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The Metal–Alkene Bond in Rh(I)(β-diketonato)(alkene)$_2$ Complexes. Correlation of ^{103}Rh-NMR Shifts with Stability Constants, Alkene Excitation Energies, and d–d Absorption Bands. An Experimental and Theoretical Study

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Abstract: Some new rhodium(I)–alkene complexes with (2,4-pentanedionato = acac) and with (1,1,1,5,5,5-hexafluoro-2,4-pentanedionato = hfacac) have been prepared and characterized by means of NMR (^{13}C, ^{1}H, and ^{103}Rh) and UV–vis spectroscopy. It was found that ^{103}Rh-NMR chemical shifts for the Rh(I)(hfacac)(alkene)$_2$ compounds (alkene = ethylene, *cis*-butene, and *trans*-butene) are linearly proportional to the wavelength of the lowest energy UV-vis absorption band. This relation is explained by the $1/\Delta E$ factor in the Ramsey equation. The Rh-NMR shifts for the compounds have been found to decrease with increasing HOMO–LUMO excitation energies for the free alkenes and with increasing equilibrium constants for the following reaction: Rh(acac)(ethylene)$_2$ + alkene $\rightleftarrows$ Rh(acac)(ethylene)(alkene) + ethylene. Ab initio quantum chemical calculations were performed for several model rhodium–alkene compounds. The calculations were executed on the CASSCF level (complete active space SCF) for all studied rhodium–alkene systems. In some cases, calculations correlating all valence electrons were performed. The rhodium–alkene bond was found to be very similar for ethylene and *cis*-butene. The rhodium–tetrafluoroethylene bond on the other hand showed a more pronounced back-bonding, but also good σ donation, leading to a stronger bond. The results of the calculations were compared to experimental data and found to be in reasonable agreement. As expected, no correlation was found between the Rh-NMR shift for a compound and the charge density on the rhodium atom. On the other hand, ^{1}H-NMR shifts and the calculated charges on the alkene protons in the rhodium–alkene compounds show a linear correlation. The correlation between the Rh-NMR shifts for the complexes and the stability constants is assumed to be caused by the differences in the rhodium–alkene bond distances.

Introduction

A crucial step in catalytic reactions of alkenes is generally assumed to be coordination of the alkene to the catalyst. The understanding of the metal–alkene bond in general[1] is based on a model proposed by Dewar[2] and applied by Chatt,[3,4] in the early 1950s. In spite of this being more than forty years ago, there is still widespread activity in the field, both theoretical and experimental.[5-8]

Because rhodium-based catalysts are widely used in industrial processes,[9] the rhodium–alkene bond has been intensively investigated.[10] Cramer pioneered these studies with research on exchange reactions, equilibria, bond strength, and isomerization reactions.[11-16] Among the most widely used probes are the Rh(β-diketonate)(alkene)$_2$ complexes.[17]

However, relatively little is known about the dynamic properties of the rhodium(I) alkene complexes in solution. Therefore, we have studied kinetics of alkene exchange for Rh(2,4-pentanedionato)(alkene)$_2$ and related complexes.[18] Following this study we recorded ^{103}Rh-NMR spectra for some rhodium(I) alkene complexes. The interpretation of ^{103}Rh-NMR chemical shifts in terms of bonding and reactivity is not clear-cut. However, we found that the shifts could be related to some physical properties of the investigated compounds, in particular stability constants and *d–d* excitation energies.

Relations between metal-NMR chemical shifts and properties of the molecules have been discussed in the literature in terms of Ramsey's equation,[19] which in its simplest form describes the chemical shift (or rather the nuclear screening) as composed of two parts, (1) the diamagnetic (σ_d), involving the free rotation of electrons, and (2) the paramagnetic (σ_p), describing the hindrance of this rotation caused by other electrons and nuclei in the molecule. Already in 1956 Griffith and Orgel interpreted

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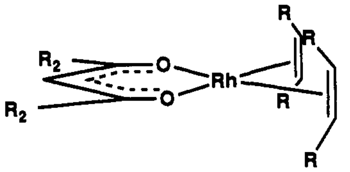
^{59}Co-NMR chemical shifts in octahedral cobalt(III) complexes using the ligand field theory.[20] Several papers have appeared during the succeeding decades, and it has been shown that in many cases a linear relationship can be found between the metal chemical shift of a compound and the reciprocal of its lowest electronic excitation energy, ΔE.[21] In Ramsey's model, only the paramagnetic part has $1/\Delta E$ dependence. Therefore, these results imply that only the latter term is of importance for the variation of the chemical shifts for transition metal nuclei.

A majority of the previous studies have dealt with octahedral complexes of d^6 metal ions where it was possible to relate the NMR shifts to ligand field parameters. Studies of other electronic configurations in this context have been scarce;[22,23] however, a number of investigators have correlated the metal shifts with geometry, substitution pattern, and reactivity.[22,24-28] In the current paper we present a ^{103}Rh-NMR study of several alkene compounds of the d^8 metal ion Rh(I): Rh(acac)(alkene)$_2$ (acac = 2,4-pentanedionato) and Rh(hfacac)(alkene)$_2$ (hfacac = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionato) complexes with ethylene, propene, *cis*- and *trans*-butene, cyclooctene, and tetrafluoroethylene. The chemical shifts are discussed in terms of structure, electronic properties of the ligands, and thermodynamic stability of the complexes.



R_2 = CH_3 or CF_3

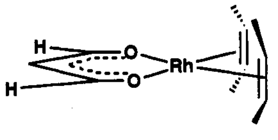
Furthermore, molecular orbital calculations may give valuable clues to the interpretation of the experimental data and yield information not available by other means. Calculations on ligated metal–alkene complexes at a higher level than Hartree–Fock are rather scarce,[29] and in direct relation to experiments extended Hückel calculations are the most common. Rhodium–ethylene complexes have been studied at the Hartree–Fock level and using second-order Möller–Plesset perturbation theory by Morokuma and others[30] in the context of olefin insertion and olefin hydrogenation (Wilkinson's catalyst). Recently, calculations including electron correlation were performed for ethylene coordination to naked metal atoms for the entire second row of transition metals.[8]

In the current paper we present SCF (self consistent field) and CASSCF (complete active space SCF) calculations on the complexes **1** and **2**, (Chart 1) where direct comparisons can be made with the experiments made on the corresponding Rh(acac)(alkene)$_2$ compounds. Correlated calculations (modified coupled pair functional, MCPF) have also been performed on ethylene, *cis*-2-butene, and tetrafluoroethylene coordinated to the naked neutral atom, Rh(0), and to the naked cation, Rh(I).

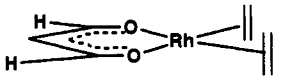
Experimental Section

Reagents and Solvents. All reagents were purchased from commercial sources and used without further purification.

Chart 1



1



2

NMR Measurements and UV–Vis Spectroscopy. ^{1}H-, ^{13}C-, and ^{103}Rh-NMR spectra were recorded at a probe temperature of 25 ± 0.5 °C (^{103}Rh-NMR at −3 °C) using a Bruker AM400 spectrometer. The temperature was calibrated using a Pt-100 resistance. The ^{13}C-NMR spectra were recorded with WALTZ-16 proton decoupling. ^{103}Rh-NMR spectra were recorded with WALTZ-16 proton decoupling, acquisition time of 0.508 s, and pulse width of 12 μs. Measuring times varied from 30 min to 12 h. Chemical shifts (δ) are reported in parts per million with the solvent as internal standard ($CHCl_3$(^{1}H) = 7.26, (^{13}C) = 77.0). For ^{103}Rh-NMR the shifts are referenced to [Ξ](^{103}Rh) = 3.16 MHz.[31] The accuracy of the measured ^{103}Rh-NMR shifts is 0.2 ppm. UV–vis measurements were made on a Cary 219 spectrometer, using chloroform as a solvent and the solutions in silica cuvettes (1-mm path).

Preparations. Rh(2,4-pentanedionato)(ethylene)$_2$,[16] Rh(2,4-pentanedionato)(propene)$_2$,[14] Rh(2,4-pentanedionato)(*cis*-2-butene)$_2$,[18] Rh(2,4-pentanedionato)(ethylene)(tetrafluoroethylene),[32] Rh(2,4-pentanedionato)(cyclooctene)$_2$,[33] and Rh(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(ethylene)$_2$,[34] were prepared and purified according to literature methods. All other complexes were prepared by a well-established ligand exchange procedure,[10] condensing (or adding if liquid) the alkene in a flask or NMR tube loaded with the appropriate ethylene complex. The mixture was subsequently allowed to reach room temperature and evaporated and the procedure repeated four to six times. This produced different amounts of bis and mixed complexes, which were all characterized by ^{1}H- and ^{13}C-NMR.

Preparation of Bis(η^2-*trans*-2-butene)(2,4-pentanedionato)rhodium(I) and (η^2-*trans*-2-Butene)(η^2-ethylene)(2,4-pentanedionato)rhodium(I). Rh(acac)(ethylene)$_2$ (0.005 g, 0.019 mmol) was added to a 5-mm NMR tube. The tube was evacuated, flushed with nitrogen, and then cooled to −70 °C (dry ice/ethanol). Gaseous *trans*-2-butene (50 mL, roughly 2 mmol) was added. The yellow solution was kept at −70 °C for some minutes and then allowed to reach room temperature while unreacted *trans*-2-butene evaporated. The solid phase was dried by vacuum pumping and the procedure repeated. Six additions gave bis(η^2-*trans*-2-butene)(2,4-pentanedionato)rhodium(I) as the major component (90% according to NMR), and four additions gave a 1:1 mixture of bis(η^2-*trans*-2-butene)(2,4-pentanedionato)rhodium(I) and (η^2-*trans*-2-butene)(η^2-ethylene)(2,4-pentanedionato)Rh(I). The products appeared as brown oils. NMR data bis(η^2-*trans*-2-butene)(2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.46 (d, J_{H-H} = 6.2 Hz, 6H), 1.60 (d, J_{HH} = 6.2 Hz, 6H), 1.88 (s, 6H), 2.09 (d of m, J_{HRh} = 1.5 Hz, 2H), 4.23 (d of m, J_{HRh} = 1.6 Hz, 2H), 5.25 (s, 1H); ^{13}C-NMR ($CDCl_3$, 0 °C) δ 19.40 (s), 27.59 (s), 69.95 (d, J_{CRh} = 14.1 Hz), 75.37 (d, J_{CRh} = 12.3 Hz), 99.27 (d, J_{CRh} = 2 Hz), 185.68 (s). NMR data (η^2-*trans*-2-butene)(η^2-ethylene)(2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.50 (broad 6H), 1.90 (s, 3H), 1.95 (s, 3H), 2.9 (very broad 4H), 3.63 (very broad 2H), 5.28 (s, 1H); ^{13}C-NMR (acetone-d_6 0 °C) δ 19.60 (s), 27.26 (s), 27.39 (s), 54.69 (d, J_{CRh} = 16.4 Hz), 59.69 (d, J_{CRh} = 13.3 Hz), 75.87 (broad), 76.2 (d, J_{CRh} = 12.3 Hz), 99.3 (d, J_{CRh} = 2 Hz), 186.56 (s), 187.27 (s).

Preparation of (η^2-*cis*-2-Butene)(η^2-ethylene)(2,4-pentanedionato)rhodium (I) (as described in ref 18). Fewer additions afforded a mixture of Rh(acac)(*cis*-butene)$_2$ and Rh(acac)(ethylene)(*cis*-butene). NMR data (η^2-*cis*-2-butene)(η^2-ethylene)(2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.48 (broad d, J_{HH} = 5.6 Hz, 12H), 1.88 (s, 3H), 1.91 (s, 3H), 2.2, 3.3 (broad), 5.26 (s, 1H); ^{13}C-NMR ($CDCl_3$, 25 °C) δ 14.50 (s), 26.98 (s), 27.17 (s), 59.50 (d, J_{CRh} = 13.2 Hz), 73.36 (broad), 98.89 (coupling not resolved), 185.91 (s), 186.21 (s).

Preparation of Bis(η^2-*trans*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I) and (η^2-*trans*-2-Butene)(η^2-ethylene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I). Rh(hfacac)(ethylene)$_2$ (0.005

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g, 0.019 mmol) was added to a small test tube. The tube was evacuated, flushed with nitrogen, and then cooled to –70 °C (dry ice/ethanol). Gaseous *trans*-2-butene (20 mL $\approx$ 1 mmol) was added. The yellow solution was kept at –70 °C for some minutes and then allowed to reach room temperature while unreacted *trans*-2-butene evaporated. The solid phase was dried by vacuum pumping and the procedure repeated. Five additions gave bis(η^2-*trans*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I) as a red solid (>95% according to NMR, quantitative yield), and two additions gave a 16:3 mixture of bis(η^2-*trans*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I) and (η^2-*trans*-2-butene)(η^2-ethylene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I). NMR data bis(η^2-*trans*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.44 (d, $J_{\text{H–H}}$ = 6.2 Hz, 6H), 1.64 (d, $J_{\text{H–H}}$ = 6.2 Hz, 6H), 2.35 (d of m, J_{HRh} unresolved, 2H), 4.41 (d of m, J_{HRh} = 1.4 Hz, 2H), 6.05 (s, 1H); ^{13}C-NMR ($CDCl_3$, 25 °C) δ 19.04 (s), 19.87 (s), 71.61 (d, J_{CRh} = 14.4 Hz), 76.94 (d, $J_{\text{C-Rh}}$ = 12.6 Hz), 89.92 (d, J_{CRh} unresolved), 117.5 (q, J_{CF} = 288 Hz), 173.87 (q, J_{CF} = 35.0 Hz). NMR data (η^2-*trans*-2-butene)(η^2-ethylene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.52 (broad d, J_{HH} = 5.9 Hz, 6H), 3.14 (broad), 6.09 (s, 1H); ^{13}C-NMR ($CDCl_3$, 25 °C) δ 19.26 (s), 19.29 (s), 60.42 (d, J_{CRh} = 14.62 Hz), 61.43 (d, J_{CRh} = 13.7 Hz), 77.88 (d, J_{CRh} = 12.7 Hz), 174.16 (q, J_{CF} = 34.7 Hz), 174.85 (q, J_{CF} = 35.0 Hz).

Preparation of Bis(η^2-*cis*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I). Rh(hfacac)(ethylene)$_2$ (0.005 g, 0.019 mmol) was added to a small test tue. The tube was evacuated, flushed with nitrogen and then cooled to –70 °C (dry ice/ethanol). Gaseous *cis*-2-butene (20 mL, roughly 1 mmol) was added. The yellow-orange solution was kept at –70 °C for some minutes and then allowed to reach room temperature while unreacted *cis*-2-butene evaporated. The solid phase was dried by vacuum pumping and the procedure repeated. Five additions gave bis(η^2-*cis*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I) as a orange solid (>95% and quantitative yield according to NMR). NMR data bis(η^2-*cis*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.44 (broad d, J_{HH} = 4.4 Hz, 12H), 2.89 (broad 4H), 5.99 (s, 1H); ^{13}C-NMR ($CDCl_3$, 0 °C) δ 15.29 (s), 75.7 (broad), 90.02 (d, J_{CRh} = 1.5 Hz), 117.53 (q, J_{CF} = 285.0 Hz), 173.54 (q, J_{CF} = 34.8 Hz).

(η^2-*trans*-2-Butene)(η^2-*cis*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I) **and (η^2-*trans*-2-Butene)(η^2-*cis*-2-butene)(2,4-pentanedionato)rhodium**(I). These complexes where detected in situ by ^{103}Rh-NMR spectroscopy in solutions of the *cis*-butene complexes where the alkene had been allowed to isomerize to give a mixture of *cis*- and *trans*-butene.

(η^2-Propene)(η^2-ethylene)(2,4-pentanedionato)rhodium(I). This complex was prepared in situ by adding 25 mL of propene gas ($\approx$ 1.1 mmol) to a cold (0 °C) solution of Rh(acac)(ethylene)$_2$ (0.043 g, 0.17 mmol, in 2.3 mL of $CDCl_3$). According to equilibrium calculations (K = 0.078),[14] this should give an approximate 1:1 mixture of the ethylene and the mixed complex, and the ^{103}Rh-NMR spectrum showed two peaks with equal integrals. The Rh(acac)(propene)(ethylene) signal was considerably broader, probably due to exchange of two rotamers. NMR data (η^2-propene)(η^2-ethylene)(2,4-pentanedionato)rhodium(I): ^{1}H-NMR ($CDCl_3$, 25 °C) δ 1.49 (d, J_{HH} = 5.7 Hz, 3H), 1.92 (broad 6H), 2.8 (broad), 2.9 (broad), 3.0 (broad), 5.29 (s, 1H); ^{13}C-NMR ($CDCl_3$, 25 °C) δ 20.24 (s), 27.24(s), 61.91 (d, J_{CRh} = 12.8 Hz), 73.07 (d, broad J_{CRh} = 14.2 Hz), 74.66 (d, broad, J_{CRh} = 13.3 Hz), 99.02 (d, J_{CRh} = 2.0 Hz), 186.27 (broad).

UV–Vis **Measurements.** Bis(η^2-*cis*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I): 270, 330 (s). Bis(η^2-*trans*-2-butene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I): 225, 275 (s), 337 (s). Bis(η^2-ethylene)$_2$(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)rhodium(I): 209, 265, 312 (s), 374 (s), 392. Bis(η^2-ethylene)(2,4-pentanedionato)rhodium(I): 207.5, 250 (s), 265, 300 (s), 391 (s), 402. Peaks corresponding to the same transitions were picked out by visual inspection of the spectra.

Computational Details. In the calculations on rhodium–alkene complexes reported in the present paper medium-sized basis sets were used in a generalized contraction scheme.[35,36] For rhodium the Huzinaga primitive basis[37] was extended by adding one diffuse *d*-function (exponent 0.0762) and two *p*-functions in the 5*p* region (exponents 0.119 and 0.0387), yielding a (17s,13p,9d) primitive basis. The core orbitals were totally contracted except for the 4s and 4p orbitals, which had to be described by at least two functions each to properly reproduce the relativistic effects.[38] The 5s and 5p orbitals were described by a double-ζ contraction, and the 4d by a triple-ζ contraction, giving a [7s,6p,4d] contracted basis. For carbon and oxygen the primitive (9s,5p) basis of Huzinaga[39] was used, contracted according to the generalized contraction scheme to [3s,2p]. In the calculations on naked rhodium–alkene complexes one d-function with exponent 0.63 was added on the alkene carbons. The hydrogens were described by the (4s) basis from ref 39 contracted to [2s] and with the exponents scaled by a factor 1.2. For all rhodium alkene systems studied, calculations were performed at the CASSCF level.[40] The active space in these calculations consists of either all rhodium 4d orbitals and the π^* orbitals on the alkene (naked rhodium and alkene) or rhodium 4d orbitals in the same symmetry as the π^* orbitals, the π and π^* orbitals on the 1,3-propanedionato ligand, and the π^* orbitals on the alkenes (for Rh(1,3-propanedionato)(alkene)$_2$). For the naked rhodium alkene complexes, correlated calculations were performed using the modified coupled pair functional (MCPF) method,[41] which is a size-consistent, single-reference-state method. The zeroth-order wave functions were determined at the SCF level. The metal valence electrons (4d and 5s) and all electrons on the alkenes except the carbon and fluorine 1s electrons were correlated. Relativistic effects were accounted for using first-order perturbation theory including the mass-velocity and Darwin terms.[42,43]

The geometries for the Rh(1,3-propanedionato)(alkene)$_2$ complexes were taken from the X-ray crystal structure determination of Rh(acac)(ethylene)$_2$.[44] The coordination around rhodium was taken to be idealized square-planar with 90° between the ligands. In the free alkenes the sp^2 bond angles were set to 120°. The following bond lengths were used: C(sp^2)–C(sp^3) = 1.51 Å, C(sp^2)–H = 1.09 Å, C(sp^3)–H = 1.11 Å, C(sp^2)–F = 1.35 Å. The carbon–carbon double bonds in the free alkenes were set as follows: ethylene 1.34 Å,[45] *cis*-butene 1.34 Å,[46] tetrafluoroethylene 1.31 Å.[47] The out-of-plane bending angle, α, is defined as the angle between the CH_2, CF_2, or CHMe plane and the extension of the carbon–carbon double bond (the original alkene plane). Additional SCF calculations on Rh(acac) and Rh(hfacac) were performed using the geometries from the aforementioned crystal structure (Rh(acac)) and from the X-ray diffraction study of a Rh(hfacac)(pyridine)(diene) complex.[48]

For naked Rh(0) and Rh(I) complexes of ethylene and *cis*-butene, the Rh–C and C–C(alkene) distances and the angle, α, were optimized using a simplex[49] procedure. For the tetrafluoroethylene and Rh(1,3-propanedionato) complexes the CASSCF energies were fitted to quadratic potentials. The carbon–carbon double-bond distance was not optimized in the Rh(1,3-propanedionato)(alkene)$_2$ complexes since computations on the simpler compounds showed this parameter to vary insignificantly between ethylene and *cis*-butene. Instead, the value from the crystal structure of Rh(acac)(ethylene)$_2$ was used.

For the compounds **1** and **2** closed-shell singlet states were considered, and the alkene bond energies of these complexes were calculated relative to the singlet state of the Rh(1,3-propanedionato) complex. We note that this might not be the ground state of the asymptote, in particular not at the SCF level. For the naked neutral rhodium atom the alkene bond energies were calculated using the ground-state asymptote, i.e. they were taken relative to the quartet ground state of the atom, although the alkene complexes are doublets. Furthermore, for the cationic naked Rh(I)–alkene complexes the singlet state was considered and the bond energies were calculated relative to the triplet ground state of the naked rhodium cation.

Results

Selected NMR data for Rh(acac)(alkene)$_2$ and Rh(hfacac)(alkene)$_2$ complexes are shown in Table 1. The ^{103}Rh-NMR

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Table 1. Selected NMR Data for Rh(I)(β-diketonato)(alkene)$_2$ Complexes (in CDCl$_3$, Concentration 0.05–0.1 M) and Experimental (UV–Vis) HOMO–LUMO Excitation Energies, $\Delta E_{\pi,\pi^*}$, for the Free Alkenes (ac = Acetylacetonato, hf = Hexafluoroacetylacetonate, et = Ethylene, pr = Propene, cb = *cis*-Butene, tb = *trans*-Butene, cot = Cyclooctatetraene, cod = Cycloocta-1,5-diene, coe = Cyclooctene, tfe = Tetrafluoroethylene)

complex	J_{RhC} (Hz)	$\Delta\delta(^{13}\mathrm{C})_{\mathrm{alk}}$[a] (ppm)	$\delta(^{103}\mathrm{Rh})$[b] (ppm)	$\Delta E_{\pi,\pi^*}$[c] (eV)
Rh(ac)(et)$_2$	13.6	63.4	1170	7.65[d]
Rh(ac)(et)(pr)	12.8[g] 13.3, 14.2	50.8[f]	1262	7.65, 7.15[d]
Rh(ac)(pr)$_2$[d]	13.7, 12.5	57.8[f]	1366, 1315[e]	7.15
Rh(ac)(et)(cb)	13.2[g]		1353	7.65, 7.10[d]
Rh(ac)(cb)$_2$	12.8	49.9	1509	7.10
Rh(ac)(et)(tb)	16.4,[g] 13.3[g] 12.3, 12.3	49.8	1386	7.65, 6.97[d]
Rh(ac)(tb)$_2$	14.1, 12.3	53.2	1603	6.97
Rh(ac)(cb)(tb)	*[n]	*	1561	7.10, 6.97
Rh(ac)(coe)$_2$	13.3	51.3	1296	6.8[h]
Rh(ac)(cot)			1743[i]	4.51[k]
Rh(ac)(cod)			1294[i]	
Rh(ac)(et)(tfe)	11.4,[g] 17.5	46.6	1171	7.65, 8.88[l]
Rh(hf)(et)$_2$	not obs[m]	60.9	1296	7.65
Rh(hf)(cb)$_2$	15.0	54.3	1644	7.10
Rh(hf)(cb)(tb)	*	*	1724	7.10, 6.97
Rh(hf)(et)(tb)	14.6,[g] 13.7[g]	62.1	1529	7.65, 6.97
Rh(hf)(tb)$_2$	14.4, 12.6	51.6	1763	6.97

[a] Difference between the ^{13}C-NMR chemical shift for the free alkene and for the alkene in the complex. [b] ^{103}Rh-NMR shifts (±0.5 ppm) are referenced to $[\Xi](^{103}\mathrm{Rh}) = 3.16$ MHz. [c] Free alkene. [d] Data from ref 59. [e] Two geometrical isomers. [f] Mean value. [g] Ethylene. [h] Extrapolated using the linear correlation between the $\Delta E_{\pi,\pi^*}$ and the difference between electron affinity and ionization potential (refs 62 and 63) for propene, *cis*- and *trans*-butene, and cyclooctene. [i] Data from ref 24. [k] Data from ref 60. [l] Data from ref 61. [m] Not observed due to broad peak. [n] * = not measured.

spectra were typically obtained with proton decoupling in order to increase the low signal-to-noise ratio due to the low sensitivity of the ^{103}Rh nucleus (20% compared to natural abundance ^{13}C). Therefore, no structural information was extracted from these spectra, although it was possible to distinguish the *cis*-butene complexes from the *trans*-butene complexes: the two rotamers of the *cis*-butene complex exchange fast enough to give an average signal in ^{103}Rh-NMR, but slow enough to cause significant line broadening, whereas the only possible rotamer of the *trans*-butene complex gives a sharp signal.

Some results of the quantum chemical calculations are summarized in Table 2, together with literature data. Geometry optimizations of the rhodium-alkene units where performed at the CASSCF level, and for the naked Rh(0) and Rh(I) complexes the binding energies were calculated at the correlated MCPF level. (See computational details.) For the larger complexes **1** and **2** it was not possible to perform correlated calculations, instead we report the SCF bond energies for these systems. The principal orbital interactions are shown in Figure 1.

Discussion

^{103}Rh-NMR Shifts, MO Calculations, and Ligand Field Theory. It is clear that factors other than charge are important for the rhodium NMR chemical shift. While the diamagnetic term (charge distribution) is a dominating factor in determining NMR shifts for light nuclei such as ^{1}H, the paramagnetic term is more important for the variation of transition metal NMR chemical shifts. Both terms are described by the Ramsey equation. Unfortunately, this equation is rather complicated and difficult to use practically, but in a simplified way we can rewrite the essential parts:[50,51]

Table 2. Summary of Quantum Chemical Calculations[m]

complex	r[a] (Å)	$r_{\mathrm{C-C}}$ (Å)	α[b] bend (deg)	ΔE[c] (kJ/mol)	method
Rh(0)(et)[d]	2.00	1.45	30	108	MCPF
Rh(0)(cb)	2.01	1.43	26	96	MCPF
Rh(0)(tfe)	1.93	1.44	39	181	MCPF
Rh(I)(et)	2.30	1.37	12	50	MCPF
Rh(I)(cb)	2.32	1.36	10	84	MCPF
Rh(prdo)(et)$_2$	2.08	*1.40*	19	58	SCF
Rh(prdo)(cb)$_2$	2.11	*1.40*	22[e]	38	SCF
Rh(Cp)(et)$_2$				130	exp[f]
Rh(Cp)(et)(tfe)	2.17	1.36	21		exp[g]
Rh(Cp)(et)(**tfe**)	2.02	1.40	37		exp[g]
Rh(ac)(et)(tfe)	2.19	1.42			exp[h]
Rh(ac)(et)(**tfe**)	2.01	1.40			exp[h]
Rh(ac)(et)$_2$	2.02	1.41			exp[h]
et		1.34			exp[l]
cb		1.34			exp[k]
tfe		1.31			exp[l]

[a] Distance Rh–(C–C) midpoint. [b] The out-of-plane bending angle, α, is defined as the angle between the CH$_2$, CF$_2$, or CHMe plane and the extension of the carbon–carbon bond (the original alkene plane). [c] Binding energy per alkene. [d] The MCPF geometry optimization in ref 8 gives slightly different values, 1.97 Å, 1.44 Å, and 22°, respectively. The MCPF energy difference between the two structures is 1 kJ/mol. [e] Methyl and H varied independently; the methyl groups bend slightly more. [f] Pyrolysis, ref 15. [g] X-ray structure, ref 77. [h] X-ray structure, ref 44. [i–l] Electron diffraction, ref 45–47. [m] Relevant experimental data are added for comparison. The geometry optimizations were made on the CASSCF level; values in italics have not been optimized. (ac = acetylacetonato, prdo = propanedionato, Cp = cyclopentadienyl, et = ethylene, cb = *cis*-butene, tfe = tetrafluoroethylene.)

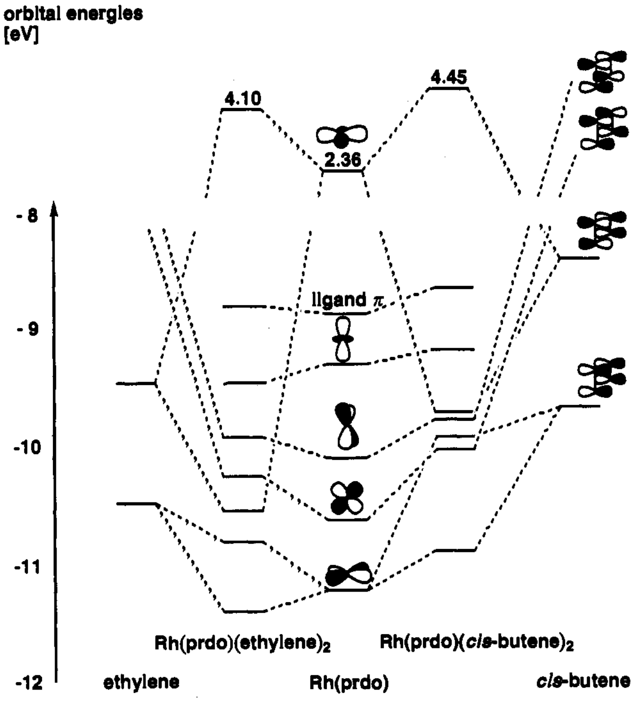

Figure 1. Principal interactions and SCF orbital energies for the Rh-(1,3-propanedionato)(alkene)$_2$ complexes and their molecular fragments: occupied orbitals with negative energies, excited levels with positive energies. Equilibrium geometries are from Table 2.

$$\delta = -A\rho_{\mathrm{electrons}} + \frac{B\langle r_{\mathrm{nd}}^{-3}\rangle D_{\mathrm{i}}}{\Delta E_{\mathrm{d-d}}} \qquad (1)$$

The first term of the equation is dependent on the electron density (diamagnetic contribution), and the other term (paramagnetic contribution) consists of the following factors: $\Delta E_{\mathrm{d-d}}$,

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(50) Adapted from the following: Jameson, C. J.; Mason, J. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: London, 1987; p 65, where the equation is written in terms of shielding, σ, instead of chemical shift, δ.

(51) The D_i factor is sometimes considered constant for transition metals: Mann, B. E. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991; Vol. 13, p 177.

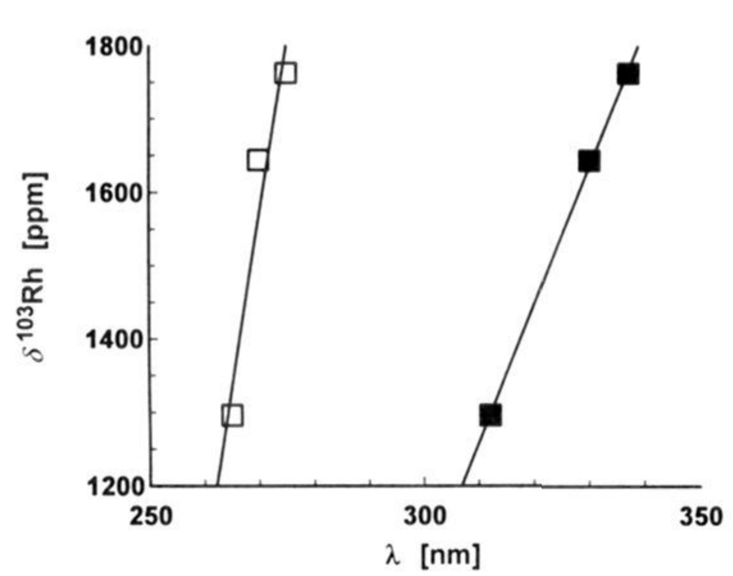

Figure 2. ^{103}Rh-NMR chemical shifts of Rh(I)(hfacac)(alkene)$_2$, alkene = ethylene (lowest shift), *cis*-butene, and *trans*-butene, plotted against the wavelengths of two UV–vis absorption bands (□ and ■), showing the dependence on the $1/\Delta E$ factor in Ramsey's equation (eq 1).

the lowest d–d excitation energy, $\langle r_{\mathrm{nd}}^{-3}\rangle$, where r is the d orbital radii, D_i, the imbalance of the d orbital electron population, and B, a constant.

Because of the expected dependence of Rh–NMR shifts on d–d transition energies (ΔE), the shifts were plotted against the UV–vis absorption bands for the compounds Rh(hfacac)(ethylene)$_2$, Rh(hfacac)(*cis*-butene)$_2$, and Rh(hfacac)(*trans*-butene)$_2$ (Figure 2).

There is an uncertainty concerning the assignment of the UV–vis bands,[52] and several possibilities can be envisaged: d–d transitions, charge-transfer bands, and ligand π-to-π^* excitations. Therefore, two different electronic transitions, found for all three compounds, are plotted in Figure 2. It seems reasonable to assume that these bands correspond to d–d excitations since they are both low in intensity and at relatively high wavelengths. In the literature concerned with the paramagnetic term of Ramsey's equation only $1/\Delta E$, representing the wavelength of the lowest energy optical transition, is considered.[53] Accordingly, we take the lowest transitions and extrapolate the corresponding straight line to $\lambda = 0$ ($1/\Delta E = 0$). The Rh chemical shift value for the $\sigma_p = 0$ standard state can thus be obtained. The extrapolation leads to $\delta = -4500 \pm 1000$ ppm, which corresponds to σ_d, the core electron diamagnetic shielding, that is, the shielding of the rhodium atom. Thus, this value should be roughly independent of the oxidation state of rhodium in the studied compounds. In fact, we have recently determined the diamagnetic shielding of rhodium from the Rh-NMR shfits of several Rh(III) complexes and obtained $\delta = -5000 \pm 1000$ ppm.[54] The agreement is remarkable indeed, and if not accidental, it constitutes an additional support for this simplified version of Ramsey's shielding model.

What consequences does this $1/\Delta E$ dependence infer for the interpretation of the Rh–alkene bonding? First, the straight line in Figure 2 indicates that for these systems the factor $\langle r_{\mathrm{nd}}^{-3}\rangle$ is constant, which implies that there are no dramatic differences in bonding when a hydrogen is substituted for a methyl in ethylene, in good agreement with the quantum chemical results presented below. Seemingly, this may have been expected, but in reality it is difficult to know a priori the sensitivity of the $\langle r_{\mathrm{nd}}^{-3}\rangle$ factor. The constancy of the $\langle r_{\mathrm{nd}}^{-3}\rangle$ factor is also supported by the small differences in ^{103}Rh–^{13}C coupling constants for these complexes (see Table 1). Also the D_i factor is constant, not surprisingly since the coordination geometry is not changed, and thus we do not expect large variations in the d orbital populations.

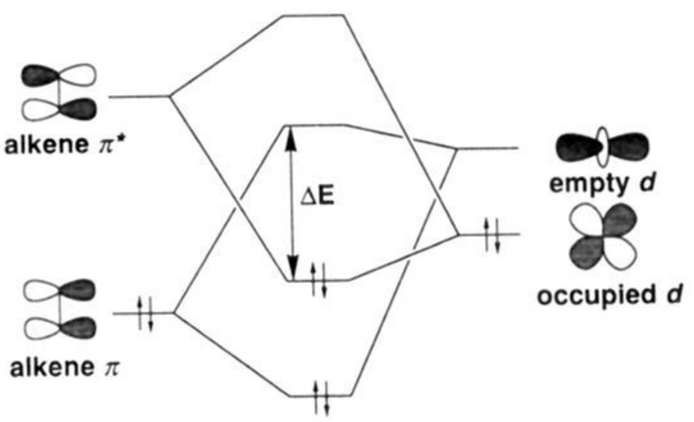

Figure 3. A simple and schematic MO treatment using the Dewar–Chatt–Duncanson model (diagram is not to scale).

Secondly, the trend in chemical shifts has to be explained. If we consider the Dewar–Chatt–Duncanson theory[2,3] within the ligand field approximation (Figure 3), we note that an increased interaction between olefin and metal means a stronger ligand field and thus gives a higher ΔE. For small perturbations the other factors in the Ramsey equation might remain essentially constant, and consequently this should lead to a lower metal chemical shift.

If we interpret our data in this way, the higher ^{103}Rh chemical shifts of the alkyl-substituted alkene complexes compared to the ethylene compounds indicate that the former are in some way weaker ligands. (One can note that methyl-substituted dienes also show higher metal-NMR shifts in Fe(CO)$_3$(1,3-diene),[55] Co(indenyl)(1,3-diene),[22a] and Rh(Cp)(1,3-diene)[24] than in the corresponding 1,3-butadiene complexes). The weaker ligand field from the alkyl-substituted alkenes might be a consequence of the lower negative charge on the alkene-carbons, as shown by the calculations (Table 3). It is also likely that the steric effects of the alkyl groups have an effect on the ligand field induced by the alkene. There are two ways in which an alkene can release the unfavorable steric interaction with the metal–ligand moiety. It can increase the metal–carbon distance, or it can increase the out-of-plane bending of the substituents. The first situation will decrease the metal–alkene interaction and lower ΔE, the second will increase the back-bonding, increase ΔE, and lower the Rh chemical shift.

Our calculations show a slightly longer rhodium–alkene distance for *cis*-butene compared to ethylene (0.01 Å in Rh(0) complexes and 0.03 Å in Rh(prdo) complexes). Additional support for longer metal–alkene bonds for alkyl-substituted ethylene comes from X-ray crystal structure determinations of Rh(acac)(ethylene)(hexafluorobutyne) and Rh(acac)(cyclooctene)(hexafluorobutyne) that show slightly longer (0.02 Å) Rh–C distances for the substituted alkene.[56]

The difference in ^{103}Rh-NMR chemical shifts between the ethylene and the *cis*-butene complexes corresponds to a difference in excitation energy on the order of 0.1–0.2 eV. Considering the difficulties in calculating d–d excitation energies in transition metal complexes, such a small shift is not likely to be reproducible at the levels of calculation possible for the complexes **1** and **2**. (Comparison of the highest occupied and lowest unoccupied d orbital gives ΔE = 13.53 eV for both complexes.) However, scrutinizing SCF orbital energies for the *cis*-butene complex at rhodium–alkene distances of 2.09 and 2.11 Å reveals a trend of decreasing ΔE with increasing bond length. When the distance is increased, all seven occupied valence orbitals that have some d character increase in energy by a total of 0.28 eV, while the energy of the excited level remains unchanged. This indicates a lowering of the ΔE with increasing rhodium–alkene distance, and thus a higher NMR chemical shift, in agreement with our simple deduction using the Dewar–Chatt–Duncanson model.

^{103}Rh-NMR Shifts and Stability Constants. Longer bond distances also imply weaker bonds, and indeed, the values for the equilibrium constants, K, for the reaction (in toluene)[14]

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Table 3. Calculated Charges and Charge Transfers (prdo = Propanedionato, et = Ethylene, cb = *cis*-Butene, tfe = Tetrafluoroethylene) Using Mulliken Population Analysis

complex	q_{Rh}[a]	qC_{alk}[b]	ΔqC_{alk}[c]	σ[d]	π[e]	total d	transfer to Rh[f]	overlap Rh–C	method
Rh(0)(et)	0.20	−0.53	+0.10	0.37	0.56	8.36	+0.19	−0.17	MCPF
Rh(0)(cb)	0.10	−0.25	+0.07	0.43	0.53	8.41	+0.10	−0.18	MCPF
Rh(0)(tfe)	0.22	+0.12	+0.08	0.50	0.67	8.28	+0.22	−0.26	MCPF
Rh(prdo)(et)$_2$	0.44	−0.35	0.00	0.33	0.25	8.04	−0.11	−0.21	SCF
Rh(prdo)(cb)$_2$	0.43	−0.11	−0.04	0.31	0.21	8.05	−0.13	−0.20	SCF
Rh(I)(et)	0.65	−0.42	+0.01	0.79	0.45	8.12	−0.35	−0.18	MCPF
Rh(I)(cb)	0.57	−0.19	+0.01	0.77	0.34	8.18	−0.43	−0.16	MCPF
et		−0.35							SCF
et		−0.43							MCPF
cb		−0.15							SCF
cb		−0.18							MCPF
tfe		+0.20							MCPF
Rh(prdo)	0.60					8.14			SCF
Rh(ac)	0.59					8.15			SCF
Rh(hf)	0.70					8.11			SCF

[a] Charge on rhodium. [b] Charge on the alkene carbon. [c] Difference in charge of the alkene carbon in coordinated and free alkene. [d] Charge transfer from alkene to rhodium through the σ bond. [e] Charger transfer from rhodium to alkene through the π bond. [f] Total charge transfer from alkene to rhodium.

$$\text{Rh(acac)(ethylene)}_2 + \text{alkene} \rightleftharpoons \text{Rh(acac)(ethylene)(alkene)} + \text{ethylene} \quad (2)$$

$$K = \frac{[\text{Rh(acac)(ethylene)(alkene)}][\text{ethylene}]}{[\text{Rh(acac)(ethylene)}_2][\text{alkene}]} \quad (3)$$

decrease with increasing Rh-NMR chemical shift (see Figure 4).

However, the conclusion that there is a relationship of higher shifts and lower stability is not always true. The first reason is that the other factors in the Ramsey equation have to remain constant. A second important consideration is that for chelating ligands such as cyclooctadiene and cyclooctatetraene there is a significant entropy contribution to the equilibrium constant.

A lower stability for complexes with higher metal NMR shifts has also been noted by v. Philipsborn and co-workers in their study of diastereomeric alkene complexes.[57] They invariably found higher shifts for the minor stereoisomers and explained this by a decrease in the orbital overlaps and an increase in the $\langle r_{nd}^{-3} \rangle$ factor. Whether this is the case or if the $1/\Delta E$ factor contributes as well may be irrelevant since both factors will work in the same direction, that is, to increase the shift with decreasing stability.

However, if the two factors could be envisaged to have opposite effects, comparisons of shifts may be difficult. An example is the Rh(acac)(ethylene)(tetrafluoroethylene) complex that has almost the same Rh shift (see Table 1) as the Rh(acac)(ethylene)$_2$ complex and clearly deviates from the trend in Figure 4. The ligand field from the fluoro-substituted alkene will be weaker because of the electron-withdrawing fluorines, thus increasing the shift due to the $1/\Delta E$. On the other hand, it has been suggested that the tetrafluoroethylene complexes are closer to the metallacyclopropane model,[7,12,32,58] and thus the $\langle r_{nd}^{-3} \rangle$ factor will decrease and lower the shift. This is also supported by our calculations that show a significantly increased orbital overlap between Rh and C, shorter Rh–alkene distance, and relative to the free alkene, a more elongated C–C bond in rhodium(0)-tetrafluoroethylene compared to the ethylene complex (Table 3 and Figure 8).

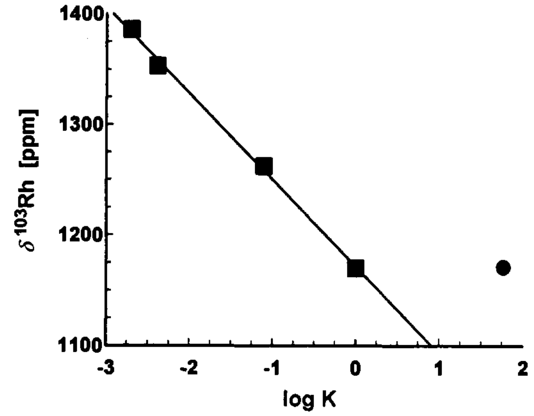

Figure 4. The equilibrium constants (at 273 K) for the reaction Rh(acac)(ethylene)$_2$ + alkene $\rightleftharpoons$ Rh(acac)(ethylene)(alkene) plotted against the corresponding ^{103}Rh-NMR chemical shifts (at 280 K) of the mixed complexes. The log K values decrease in the order ethylene > propene > *cis*-butene > *trans*-butene (■). The data point at log $K \approx 1.8$ is the tetrafluoroethylene mixed complex (●).

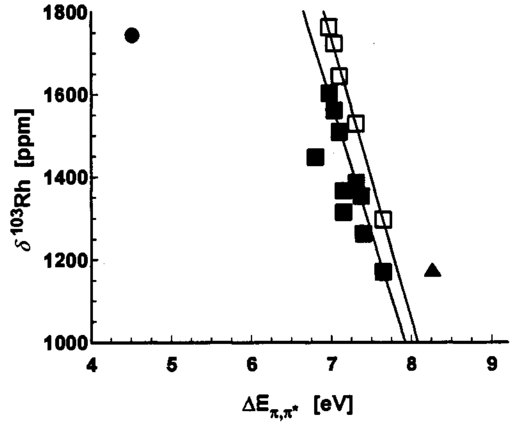

Figure 5. ^{103}Rh-NMR chemical shifts at 280 K of some Rh(I)(β-diketonato)(alkene)$_2$ complexes plotted against the HOMO–LUMO excitation energies (mean values for mixed complexes) of the free alkenes: ■, Rh(acac)(alkene)$_2$; □, Rh(hfacac)(alkene)$_2$; ●, Rh(acac)(cyclooctatetraene); ▲, Rh(acac)(ethylene)(tetrafluoroethylene). Straight lines mark the ethylene and *cis*- and *trans*-butene complexes.

^{103}Rh-NMR Parameters and Free Alkene Excitation Energies. Another interesting correlation is that the ^{103}Rh-NMR chemical shifts of the complexes decrease with increasing excitation energies of the free alkenes (the $\Delta E_{\pi,\pi^*}$ excitation),[59-63] see Figure 5.

The propene and cyclooctene complexes deviate from the straight line, however, the trend is the same; a decrease in $\Delta E_{\pi,\pi^*}$

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leads to an increase in the Rh-NMR shift. It has been proposed that increasing numbers of alkyl substituents on the double bond should decrease the $\Delta E_{\pi,\pi^*}$ due to the hyperconjugation effect.[64,65] It was also concluded earlier that the steric requirements of the methyl-substituted alkenes force subtle increases in the Rh-alkene causing the ^{103}Rh-NMR chemical shifts to increase. Thus, increasing shifts with decreasing $\Delta E_{\pi,\pi^*}$ energies of the free alkenes seem reasonable.

Tetrafluoroethylene and cyclooctatetraene on the other hand show larger deviations, probably because of different bonding mechanisms, as discussed above for tetrafluoroethylene, and, or, because of different factors controlling the $\Delta E_{\pi,\pi^*}$, apart from hyperconjugation.

There are examples of correlations of metal–ligand spin–spin coupling constants with metal–ligand distances.[66–68] In the case of rhodium–alkene complexes we have not found any simple relation between ^{103}Rh–^{13}C one-bond coupling constants and the Rh–C distance.[44,48,69–71] This is probably because the coupling is sensitive not only to the bond strength but also to the hybridization on the carbon. Small differences in σ and π bonding may thus also influence the coupling constants.

The difference in ^{13}C-NMR chemical shifts for free and coordinated alkenes has been interpreted in many ways, and the significance of this parameter to the metal–alkene bonding is unclear.[72]

Quantum Chemical Results. The bonding in metal alkene complexes is usually described by the Dewar–Chatt–Duncanson model including a σ donation of electrons from the olefin π orbital to empty orbitals on the metal and a π back-donation from an occupied d orbital on the metal to the π^* orbital on the alkene. Both types of donations weaken the olefin π bond, and the larger the donations are the more perturbed is the coordinated olefin compared to the free molecule. In the limiting case a metallacyclopropane structure is obtained with a C–C distance corresponding to a single bond (1.54 Å). For the simple model systems studied here, Rh(0)(alkene), the C–C distances are optimzied and the resulting distances, 1.43–1.45 Å, indicate an intermediate weakening of the π bond, in agreement with previous results for metals to the right in the periodic table.[8] Similar results have also been obtained for an $Os(CO)_4(C_2H_4)$ complex, yielding a theoretical C–C distance of 1.44 Å.[6] The present results indicate that the tetrafluoroethylene is somewhat more perturbed than ethylene and *cis*-butene in the rhodium complexes, since the C–C distances in fluoro-substituted hydrocarbons are shorter than in the corresponding unsubstituted system, about 0.03 Å for both double bonds and single bonds. In Table 3 it can be seen that the π back-donations for Rh(0)ethylene and Rh(0)*cis*-butene are very similar, about 0.55 electrons, and that the π back-donation for Rh(0)tetrafluoroethylene is larger, 0.67 electrons, in agreement with the larger geometric perturbation obtained for the tetrafluoroethylene system.

We note that the formulation of Rh–tetrafluoroethylene complexes as metallacyclopropanes would explain some experimental observations: (1) The second ethylene cannot be exchanged for another tetrafluoroethylene in Rh(acac)(ethylene)(tetrafluoroethylene),[12] because this would mean formal oxidation to Rh(V). (2) The increased Rh–C bond distances in Rh(acac)(ethylene)$_2$ as compared to Rh(acac)(ethylene)(tetrafluoroethylene) (+0.17 Å for ethylene), and in Rh(Cp)(ethylene)(tetrafluoroethylene) the short C–C bond in ethylene, are consistent with a more charged metal ion (Rh(III)) and thus a weaker, more electrostatic bond (Table 2).

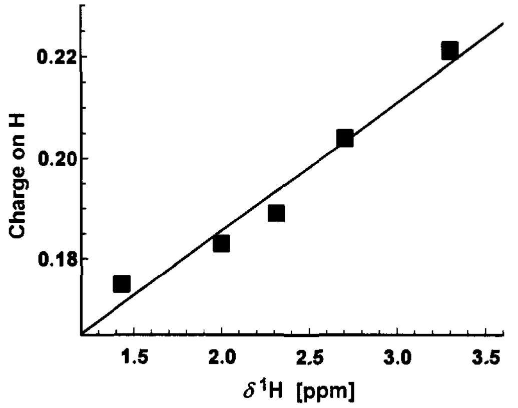

Figure 6. The ^{1}H-NMR chemical shift is normally proportional to the charge density on the hydrogen. Here, the charges obtained by Mulliken population analysis on Rh(prdo)(ethylene)$_2$, Rh(prdo)(*cis*-butene)$_2$-[alkene protons], and Rh(acac)(ethylene)$_2$[acac-methyl protons] have been used.

For some of the quantum chemical results summarized in Table 2, comparison can be made with experimental data for rhodium–alkene complexes. For example, the bond energy difference between ethylene and *cis*-butene in Rh(acac)(alkene)$_2$ can be estimated at 8 ± 3 kJ/mol per alkene using Cramer's equilibrium data.[14] The calculated difference in alkene binding energy between **1** and **2** is 20 kJ/mol at the SCF level. However, calculations on the naked Rh(0) compounds show that the correlation effects on the rhodium–alkene bond energy are larger by 13 kJ/mol for *cis*-butene than for ethylene. If this correlation energy difference is subtracted from the SCF value, the difference in bond energy between Rh(prdo)(ethylene)$_2$ and Rh(prdo)(*cis*-butene)$_2$ is estimated to 7 kJ/mol per alkene, in excellent agreement with Cramer's data.

For the coordination of tetrafluoroethylene to rhodium it was not possible to perform calculations on the larger Rh(prdo) complexes, but we note that the calculations on the naked Rh(0) compounds give the same trend in complex stabilities as experiment, tetrafluoroethylene > ethylene > *cis*-butene.[14] The calculated ethylene bond energy to the naked Rh atom, 108 kJ/mol, can be compared to the corresponding theoretical value of 129 kJ/mol obtained in ref 8. This value is very close to the experimental bond energy in Rh(Cp)(ethylene)$_2$, 130 kJ/mol.[15] The difference in the two calculated values is due to the larger basis set used in ref 8.

As discussed above, the ^{103}Rh-NMR chemical shifts of the Rh(acac)(alkene)$_2$ complexes plotted against the lowest d–d absorption bands give a straight line (Figure 2). Considering the Ramsey equation, this result indicates that the electronic structure on the rhodium atom is the same for the different alkene complexes. In agreement with this the calculated wave functions for the ethylene and the *cis*-butene complexes of Rh(prdo) are very similar, shown by close values of charge transfers, d orbital populations, and overlap (Table 3 and Figure 8). For example, the charge on the rhodium atom is +0.44 in the ethylene case and +0.43 in the butene case. Thus, as expected for transition metals, there is no correlation between the charge on the rhodium atom and the NMR shift. On the other hand, proton shifts and calculated charges on the alkene protons correlate very nicely (cf. Figure 6).

In Table 2 also the optimized geometric parameters are given. The calculated rhodium–ethylene bond distance in Rh(prdo)(ethylene)$_2$ is 2.08 Å, which is somewhat longer than the 2.02 Å found in the X-ray structure of Rh(acac)(ethylene)$_2$.[44] Also in other alkene complexes of similar type the rhodium–alkene bond

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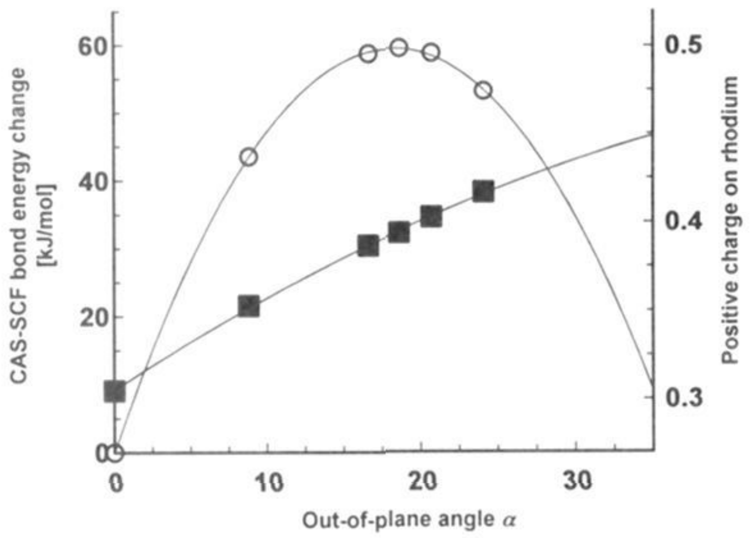

Figure 7. CASSCF energy change upon increased out-of-plane bending angle α, ○, and the corresponding change in rhodium charge (from Mulliken population analysis), ■, for Rh(1,3-propanedionato)(ethylene)$_2$.

length is around 2.02 Å.[44,69,73,74] This moderate difference between calculated and experimental bond lengths can probably be ascribed to the fact that correlation effects are neglected and that the alkene–rhodium–alkene bond angle is not optimized. Furthermore, the potential energy surface for the rhodium alkene interaction is rather flat, which can lead to rather large effects on the bond distance from small changes in the interaction energy.

The naked Rh(0)alkene complexes give rather similar rhodium–alkene bond distances to the ligated Rh(prdo) complexes, shorter by about 0.1 Å; see Table 2. The difference between ethylene and *cis*-butene, obtained as 0.03 Å for the Rh(prdo) complexes, is much smaller in the naked Rh(0)alkene complexes, giving a difference of only 0.01 Å. This indicates that the longer Rh–(*cis*-butene) bond in the prdo complex is mainly due to ligand–ligand repulsion.

On the other hand, naked cationic Rh(I)alkene complexes give a very different picture of the rhodium–alkene bonding. The Rh–C bond distances are much longer for the cationic complexes compared to the neutral complexes, and the C–C distances are shorter and the out-of-plane bending smaller, indicating less perturbed alkenes in the case of the cationic compounds.

In the cationic complexes the bonding is dominated by charge-induced dipole interaction. This explains that the alkenes are less distorted than in the neutral compounds where the bonding occurs through a donation–back-donation between the metal and the alkene, leading to an increased C–C distance compared to the free alkene. Moreover, the larger polarizability of *cis*-butene compared to ethylene leads to a stronger bond to the rhodium cation, 84 kJ/mol versus 50 kJ/mol for ethylene.

In conclusion we note that the naked neutral rhodium is a rather good model for the larger complexes, while the naked cationic complexes, formally having the same oxidation state as **1** and **2**, give a different kind of bonding. The same observation has been made in some other recent studies.[75,76]

As would be expected and in agreement with Morokuma and Borden, who recently performed some calculations on platinum(0)ethylene complexes,[5] we find a sizable increase in bonding energy with increased out-of-plane bending ("pyramidalization", α) (Figure 7). On the CASSCF level the bending actually accounts for 75% of the total bond energy. In correspondence with what was noted by Svensson et al.,[8] we see a linear correlation between longer C–C distances and increased angle α, for ethylene and *cis*-butene, respectively (Table 2).

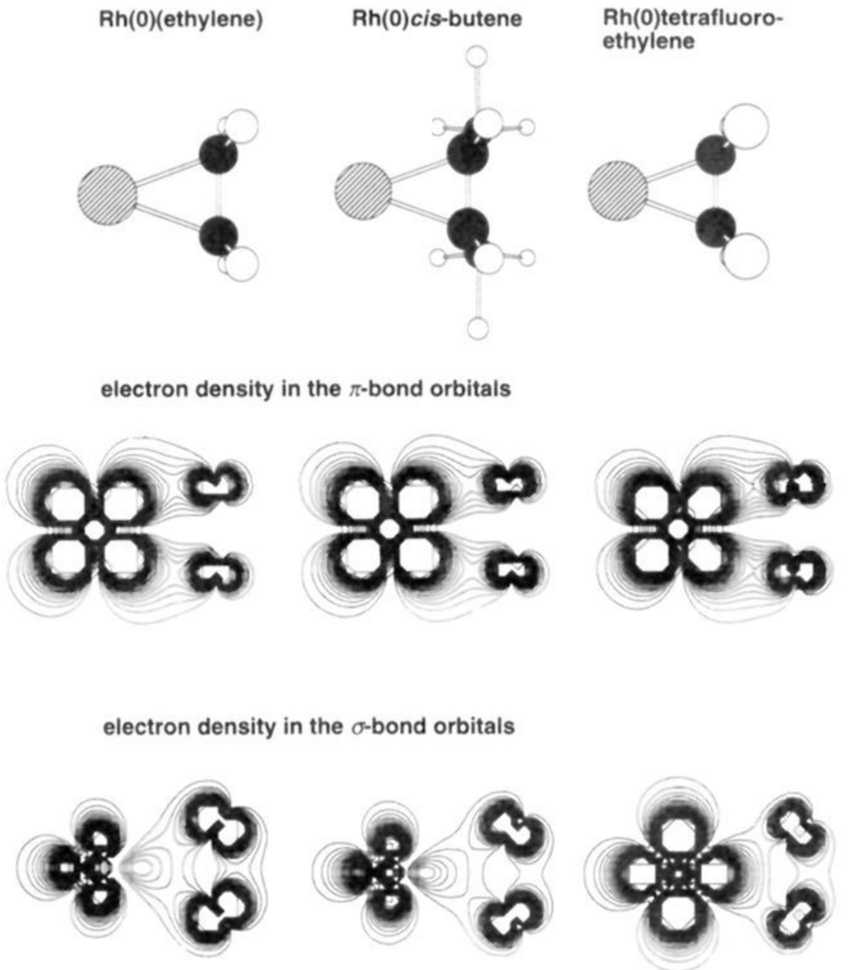

Figure 8. Equilibrium geometries and electron density plots of the principal binding SCF orbitals of Rh(0)ethylene, Rh(0)*cis*-butene, and Rh(0)-tetrafluoroethylene in the Rh–C–C plane. The density plots are all executed using the same linear scale and cut-off level.

As predicted, the electron donation from rhodium to the alkene increases with increasing out-of-plane bending (Figure 7). Our trend of 0.004 electrons/degree is close to the one computed by Morokuma and Borden, 0.005 electrons/degree. The calculated values of α are also quite close to the experimental findings.[77]

Some further comparisons of the different alkene complexes can be made from the population analysis results of the calculated wave functions that are listed in Table 3. For the free alkenes it can be seen that the methyl groups decrease the negative charge on the olefinic carbons by about 0.25 electrons per carbon compared to ethylene. This difference in charge, which remains after coordination to the metal, is expected to lead to a weaker ligand field for *cis*-butene than for ethylene, a difference that will be further strengthened by the longer rhodium–alkene distance for *cis*-butene, as discussed above.

The fluoro substituents have a large electron-withdrawing effect, leading to a positively charged olefinic carbon. Therefore, tetrafluoroethylene is expected to give rise to the weakest ligand field upon complexation. However, tetrafluoroethylene also forms the strongest bond to rhodium, yielding the shortest Rh–C bond distance (see Table 2). This will have an opposite effect on the ligand field, and thus the difference in ligand field between ethylene and tetrafluoroethylene is likely to be less than what is indicated by the carbon charges.

A graphical comparison of the complexes of ethylene, *cis*-butene, and tetrafluoroethylene with rhodium(0) is given in Figure 8, where the electron densities of the principal bonding orbitals are plotted. Here the resemblance between the ethylene and the *cis*-butene on one hand, and the contrast to the tetrafluoroethylene complex on the other hand, is clear. As would be expected, the back-bonding is more pronounced for the tetrafluoroethylene compound. Judging from the electron density in the Rh–tetrafluoroethylene bond, this leads to a stronger Rh–alkene bond, in accordance with experiment.[14] One also notes that the carbon p orbitals in the σ bond are kept perpendicular to the CH_2, CHMe, and CF_2 plane, respectively, while in the π bond the p orbitals are oriented to maximize the overlap with the rhodium d orbital.

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A trend of decreasing double-bond strength with increasing out-of-plane bending may also be indicated by the decreasing electron density between the carbon atoms.

The orbital interaction diagram in Figure 1 merits a few comments. First, we notice that the metal *d* orbitals and the alkene π orbitals combine in the expected way. One would expect the d_{z^2} orbital (perpendicular to the coordination plane) to remain more or less constant. It does change much less than most of the other d orbitals, but it moves in different directions for the ethylene and the *cis*-butene complexes. Second, and more significant, the HOMO of the complex is a propanedionato π orbital with very little rhodium contribution. These complexes are therefore exceptions to the rule that the HOMO is normally metal centered.[78] We note that this might have important implications for the reactivity of Rh(acac)(alkene)$_2$ complexes toward electrophiles.[79–81]

Finally, the force constant for the rhodium–carbon bond in Rh(acac)(ethylene)$_2$ (Rh–C) has recently been determined to be 147 N/m.[82] From our optimization of the Rh(prdo)(ethylene)$_2$ complex we can estimate the force constant to be 121 N/m.

Alkene Exchange. The alkene self-exchange reaction of Rh(acac)(alkene)$_2$ has been studied in some detail.[14,18] The exchange of the *cis*-butene complex is slower than for the ethylene compound. This could be attributed to steric effects. However, the reaction is speeded up considerably when the acetylacetonate is substituted for hexafluoroacetylacetonate, hfacac.[83,84] This suggests that there is also an electronic effect influencing the rate.

An electronic difference in reactivity between ethylene and *cis*-butene could possibly be detected using model calculations on naked metals. We calculated reaction coordinates for the association of one alkene with the naked metal, Rh(0) or Rh(I), on the CASSCF level. No substantial activation barrier was found for either of the alkenes, neither when we adjusted bond lengths and angles to obtain a smooth "docking" or when the unperturbed alkene was brought into bonding distance to rhodium.

The suggestion that the difference in reactivity may originate from higher electron density at the metal with the more electron-rich alkenes, slowing down a nucleophilic attack,[18] can also be refuted on the basis of the very similar charges obtained in the MO calculations (Table 3).

We therefore propose that the exchange rates are mainy governed by steric factors.

Concluding Remarks

The results from the present study indicate that the correlation between ^{103}Rh-NMR shifts and the stability constants found for some rhodium(I) alkene complexes is due to the similarity of metal–alkene bonding in the different compounds and to slightly longer rhodium–alkene bonds for the methyl-substituted ethylenes. The trend of increasing shifts with decreasing $\Delta E_{\pi,\pi^*}$ excitation energies of the free ligand, on the other hand, is probably caused by the covariation of the $\Delta E_{\pi,\pi^*}$ with the number of alkyl substituents. Alkenes with electronic properties that are clearly different deviate from these correlations. Thus, it is possible to distinguish classes of alkene complexes in this way.

In Rh(β-diketonato)(alkene)$_2$ complexes, when the alkenes bind in the same way, the changes in Rh-NMR shifts are most likely determined by the d–d excitation energy contribution to the paramagnetic term in the Ramsey equation, all other terms being essentially constant. Together with the previous results from other studies of metal-NMR chemical shifts,[21,54] the present finding has an important implication for the validity of the simplified Ramsey model.

In conclusion, the metal-NMR chemical shift for a particular metal ion has a potential as a working tool when the chemical properties of metal compounds are studied. The diamagnetic term is determined mainly by the inner electrons of the metal, and their configuration is not expected to change much between the different complexes of the same metal ion. On the contrary, the paramagnetic term is mainly determined by the outer electrons, which can participate in chemical bonds. For example, the trend of decreased stability with increased chemical shifts may be quite general for transition metal complexes with the same type of bonding since both important parameters in the Ramsey equation, $1/\Delta E$ and $\langle r_{\mathrm{nd}}^{-3}\rangle$, in that case work in the same direction. Chelating ligands and other cases where significant changes in entropy might be envisaged must, however, be treated cautiously.

The molecular orbital calculations on **1** and **2** suggest that the rhodium–alkene bonds are very similar. The close correspondence between metal charges, d orbital populations, and Rh–C overlaps implies constant (σ_{d}), $\langle r_{\mathrm{nd}}^{-3}\rangle$, and D_i in Ramsey's equation (eq 1), thus leaving ΔE as the major variable in this case, in agreement with the experimental findings.

The model calculations on naked rhodium alkene complexes give further support for this and suggest important differences in the bonding of tetrafluoroethylene to rhodium, in agreement with empirical evidence. In this type of complex the back-bonding is dominant, but also the σ donation is strong.

In general, we note the close correspondence of the molecular orbital calculations with the Dewar–Chatt–Duncanson model, and we are also satisfied with the reasonable agreement between theory and experiment.

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