rh1-O5 173.00(15)	O3-Rh1-O4 81.37(12)	O3-Rh1-O5 83.19(12)
O5-Rh1-O4 80.61(12)	P2-Rh1-O5 98.19(9)	P2-Rh1-O4 104.04(9)
C21-P2-Rh1 111.59(15)	C11-C10-Rh1 116.9(3)	C10-C11-C16 120.5(4)

promoted by the cationic rhodium center acting as a Lewis acid. The chelating ketol moiety probably contributes to the stabilization of this complex. The Rh1–C10 bond length of 2.045(5) Å is similar to Rh–benzyl bond lengths in comparable chelate environments.[12a,b] Bond angles of the six-membered chelate ring indicate that it is not significantly strained. There is no evidence for agostic interactions in **2d**.

Spin saturation transfer studies: mechanism of reversible C–H bond elimination: Although an unsaturated cationic rhodium center is expected to undergo rapid reductive C–H elimination,[8] the hydride complexes **2a–c**, containing labile solvent molecules, are the only species observed. In order to probe the system for reversible C–H elimination/activation we performed spin saturation transfer (SST) experiments (for details see Experimental Section), involving selective irradiation of the hydride ligand in **2.**[16] The results of these experiments indicate that a chemical exchange between the hydride and the methylene protons takes place. The most interesting feature of this exchange process is its selectivity: *only one of the two methylene protons is involved in the exchange* up to a certain temperature (Figure 3, Scheme 2). To confirm that the observed selectivity is due to the chemical exchange and not caused by an intrinsic difference in relaxation times, T_1 values for the two methylene protons were measured in the absence of the exchange ($-10\,^{\circ}C$, CD_3OD). Indeed, very similar T_1 values were obtained (signal at $\delta = 2.81$, $T_1 = 343$ ms; $\delta = 2.70$, $T_1 = 329$ ms).

The temperature at which the second methylene proton, which was not involved in the exchange, starts to exchange with the hydride (as indicated by SST) strongly depends on the solvent and is -10, 7, and 27 °C for acetone, THF, and methanol, respectively. At this point the protons of the other methyl group, which are equivalent (in the case of full

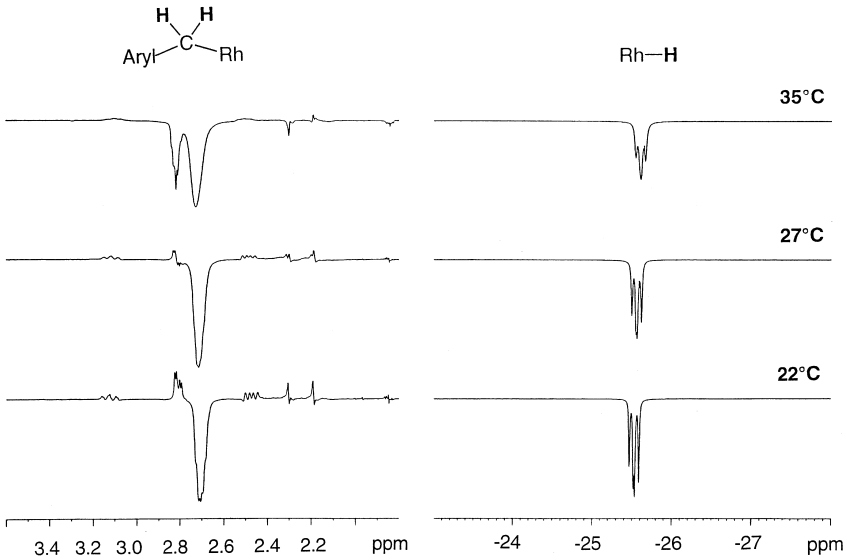
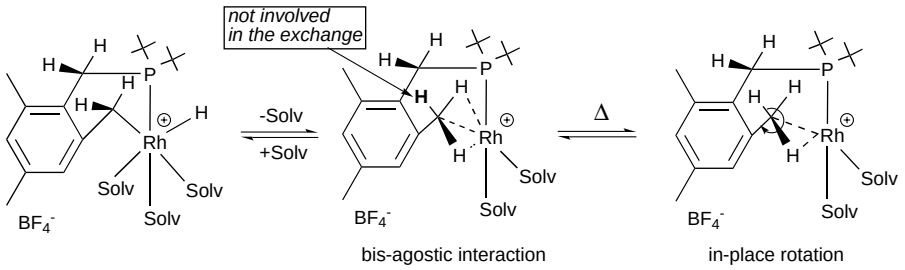


Figure 3. Difference spectra of spin saturation transfer measurements in CD_3OD at various temperatures, showing the inverted hydride signal and the methylene protons response. This response was detected by comparison (subtraction) with a control experiment, in which the signal-free area was irradiated under the same conditions. 22 °C: Observation of a small positive NOE of one of the methylene protons (due to proximity to the hydride and/or secondary NOE) and a strong negative signal due to chemical exchange for another methylene proton. 27 °C: The small positive NOE disappears, the negative signal increases. 35 °C: Observation of negative signals of both methylene protons and a small negative signal of the methyl protons (signal at $\delta = 2.3$). The small out-of-phase signals are due to subtraction inaccuracy, caused by the phasing of the parent spectra.



Scheme 2. Mechanism of reversible C–H bond elimination.

opening) to the ones being activated, do not show any exchange with the hydride. A higher temperature is needed in order to observe some exchange effect with this methyl group (e.g. in CD_3OD it is observed above 35 °C); however, at these temperatures slow decomposition starts to take place. A plausible explanation for the observed exchange selectivity is that when C–H reductive elimination occurs, the C–H bond *is not detached from the cationic metal center,* but rather held by an agostic interaction,[17] *playing the role of a stabilizing ligand*. The same interaction may take place with another C–H bond of the reductively eliminated methyl group, creating a double agostic interaction (η^2-H,H; Scheme 2), precedented in the case of various unsaturated complexes[3, 18] and reactive intermediates.[19] Thus, one of the methyl C–H bonds is not involved in an agostic interaction and, hence, it is excluded from the C–H activation process (Scheme 2). At a higher temperature, dependent upon the solvent, detachment of the agostic bonds starts to take place and the third C–H bond becomes involved in activation by the metal center (methyl in-place rotation).[17a, 20] At still higher temperatures complete detachment of the methyl group, rotation, and activation of the other methyl group starts to take place.

Another possible mechanism can involve a single agostic interaction with one of the diastereotopic benzylic protons (Scheme 3). Upon detachment of this agostic bond the metal immediately binds only one of the available C–H bonds of the benzyl group, which is sterically predisposed for the bonding with the metal center. If the rate of methyl rotation is significantly slower than the on-off metal – C–H agostic bonding, the third C–H bond is excluded from the exchange. At higher temperatures rotation and activation of the third C–H bond takes place.

To get more information about the reaction mechanism, spin saturation transfer kinetic experiments were performed with **2c** in CD_3OD between 0 to 20 °C (conditions at which the second methylene proton does not undergo exchange, Table 3). The activation parameters obtained from an Eyring plot are $\Delta H^{\neq}_{obs} = 14.79 \pm 2.57$ kcal mol^{-1}, $\Delta S^{\neq}_{obs} = -6.03 \pm 1.08$ e.u., $\Delta G^{\neq}(293) = 16.57 \pm 2.89$ kcal mol^{-1} (Figure 4). The mildly negative value of $\Delta S^{\neq}_{obs}$ indicates that the reductive elimination and the resulting agostic exchange is not the only measured process, since a more negative activation entropy value is expected for the organized transition state.[21] Most probably, predissociation of the coordinated solvent (positive entropy change) followed by C–H reductive elimination and agostic bond exchange takes place. Thus, the observed kinetic parameters seem to relate to a complex process. Solvent dissociation is necessary in order to create an empty coordination site for agostic C–H bonding and it is also expected to promote C–H reductive elimination.[8] The temperature at which the exchange starts to take place is significantly lower for acetone than for THF or MeOH, which is consistent with the stronger coordination ability of THF and MeOH to the cationic metal center.

Table 3. Kinetic data for the exchange process between the hydride ligand and one of the methylene protons, yielding $\Delta H^{\neq}_{obs} = 14.79$ kcal mol^{-1}, $\Delta S^{\neq}_{obs} = -6.03$ e.u., $\Delta G^{\neq}(293) = 16.57$ kcal mol^{-1}.

T [°C]	0	5	10	20
k [s^{-1}]	0.386	0.617	1.290	2.557

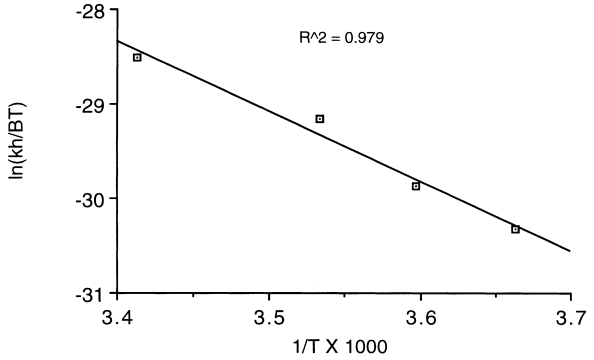
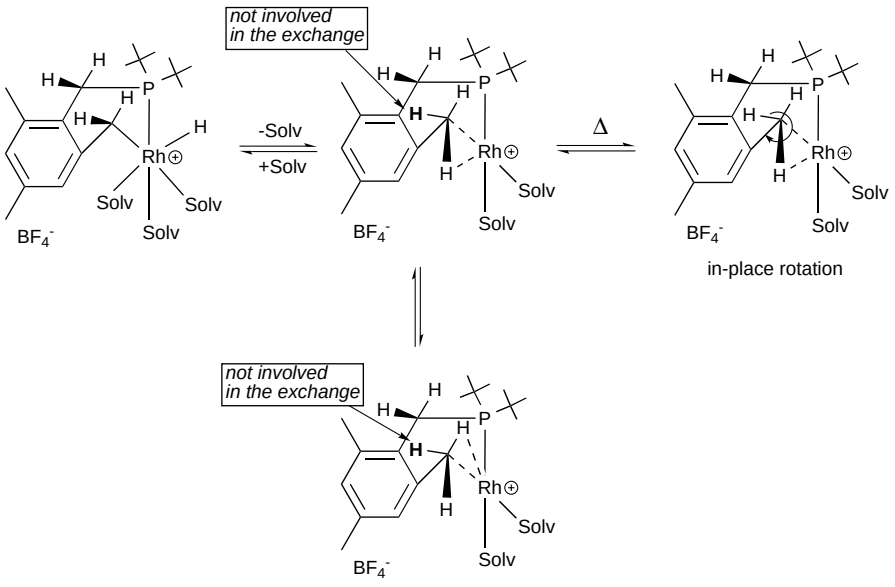


Figure 4. Eyring plot for the exchange process between the hydride ligand and one of the methylene protons.



Scheme 3. Alternative mechanism for the C–H bond elimination involving a single agostic interaction with one of the diastereotopic benzylic protons.

A comparison of the rates of the exchange of the two methylene protons was performed at 33 °C in methanol by SST. A ratio of $k_1/k_2 = 20.24$ (k_1 and k_2 are the observed rate constants for the first and second exchange processes, respectively) was observed, corresponding to $\Delta\Delta G^{\neq}(306) = 1.83 \pm 0.32$ kcal mol^{-1}. Such a significant difference in reaction rates testifies that the agostic bonding, responsible for the first exchange process, is strong at the temperature of measure-

0947-6539/00/0617-3290 $ 17.50+.50/0 *Chem. Eur. J.* **2000**, *6*, No. 17

ment. We believe that this considerable difference tends to support the double agostic (η^2-H,H) hypothesis, rather than a single agostic interaction (η^1-C,H) based on diastereotopic selectivity. A comparison of the two exchange processes at higher temperatures by SST was impossible due to significant broadening and overlapping of the two methylene proton signals.

It should be noted that despite the reversible C–H elimination, the alkyl hydride complexes **2a–c** are stable. Agostic bonding appears to play an important role in this stabilization, since under conditions of full detachment of the agostic bonds the complexes **2a–c** start to decompose. Upon solvent dissociation and C–H reductive elimination the metal-bound agostic C–H bond plays the role of a stabilizing ligand.

Conclusion

Unexpectedly stable solvento alkylrhodium(III) hydride complexes were synthesized and fully characterized. Their stability is solvent dependent, and follows the trend ethylene glycol > methanol > THF > acetone. Selective, temperature and solvent-dependent Rh–H/C–H exchange processes have been identified. The inequivalence of the two benzyl C–H bonds in the exchange with the hydride indicates that the C–H reductive elimination results in double agostic interaction or fast on-off agostic bonding of diastereotopic C–H bonds. This interaction plays an important role in controlling the C–H bond activation selectivity. The bond which is not involved in the agostic interaction in our system cannot be activated by the metal center, supporting the notion that C–H agostic interaction is a prerequisite for C–H bond activation. Thus, this study indicates several stages in the reductive elimination/C–H activation of a methyl group: 1) solvent dissociation; 2) selective formation of one or, more likely, two agostic bonds, one proton being unaffected; 3) upon heating, agostic bond rupture and formation involving all three protons without detachment of the methyl group; 4) complete detachment of the methyl group at higher temperature and activation of another methyl group.

Experimental Section

All experiments with metal complexes and the phosphane ligand 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 in a MBraun MB 150B-G glove box. The complex $[\{Rh(coe)_2Cl\}_2]$ was prepared according to a literature procedure.[22]

^{1}H, ^{13}C, ^{31}P NMR spectra were recorded at 400, 100, and 162 MHz respectively, using a Bruker Avance-400 NMR spectrometer. ^{1}H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are reported in ppm downfield from tetramethylsilane. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signal of the deuterated solvents and in $^{13}C\{^1H\}$ NMR the ^{13}C signal of the deuterated solvents was used as a reference. ^{31}P NMR chemical shifts are reported in ppm downfield from H_3PO_4 and referenced to an external 85% solution of phosphoric acid in D_2O. $^{13}C-^1H$ heteronuclear correlation was measured using a 5 mm inverse probehead with a z-gradient coil. Abbreviations used in the description of NMR data: Ar: aryl; br: broad; dist.: distorted; s: singlet; d: doublet; m: multiplet. Elemental analyses were performed at the Hebrew University of Jerusalem.

Synthesis of ligand 1: A solution of α-bromoisodurene (6.72 g, 31.5 mmol)[23] in dry acetone (14 mL) was added to di-*tert*-butylphosphane (4.6 g, 31.5 mol) under a nitrogen atmosphere.[24] A violent reaction occurred immediately and a white precipitate was formed within one minute. The precipitate was filtered off, washed with cold acetone, and dried in vacuum to give the pure phosphonium salt (9.0 g; yield 79.4%).

A solution of the phosphonium salt (9.0 g, 25 mmol) in degassed water (30 mL) was treated with a solution of sodium acetate (8.2 g, 100 mmol) in degassed water (20 mL) under argon. A white precipitate was rapidly formed. Dry diethyl ether (30 mL) was added, producing two transparent layers. The diethyl ether layer was separated by cannula transfer, the water layer was washed with another portion of diethyl ether (20 mL) and both diethyl ether fractions were combined and dried over anhydrous sodium sulfate. Evaporation of diethyl ether gave pure **1** (6.0 g; yield 86.5%). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta = 25.68$ (s); ^{1}H NMR ($CDCl_3$): $\delta = 6.76$ (s, 2H; Ar-H), 2.86 (d, J(P,H) = 10.3 Hz, 2H; Ar-CH_2-P), 2.43 (s, 6H; CH_3-Ar), 2.2 (s, 3H; CH_3-Ar), 1.25 (d, 18H, J(P,H) = 10.6 Hz; 2 *t*Bu).

Reaction of $[Rh(coe)_2(solv)_n]BF_4$ with ligand 1 in THF: formation of complex 2: To a solution of $[Rh(coe)_2(solv)_n]BF_4$ (obtained in situ from $[\{Rh(coe)_2Cl_2\}_2]$ (22 mg, 0.031 mmol) and $AgBF_4$ (12 mg, 0.062 mmol)) in THF (2 mL) was added a solution of the ligand **1** (17 mg, 0.061 mmol) in THF (2 mL). After 1 h at room temperature the color of the mixture changed from orange to brown. Evaporation of the solvent resulted in the formation of **2** as a dark solid. Complex **2** is soluble in acetone, THF, methanol, quantitatively forming **2a**, **2b**, and **2c**, respectively; it decomposes in benzene, dichloromethane, chloroform.

2a: $^{31}P\{^1H\}$ NMR ([D_6]acetone, −20 °C): $\delta = 124.59$ (d, ^1J(Rh,P) = 191.8 Hz); ^{1}H NMR ([D_6]acetone, −20 °C): $\delta =$ 6.83 (s, 1H; Ar), 6.74 (s, 1H; Ar), 3.14 (m, 1H; Ar-CH_2-P), 2.90 (m, 1H; Rh-CH_2-Ar), 2.76 (m, 2H; overlapped 1 Ar-CH_2-P and 1 Rh-CH_2-Ar), 2.34 (s, 3H; Ar-CH_3), 2.16 (s, 3H; Ar-CH_3), 1.46 (d, J(P,H) = 12.6 Hz, 9H; $(CH_3)_3$C-P), 1.15 (d, J(P,H) = 13.1 Hz, 9H; $(CH_3)_3$C-P), −24.47 (dd, J(Rh,H) = 17.7 Hz, J(P,H) = 5.5 Hz; Rh-H). Assignment of the ^{1}H NMR signals was confirmed by a $^{13}C-^1H$ heteronuclear correlation. $^{13}C\{^1H\}$ NMR: $\delta = 149.27$ (d, J = 6.1 Hz; Ar), 134.54 (s; Ar), 134.30 (d, J = 5.2 Hz; Ar), 131.08 (s; Ar), 127.07 (s; Ar), 124.69 (s; Ar), 37.22 (d, J(P,C) = 24.4 Hz; $(CH_3)_3C$-P), 36.96 (d, J(P,C) = 16.3 Hz; $(CH_3)_3C$-P), 29.12 (s; $(CH_3)_3$C-P), 29.10 (s; $(CH_3)_3$C-P), 20.24 (s; CH_3-Ar), 19.80 (s; CH_3-Ar), 18.97 (d, J(P,C) = 27.9 Hz; Ar-CH_2-P), 13.80 (br. d, ^1J(Rh,C) = 25.9 Hz; Rh-CH_2-Ar). Assignment of the $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT 135 and $^{13}C-^1H$ heteronuclear correlations. IR (film): $\tilde{\nu} = 1664.8$ (s) $\nu_{C=O}$, coordinated acetone. Elemental analysis calcd. (for two coordinated acetone molecules) C 48.41, H 7.26; found: C 48.19, H 7.20. Upon drying the compound does not retain the third coordinated acetone molecule.

2b: $^{31}P\{^1H\}$ NMR ([D_8]THF, −10 °C): $\delta = 127.17$ (d, ^1J(Rh,P) = 200.0 Hz); ^{1}H NMR ([D_8]THF, −10 °C): $\delta = 7.03$ (s, 1H; Ar), 6.93 (s, 1H; Ar), 3.21 (m, 1H; Ar-CH_2-P), 3.00 (m, 1H; Rh-CH_2-Ar), 2.88 (m, 1H; Rh-CH_2-Ar), 2.65 (m, 1H; Ar-CH_2-P), 2.24 (s, 3H; Ar-CH_3), 2.21 (s, 3H; Ar-CH_3), 1.53 (d, J(P,H) = 12.6 Hz, 9H; $(CH_3)_3$C-P), 1.14 (d, J(P,H) = 13.1 Hz, 9H; $(CH_3)_3$C-P), −26.37 (br unresolved dd, J(Rh,H) = 18.4 Hz; Rh-H). Assignment of the ^{1}H NMR signals was confirmed by a $^{13}C-^1H$ heteronuclear correlation. $^{13}C\{^1H\}$ NMR: $\delta = 150.77$ (d, J = 5.8 Hz; Rh-Ar), 135.53 (s; Ar), 134.99 (d, J = 5.2 Hz; Ar), 132.41 (s; Ar), 127.82 (s; Ar), 124.76 (s; Ar), 38.04 (d, J(P,C) = 24.8 Hz; $(CH_3)_3C$-P), 37.34 (d, J(P,C) = 16.3 Hz; $(CH_3)_3C$-P), 29.79 (br. s; $(CH_3)_3$C-P), 21.16 (s; CH_3-Ar), 20.58 (s; CH_3-Ar), 20.16 (d, J(P,C) = 27.9 Hz; Ar-CH_2-P), 15.41 (br. d, ^1J(Rh,C) = 26.6 Hz; Rh-CH_2-Ar). Assignment of the $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT 135 and $^{13}C-^1H$ heteronuclear correlations.

2c: $^{31}P\{^1H\}$ NMR ([D_4]methanol, 22 °C): $\delta = 125.67$ (d, ^1J(Rh,P) = 197.0 Hz); ^{1}H NMR ([D_4]methanol, 22 °C): $\delta = 6.92$ (s, 1H; Ar), 6.72 (s, 1H; Ar), 3.13 (m, 1H; Ar-CH_2-P), 2.82 (dd, J = 9.0 Hz, J = 3.5 Hz, 1H; Rh-CH_2-Ar), 2.70 (m, 1H; Rh-CH_2-Ar), 2.49 (m, 1H; Ar-CH_2-P), 2.31 (s, 3H; Ar-CH_3), 2.20 (s, 3H; Ar-CH_3), 1.45 (d, J(P,H) = 12.4 Hz, 9H; $(CH_3)_3$C-P), 1.14 (d, J(P,H) = 13.0 Hz, 9H; $(CH_3)_3$C-P), −25.52 (dd, J(P,H) = 6.9 Hz, J(Rh,H) = 20.6 Hz; Rh-H). Assignment of the ^{1}H NMR signals was confirmed by a $^{13}C-^1H$ heteronuclear correlation. $^{13}C\{^1H\}$ NMR: $\delta =$ 150.91 (d, J = 5.8 Hz; Ar), 136.06 (d, J = 1.4 Hz, Ar), 135.40 (d, J = 5.2 Hz; Ar), 132.20 (s; Ar), 127.93 (s; Ar), 125.29 (s; Ar), 38.26 (d, J(P,C) = 24.8 Hz; $(CH_3)_3C$-P), 37.56 (d, J(P,C) = 15.7 Hz; $(CH_3)_3C$-P), 30.02 (br. s; $(CH_3)_3$C-P), 20.96 (s; CH_3-Ar), 20.50 (d, J(P,C) = 27.4 Hz;

Ar-CH_2-P), 20.41 (s; CH_3-Ar), 15.25 (br. d, ^1J(Rh,C) = 31.2 Hz; Rh-CH_2-Ar). Assignment of the $^{13}C\{^1H\}$ NMR signals was confirmed by ^{13}C DEPT 135 and $^{13}C-^1H$ heteronuclear correlations.

X-ray analysis of the structure of 2d: Complex **2d** was crystallized from acetone at room temperature. Crystal data: $C_{27}H_{47}BF_4O_3PRh$, yellowish needles, $0.1 \times 0.05 \times 0.01$ mm^3, triclinic, $P\bar{1}$ (no. 2), $a = 8.837(2)$, $b = 9.535(2)$, $c = 18.409(4)$ Å, $\alpha = 92.36(3)$, $\beta = 90.54(3)$, $\gamma = 90.70(3)^\circ$, from 20 degrees of data, $T = 120$ K, $V = 1549.6(6)$ Å^3, $Z = 2$, $F_w = 642.35$, $\rho_{calcd} = 1.377$ Mg m^{-3}, $\mu = 0.652$ mm^{-1}. Data collection and treatment: Nonius KappaCCD diffractometer, $Mo_{K\alpha}$, graphite monochromator ($\lambda = 0.71073$ Å), 11133 reflections collected, $0 < h < 10$, $-10 < k < 10$, $-20 < l < 20$, frame scan width = 1.6°, scan speed 1° per 60 s, typical peak mosaicity = 0.9°, 4649 independent reflections. Data were processed with Denzo-Scalepack. Solution and refinement: The structure was solved by direct methods (SHELXS-97). Full-matrix least-squares refinement was based on F^2 (SHELXL-97). Idealized hydrogen atoms were placed and refined in a riding mode, with the exception of H1 and H3, which were located in the difference Fourier map and refined independently. 342 parameters with 0 restraints, final $R_1 = 0.0446$ (based on F^2) for data with $I > 2\sigma I$ and $R_1 = 0.0600$ for all data based on all independent reflections, goodness-of-fit on $F^2 = 1.015$, largest electron density = 1.495 e Å^{-3}. The data were not corrected for absorption of the crystal. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140846. Copies of data can be obtained free of charge on application to CCDC 12 Union Road Cambridge CB2, 1EZ, UK (fax: (+44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Spin saturation transfer experiments: Saturation transfer experiments were performed by selective saturation of the hydride resonance. The response of the signal of the methylene protons was detected by comparison (difference spectrum) with a control experiment, in which the signal free area was irradiated under the same conditions. The relaxation time (T_{obs}) of the olefinic protons was measured by using the standard inversion-recovery technique combined with the saturation of the hydride resonance. The k_{obs} value was calculated from the saturation transfer (Forsen–Hoffman) equation: $I^s/I^c = \tau/(\tau + T_{obs})$, where $\tau = 1/k_{obs}$, I^s is the intensity of the benzylic protons signal under the saturation of the hydride resonance, I^c is the one in the control experiment.[16]

Acknowledgement

This work was supported by the U.S.–Israel Binational Science Foundation, Jerusalem, Israel, and by the MINERVA Foundation, Munich, Germany. L. K. thanks the Ministry of Absorption of Israel for financial support. D.M. is the holder of the Israel Matz professorial chair of organic chemistry.

[1] Examples of solvent-stabilized cationic complexes in alkane C–H activation: a) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *Angew. Chem.* **1998**, *110*, 2298; *Angew. Chem. Int. Ed.* **1998**, *37*, 2180; b) B. A. Arndtsen, R. G. Bergman, *Science* **1995**, *270*, 1970.

[2] For a review see: G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem.* **1999**, *111*, 448; *Angew. Chem. Int. Ed.* **1999**, *38*, 428.

[3] a) A. C. Cooper, W. E. Streib, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, *119*, 9069; b) A. C. Cooper, E. Clot, J. C. Huffman, W. E. Streib, F. Maseras, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1999**, *121*, 97.

[4] R. H. Crabtree, E. M. Holt, M. Lavin, S. M. Morenhouse, *Inorg. Chem.* **1985**, *24*, 1986.

[5] a) A. C. Albeniz, G. Schulte, R. H. Crabtree, *Organometallics* **1992**, *11*, 242; b) M. Cree-Uchiyama, J. R. Shapley, G. J. M. St. George, *J. Am. Chem. Soc.* **1986**, *108*, 1316.

[6] For a review see: C. Hall, R. N. Perutz, *Chem. Rev.* **1996**, *96*, 3125.

[7] B. Rybtchinski, D. Milstein, *J. Am. Chem. Soc.* **1999**, *121*, 4528.

[8] D. Milstein, *Acc. Chem. Res.* **1984**, *17*, 221.

[9] For examples, see: a) D. Milstein, *J. Am. Chem. Soc.* **1982**, *104*, 5227; b) W. D. Jones, E. T. Hessel, *J. Am. Chem. Soc.* **1993**, *115*, 554; c) C. Wang, J. W. Ziller, T. C Flood, *J. Am. Chem. Soc.* **1995**, *117*, 1647; d) D. D. Wick, K. A. Reynolds, W. D. Jones, *J. Am. Chem. Soc.* **1999**, *121*, 3974.

[10] $[Rh(coe)_2(solv)_n]BF_4$ was obtained in THF by chloride abstraction from $[Rh(coe)_2Cl]_2$ analogously to a reported procedure: R. R. Schrock, J. A. Osborn, *J. Am. Chem. Soc.* **1971**, *93*, 3089.

[11] See Experimental Section for the detailed procedure.

[12] Intramolecular benzylic C–H activation to give alkyl hydride complexes has been reported, for example: a) T. H. Tulip, D. L. Thorn, *J. Am. Chem. Soc.* **1981**, *103,* 2448; b) Sh.-Y. Liou, M. Gozin, D. Milstein, *J. Am. Chem. Soc.* **1995**, *117*, 9774. 1965; c) B. Rybtchinski, A. Vigalok, Y. Ben-David, D. Milstein, *J. Am. Chem. Soc.* **1996**, *118*, 12406.

[13] Dicationic rhodium(III) complexes $[Cp^*Rh(solvent)_3][PF_6]_2$ were reported: a) S. J. Thompson, P. M. Bailey, C. White, P. M. Maitlis, *Angew. Chem.* **1976**, *88*, 506; *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 490; b) C. White, S. J. Thompson, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* **1977**, 1654.

[14] M. E. van der Boom, Sh.-Y. Liou, L. J. W. Shimon, Y. Ben-David, D. Milstein, *Organometallics* **1996**, *15*, 2562.

[15] Most of the material was not crystalline, and our spectroscopic data indicates no ketol moiety: (based on the ^1H NMR spectrum of complex **2a** in non-deuterated acetone). We believe that preferential crystallization of **2d** can be explained by the stabilization and higher rigidity provided by the ketol chelate.

[16] For examples of spin saturation transfer in chemical exchange studies, see: a) M. Portnoy, D. Milstein, *Organometallics* **1993**, *12*, 1665; b) M. Ogasawara, M. Saburi, *Organometallics*, **1994**, *13*, 1911; c) A. Vigalok, H.-B. Kraatz, L. Konstantinovski, D. Milstein, *Chem. Eur. J.* **1997**, *3*, 253.

[17] For reviews, see: a) M. Brookhart, M. L. H. Green, L.-L. Wong, *Progr. Inorg. Chem.* **1988**, *36*, 1; b) R. H. Crabtree, *Angew. Chem.* **1993**, *105*, 828; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 789.

[18] Double agostic complexes: a) W. A. King, X.-L. Luo, B. L. Scott, G. J. Kubas, K. W. Zilm, *J. Am. Chem. Soc.* **1996**, *118*, 6782; b) W. Baratta, E. Herdtweck, P. Rigo, *Angew. Chem.* **1999**, *111,* 1733; *Angew. Chem. Int. Ed.* **1999**, *38*, 1629. Alkane–metal η^2-H,H complexes: c) S. Geftakis, G. E. Ball, *J. Am. Chem. Soc.* **1998**, *120*, 9953; d) D. R. Evans, T. Drovetskaya, R Bau, C. A. Reed, P. D. W. Boyd, *J. Am. Chem. Soc.* **1997**, *119,* 3633.

[19] a) T. A. Mobley, C. Schade, R. G. Bergman, *Organometallics*, **1998**, *17*, 3574; b) S. S. Stahl, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.* **1996**, *118*, 5961.

[20] D. J. Tempel, M. Brookhart, *Organometallics*, **1998**, *17*, 2290.

[21] T. G. P. Harper, P. J. Desrosiers, T. C. Flood, *Organometallics*, **1990**, *9*, 2523.

[22] J. L. Herde, C. V. Senoff, *Inorg. Nucl. Chem. Letters* **1971**, *7*, 1029.

[23] A. W. van der Made, R. H. van der Made, *J. Org. Chem.* **1993**, *58*, 1262.

[24] For a general procedure of benzylphosphane synthesis see: C. J. Moulton, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1976**, 1020.

Received: February 21, 2000 [F2312]

  0947-6539/00/0617-3292 $ 17.50+.50/0