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Relative Stability Constants of Olefin–Rhodium(II) vs. Olefin–Rhodium(I) Coordination As Determined by Complexation Gas Chromatography

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Relative stability constants of π-complexation of 40 acyclic and cyclic monoolefins (and alkynes) with dirhodium(II) tetrakis-(heptafluorobutyrate) (**1c**) (Rh(II)) and dicarbonylrhodium(I) 3-(trifluoroacetyl)-($1R$)-camphorate (**2d**) (Rh(I)) are determined from retention data by complexation gas chromatography and compared with that of AgNO$_3$ (**3**) (Ag(I)). Contrary to the cases of Rh(I) and Ag(I), increasing alkyl substitution at the carbon–carbon double bond of the olefin favors coordination with Rh(II). Thus, it is proposed that σ-bonding is important in determining the stability of olefin–Rh(II) π-complexes. The fast and reversible interaction of olefins with **1c** can also be detected by ^{1}H NMR spectroscopy.

Introduction

The demonstration of coordination of olefins with dirhodium(II) tetracarboxylates (**1**) is of both practical and theoretical interest in view of the catalytic activity of Rh(II) toward olefin transformations.[1] The first evidence of olefin coordination with Rh(II), the carboxylates of which were previously regarded as incapable of olefin complexation,[2] was claimed by Doyle and co-workers in 1984.[3] We wish to draw attention to our chromatographic work carried out in 1973 that unambiguously established the propensity of olefins to coordinate reversibly and rapidly with Rh(II) compounds such as dirhodium(II) tetrabenzoate (**1a**)[4] and
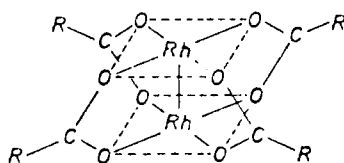
1a, R = C$_6$H$_5$
  b, R = CH$_3$
  c, R = CF$_2$CF$_2$CF$_3$
  d, R = CF$_2$CF$_2$CF$_2$CF$_2$CF$_3$
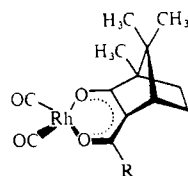
2a, R = H
  b, R = CH$_3$
  c, R = C$_6$F$_5$
  d, R = CF$_3$
  e, R = CF$_2$CF$_2$CF$_3$

AgNO$_3$

3

dirhodium(II) tetraacetate (**1b**).[5] We had also noticed[4,6] that the selectivity of Rh(II) toward alkyl-substituted ethenes differed markedly and unexpectedly from that observed for Rh(I), e.g. **2d**,[7] and for Ag(I), e.g. **3**.[8] In particular, the unusual trend in ole-fin–Rh(II) coordination, that is the stabilization of the complexes with increasing alkyl substitution at the carbon–carbon double bond, observed in many instances,[4,6] was attributed to predominant olefin–metal σ-bonding in determining the stability of olefin–rhodium(II) coordination.[4,6] This interpretation, incidentally, appears to be in contradiction to a more recent proposal of the importance of π-back-bonding in determining the stability of rhodium(II) carboxylates (**1**) with axial ligands,[9] an assertion that had been challenged by others.[10]

In this work we not only wish to recall these earlier studies, which apparently remained unnoticed, but also to take the opportunity of disclosing hitherto unpublished results of a detailed gas chromatographic study of olefin coordination with rhodium(II), e.g. **1c**, in comparison to that with rhodium(I), e.g. **2d**.[11] The method, pioneered by Muhs and Weiss[8] in "argentation" gas chromatography, provides a comprehensive set of stability data of olefin–rhodium π-complexation not available by other techniques thus far.

Experimental Section

Materials. Dirhodium(II) tetracarboxylates (**1**) were prepared according to the general procedure of Johnson and co-workers,[12] as described for dirhodium tetrafluoroacetate.

Dirhodium(II) Tetrakis(heptafluorobutyrate) (1c).[11] A 0.5-g sample of rhodium acetate (**1a**) (Johnson Matthey Chemicals Ltd., Royston, England) was treated with 10 mL of heptafluorobutyric acid (Fluka, Buchs, Switzerland) at 160 °C under refluxing for 24 h. The excess acid was allowed to distill off, and the residue was vacuum-treated (10 mmHg) until dryness. The green residue was collected and Soxhlet-extracted with dry *n*-hexane/benzene (3:1 v/v). Concentration of the solution afforded a green hygroscopic crude powder that resisted all attempts of further purification by crystallization or sublimation.

Anal. Calcd for Rh$_2$C$_{16}$F$_{28}$O$_8$: Rh, 19.5; C, 18.2; H, 0. Found: Rh, 20.7; C, 18.6; H, 0.6. The compound is highly hygroscopic. Although no satisfactory fluorine analysis had been obtained, the completion of the carboxylate-exchange reaction is indicated by the absence of CH$_3$ absorptions in the ^{1}H NMR spectrum.

Dicarbonylrhodium(I) 3-Acyl-($1R$)-camphorates (2). Dicarbonylrhodium(I) 3-(trifluoroacetyl)-($1R$)-camphorate (**2d**) has been prepared from barium bis(3-(trifluoroacetyl)-($1R$)-camphorate) and Rh$_2$(CO)$_4$-Cl$_2$.[13] The other dicarbonylrhodium(I) 3-acyl-($1R$)-camphorates have been prepared from the sodium salt of 3-acyl-($1R$)-camphorates[14] and Rh$_2$(CO)$_4$Cl$_2$. The chelates gave satisfactory elemental analyses and spectroscopic data.

Gas Chromatography. (a) Packed Columns. A 3 m × 2 mm glass column was filled with Chromosorb P, AW, DMCS, 80–100 mesh, which

(1) (a) Cotton, F. A. "Multiple Bonds between Metal Atoms"; Wiley: New York, 1982; Chapter 7 and references cited therein. (b) Felthouse, T. R. *Prog. Inorg. Chem.* **1982**, *29*, 73–166 and references cited therein.
(2) (a) Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petiniot, N.; Teyssié, P. *J. Org. Chem.* **1980**, *45*, 695. (b) Doyle, M. P.; Griffin, J. H.; Baghesi, V.; Dorow, R. L. *Organometallics* **1984**, *3*, 53.
(3) Doyle, M. P.; Colsman, M. R.; Chinn, M. S. *Inorg. Chem.* **1984**, *23*, 3684.
(4) Schurig, V.; Bear, J. L.; Zlatkis, A. *Chromatographia* **1972**, *5*, 301.
(5) Mikeš, F.; Schurig, V.; Gil-Av, E. *J. Chromatogr.* **1973**, *83*, 91.
(6) Schurig, V. *Chem.-Ztg.* **1977**, *101*, 173.
(7) (a) Schurig, V.; Gil-Av, E. *J. Chem. Soc., Chem. Commun.* **1971**, 650. (b) Gil-Av, E.; Schurig, V. *Anal. Chem.* **1971**, *43*, 2030. (c) Schurig, V.; Gil-Av, E. *Isr. J. Chem.* **1971**, *9*, 220.
(8) Muhs, M. A.; Weiss, F. T. *J. Am. Chem. Soc.* **1962**, *84*, 4697.

(9) (a) Drago, R. S.; Tanner, S. P.; Richman, R. M.; Long, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 2897. (b) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1981**, *20*, 2920. (c) Drago, R. S.; Long, J. R.; Cosmano, R. *Inorg. Chem.* **1982**, *21*, 2196. (d) Drago, R. S. *Inorg. Chem.* **1982**, *21*, 1697.
(10) Burston, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.
(11) Schurig, V. Habilitation Thesis, University of Tübingen, Tübingen, FRG, 1974.
(12) Johnson, S. A.; Hunt, H. R.; Neumann, H. M. *Inorg. Chem.* **1963**, *2*, 960.
(13) Schurig, V. *Inorg. Chem.* **1972**, *11*, 736.
(14) Schurig, V.; Bürkle, W. *J. Am. Chem. Soc.* **1982**, *104*, 7573.

was coated (a) with Fluorolube (15% w/w) as the reference column and (b) with 5×10^{-3} *m* (mol/kg of solvent) dirhodium(II) tetrakis(heptafluorobutyrate) (**1c**) in Fluorolube (15% w/w) as the olefin-interacting column.[4] Fluorolube (a difluorovinyl chloride polymer)[15] has been obtained from Hewlett-Packard, Böblingen, FRG, and it had the following McReynold constants: X'(benzene), 51; Y'(1-butanol), 68; Z'(2-pentanone), 114; U'(nitropropane), 144; S'(pyridine), 118.

(b) **Open Tubular (Capillary) Columns.**[16] A 200 m × 0.5 mm stainless-steel capillary column (Handy and Harmon Tube Co. Norristown, PA) was dynamically coated[16] with 1 g of squalane (Applied Science Laboratories) dissolved in 10 mL of $CHCl_3$ at 25 °C and at 60 psig to give the reference column. A 200 m × 0.5 mm stainless-steel capillary column was dynamically coated[16] with 5 mg of dicarbonylrhodium(I) 3-(trifluoroacetyl)-(1*R*)-camphorate (**2d**), and 250 mg of squalane (5 × 10^{-2} *m*) dissolved in 5 mL of $CHCl_3$ to give the olefin-interacting column. The latter column was conditioned at 50 °C for 120 h. The carrier gas for coating and conditioning was high-purity-grade nitrogen. Olefins were injected as diluted vapors by using a split ratio of 1:100. The instrument was operated at highest sensitivity in order to avoid overloading conditions, which result in peak tailing for interacting olefins.

Determination of the Retention Increase *R′*. Methane (for measuring the gas holdup, "dead volume") and methylcyclohexane (as noninteracting reference standard) were always coinjected with the olefins. The relative retention r_0 of an olefin with respect to methylcyclohexane is calculated from the ratio t_0'(olefin)/t_0'(methylcyclohexane) obtained on the reference column. The relative retention *r* of an olefin with respect to methylcyclohexane is calculated from the ratio t'(olefin)/t'(methylcyclohexane) obtained on the olefin-interacting, rhodium-containing column. The retention increase *R′* is calculated from the equation $R' = (r - r_0)/r_0$. Note that the retention times t' are measured from the methane peak (adjusted retention times).

Instrumentation. A Carlo Erba Fractovap 2101 instrument equipped with a FID detector was used. Retention times t' have been determined graphically (chard speed 2 cm/min).

Gas Chromatographic Parameters. (a) Packed column coated with **1c** in Fluorolube: temperature, 100 °C; N_2 flow, 0.4 bar of N_2 (overpressure) or 4 mL/min. The relative retention, *r*, is independent of the carrier-gas flow (1 bar vs. 0.4 bar of N_2).

(b) Open tubular (capillary) column coated with **2d** in squalane: temperature, 50 °C; N_2 flow, 1.5 bar of N_2 (overpressure) or 6 mL/min; split ratio, 1:100; dead volume, 12 min; t'(methylcyclohexane), 9.5 min; number of theoretical plates for methylcyclohexane, 180 000. The relative retention, *r*, is independent of the carrier-gas flow (1.5 bar vs. 0.4 bar of N_2).

Results and Discussion

The fast and reversible coordination of olefins (and alkynes) with dirhodium(II) tetracarboxylates (**1**) can readily be demonstrated by *complexation gas chromatography*.[4,6,11] Thus, when dirhodium(II) tetrakis(heptafluorobutyrate) (**1c**)[11] is added to the liquid-stationary-phase Fluorolube (a fluid difluorovinyl chloride polymer), the observed overall retention of the olefin in the gas chromatographic experiment is determined by two independent equilibria: (i) the *physical* partition of the olefin between the gaseous and liquid phases (separation according to boiling points) and (ii) the fast and reversible *chemical* association between the olefin B and the metal ion A (separation according to the chemical equilibrium), i.e.

$$A + B \rightleftharpoons AB \quad K$$
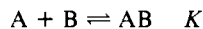
The chemical equilibrium causes a *retention increase R′* (or retention factor)[4] for the olefin, which is easily determined from relative retention data (cf. Experimental Section) according to the simplified equation[16,17]
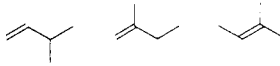
$$Ka_A = (r - r_0)/r_0 = R' \quad (1)$$

With

$$K = a_{AB}/(a_A a_B) \quad (2)$$

it follows from eq 1 that the retention increase *R′* represents the

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(16) (a) Schurig, V.; Chang, R. C.; Zlatkis, A.; Gil-Av, E.; Mikeš, F. *Chromatographia* **1973**, *6*, 223. (b) Schurig, V. *Chromatographia* **1980**, *13*, 263.
(17) Schurig, V.; Chang, R. C.; Zlatkis, A.; Feibush, B. *J. Chromatogr.* **1974**, *99*, 147.

Chart I. π-Complexation Selectivity of Methylbutenes with Rh(II), Rh(I), and Ag(I) (Data from Table II)

alkyl substitution at the double bond	mono	di	tri
Rh(II)	0.12	0.50	0.66
Rh(I)	2.85	0.12	0.04
Ag(I)	0.95	0.55	0.15

fraction of complexed to uncomplexed olefin B in the liquid phase, i.e.

$$R' = a_{AB}/a_B \quad (3)$$

Since the metal complex A is employed in high dilution and the olefin is injected in minute amounts (10^{-9} g), eq 1 and 3 may be rewritten:

$$R' = K_m m_A = m_{AB}/m_B = (r - r_0)r_0 \quad (4)$$

Note that in eq 4 the molality concentration scale *m* (mol/kg of solvent) has been employed since this quantity is temperature-independent and, for practical purposes, the weight of the solvent is determined. According to eq 4 the equilibrium constant K_m and, at variable temperatures, the Gibbs–Helmholtz parameters of molecular association may be measured[7c] from relative retention data where *r* = relative dead volume adjusted retention of the olefin B with respect to an inert reference standard (not interacting with the metal ion A) measured on a column containing the molal concentration *m* of the metal coordination compound A in the nonvolatile solvent S and r_0 = relative adjusted retention of the same olefin B with respect to the inert reference standard on a reference column containing the pure solvent S. *r* and r_0 are measured at the same temperature.

The comparison of the retention increases *R′* for two olefins, 1 and 2, provides a direct measure for the difference in their abilities to coordinate with the metal compound, and the difference in the free enthalpy changes may be calculated according to eq 5.

$$-\Delta_{2,1}(\Delta G°) = RT \ln (R'_2/R'_1) = RT \ln (K_{m2}/K_{m1}) \quad (5)$$

Although, in principle, absolute stability constants *K* may be obtained from eq 1, such data may bear a systematic error due to uncertainties in the amount of the metal complex activity that may be caused by partial insolubility, decomposition, activation,[16b] or losses of stationary phase. However, relative stability constants, which are directly proportional to relative retention increases *R′*, are considered to be highly reliable, notably in those cases where the olefins were simultaneously injected or measured in close succession. In the present measurements, (*Z*)-2-butene (*cis*-2-butene) has always been coinjected to check the constancy of the retention increase *R′*.

In Table I retention data of 40 olefins on dirhodium(II) tetrakis(heptafluorobutyrate) (**1c**) in Fluorolube (100 °C) are compared with those on dicarbonylrhodium(I) 3-(trifluoroacetyl)-(1*R*)-camphorate (**2d**) in squalane (50 °C). The relative stability constants for Rh(I)[7b] have been confirmed by employing a high-resolution 200-m capillary column. In Table II relative stability constants of 40 olefins with Rh(II), Rh(I), and Ag(I),[8] normalized to (*Z*)-2-butene, are compared. Repeated measurements at different concentrations, performed for both Rh(II) and Rh(I), not only confirmed the validity of eq 4 but also established a precision of the relative stability constants of approximately 5%. Retention data for ethene and propene and Rh(II) are not included in Table I since these highly volatile olefins exhibited only a small chemical interaction with **1**, rendering the determination of the retention increase *R′* somewhat inaccurate.

The results contained in Table II merit the following comments. The decrease of olefin interaction upon alkyl substitution at the double bond, as observed with Rh(I) and Ag(I), is not found for Rh(II). Thus, e.g., 2-methyl-2-butene and 2,3-dimethyl-2-butene interact quite strongly with Rh(II) but not with Rh(I) and Ag(I).

Olefin–Rh(II) vs. Olefin–Rh(I) Coordination

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Table I. Gas Chromatographic Retention Data of C_2–C_7 Monoolefins[a]

olefin	bp,[b] °C	$r_0^{c,d}$	$r^{c,e}$	$r_0^{c,f}$	$r^{c,g}$
ethene	−103.7		h	0.002	0.159
propene	−47.7		h	0.01	0.125
2-methylpropene	−6.9	0.087	0.295	0.03	0.045
1-butene	−6.3	0.087	0.144	0.03	0.392
(E)-2-butene	0.9	0.109	0.170	0.04	0.105
(Z)-2-butene	3.7	0.115	0.406	0.045	0.195
1-pentene	30.0	0.187	0.279	0.085	1.105
(E)-2-pentene	36.4	0.217	0.279	0.105	0.31
(Z)-2-pentene	36.9	0.230	0.577	0.11	0.73
3-methyl-1-butene	20.1	0.148	0.193	0.06	0.63
2-methyl-1-butene	31.2	0.200	0.452	0.09	0.125
2-methyl-2-butene	38.6	0.252	0.675	0.12	0.135
1-hexene	63.5	0.381	0.567	0.24	3.32
(E)-2-hexene	67.9	0.428	0.567	0.28	0.84
(Z)-2-hexene	68.8	0.450	1.06	0.295	1.655
(E)-3-hexene	67.1	0.409	0.489	0.27	0.925
(Z)-3-hexene	66.4	0.390	0.801	0.27	2.605
4-methyl-1-pentene	53.9	0.309	0.438	0.17	2.00
3-methyl-1-pentene	54.1	0.318	0.377	0.18	1.42
2-methyl-1-pentene	60.7	0.394	0.807	0.24	0.305
2-methyl-2-pentene	67.6	0.459	0.896	0.28	0.335
3,3-dimethyl-1-butene	41.2	0.238	0.257	0.115	0.165
2,3-dimethyl-1-butene	55.7	0.347	0.465	0.195	0.225
2,3-dimethyl-2-butene	73.2	0.607	1.491	0.375	0.375
2-ethyl-1-butene	64.7	0.430	0.676	0.265	0.31
(E)-4-methyl-2-pentene	58.6	0.344	0.380	0.195	0.475
(Z)-4-methyl-2-pentene	56.3	0.332	0.406	0.185	1.44
(E)-3-methyl-2-pentene	70.5	0.508	0.873	0.325	0.36
(Z)-3-methyl-2-pentene	67.6	0.482	0.928	0.295	0.34
cyclopentene	44.2	0.320	0.828	0.175	0.305
cyclohexene	83.0	0.728	1.372	0.585	0.615
cycloheptene	116.4	1.518	3.26	1.625	7.045
methylenecyclobutane	41.2	0.278	0.9[i]	0.14	10.5
methylenecyclopentane	75.7	0.613	1.1[i]	0.43	1.235
methylenecyclohexane	103.3	1.140	2.3[i]	1.055	3.845
1-methylcyclopentene	75.8	0.627	1.00	0.45	0.46
3-methylcyclopentene	65.0	0.459	0.888	0.295	0.51
1,2-dimethylcyclopentene	105.8	1.311	1.64	1.19	1.19
1-ethylcyclopentene	106.3	1.266	1.588	1.23	1.24
1-methylcyclohexene	110.0	1.445	1.74	1.42	1.42
3-methylcyclohexene	104.0	1.137	1.803	1.05	1.095
4-methylcyclohexene	102.7	1.158	2.256	1.075	1.13
methylcyclohexane	*100.9*	*1.00*	*1.00*	*1.00*	*1.00*

[a] Reference standard: methylcyclohexane. [b] r_0 values reflect volatility as expressed by boiling points. [c] Mean from four measurements (±0.005); cf. Experimental Section. [d] On Fluorolube (100 °C). [e] On dirhodium(II) tetrakis(heptafluorobutyrate) in Fluorolube (5×10^{-3} m, 100 °C). [f] On squalane (50 °C). [g] On dicarbonylrhodium(I) 3-(trifluoroacetyl)-(1R)-camphorate in squalane (5×10^{-2} m, 50 °C)[7b] [h] Low retention increase and high volatility; cf. text. [i] Excessive peak broadening.

In some cases, e.g. for isomeric methylbutenes, interaction with Rh(II) even increases as alkyl substitution at the double bond is increased (cf. Chart I). Inspection of Table II will reveal other examples that establish the striking differences of olefin coordination with Rh(I) and Ag(I) on the one hand and with Rh(II) on the other. Doyle and co-workers[3] have also concluded from spectroscopic evidence that increasing alkyl substitution at the carbon–carbon double bond favors coordination of olefins with 1 (R = CF_3).

The selectivity of olefin coordination with Ag(I) and Rh(I) has been discussed previously[7,8] as depending on a complex interplay among electronic, steric, and, occasionally, strain effects. The decrease of interaction with Ag(I) and Rh(I) upon alkyl substitution at the double bond of the olefins has been ascribed to a steric effect that overrides the electronic effect of alkyl groups (+I).[7,8] The observation of an "inverse" secondary isotope effect for ethene/ethene-d_4 with Ag(I) ($K_{C_2D_4}/K_{C_2H_4}$ = 1.13 (25 °C) for 3)[18] and with Rh(I) ($K_{C_2D_4}/K_{C_2H_4}$ = 1.21 (25 °C) for 2d)[19] has been attributed as arising from a prevalent σ-bonding contribution in determining the stability of olefin silver(I) and rhodium(I) complexes. The observed stabilization of olefin interaction

with dirhodium(II) tetracarboxylates 1 with increasing alkyl substitution at the double bond (cf. Chart I) would indicate an even more pronounced importance of σ-bonding in olefin rhodium(II) coordination as opposed to the recent claim of the importance in π-back-bonding in adducts of 1 with axial ligands.[9] It should be mentioned that with increasing alkyl substitution at the double bond the interaction of olefins with oxodiperoxomolybdenum(VI) hexamethylphosphoric triamide, which is devoid of d electrons capable of back-bonding, has also been found to increase remarkably.[20] It is suggested that in the complexation of olefins to dirhodium(II) tetracarboxylates 1 the alkene is mainly acting as a σ-donor molecule.

Some common features of olefin complexation selectivity are found for the three ions Ag(I), Rh(I), and Rh(II). Thus, cis (Z) olefins are always undergoing stronger coordination than are the trans (E) isomers. While with Ag(I) and Rh(II) an almost invariable ratio is observed (i.e. Ag(I) 4:1 and Rh(II) 5:1), a steady increase between the stability constants of cis. vs. trans olefins with increasing bulk of the alkyl substituent at the double bond is observed for Rh(I). In fact, in cis olefins, interaction increases as the steric hindrance of the alkyl substituents increases (cf. Chart II).

(18) Cvetanović, R. J.; Duncan, F. J.; Falconer, W. E.; Irwin, R. S. *J. Am. Chem. Soc.* 1965, 87, 1827.
(19) Schurig, V. *Angew. Chem., Int. Ed. Engl.* 1976, 15, 304.

(20) Arakawa, H.; Moro-aka, Y.; Ozaki, A. *Bull. Chem. Soc. Jpn.* 1974, 47, 2958.

Table II. Relative Stability Constants K of Olefin–Metal π-Complexation Calculated from Data of Table I[a]

| olefin	Rh(II)	Rh(I)	Ag(I)
ethene		23.19	4.13
propene		3.40	1.68
2-methylpropene	0.94	0.15	0.72
1-butene	0.26	3.62	1.43
(*E*)-2-butene	0.22	0.49	0.26
(*Z*)-2-butene	1.00	1.00	1.00
1-pentene	0.19	3.60	0.91
(*E*)-2-pentene	0.11	0.59	0.20
(*Z*)-2-pentene	0.60	1.69	0.80
3-methyl-1-butene	0.12	2.85	0.95
2-methyl-1-butene	0.50	0.12	0.55
2-methyl-2-butene	0.66	0.04	0.15
1-hexene	0.19	3.85	0.80
(*E*)-2-hexene	0.13	0.60	0.15
(*Z*)-2-hexene	0.53	1.38	0.57
(*E*)-3-hexene	0.08	0.73	0.18
(*Z*)-3-hexene	0.42	2.60	0.72
4-methyl-1-pentene	0.17	3.23	0.52
3-methyl-1-pentene	0.07	2.07	0.63
2-methyl-1-pentene	0.41	0.08	0.39
2-methyl-2-pentene	0.38	0.06	0.11
3,3-dimethyl-1-butene	0.03	0.13	0.67
2,3-dimethyl-1-butene	0.13	0.05	0.44
2,3-dimethyl-2-butene	0.57	0.00	0.02
2-ethyl-1-butene	0.23	0.05	0.65
(*E*)-4-methyl-2-pentene	0.04	0.43	0.13
(*Z*)-4-methyl-2-pentene	0.09	2.04	0.57
(*E*)-3-methyl-2-pentene	0.28	0.03	0.13
(*Z*)-3-methyl-2-pentene	0.37	0.05	0.13
cyclopentene	0.63	0.22	1.35
cyclohexene	0.35	0.02	0.67
cycloheptene	0.45	1.00	2.37
methylenecyclobutane	0.88	22.2	1.07
methylenecyclopentane	0.31	0.56	0.74
methylenecyclohexane	0.40	0.79	1.11
1-methylcyclopentene	0.24	0.01	0.35
3-methylcyclopentene	0.37	0.22	
1,2-dimethylcyclopentene	0.10	0.00	
1-ethylcyclopentene	0.10	0.01	0.43
1-methylcyclohexene	0.08	0.00	0.09
3-methylcyclohexene	0.23	0.01	0.65
4-methylcyclohexene	0.37	0.01	0.70

[a] Complex: Rh(II) (dirhodium(II) tetrakis(heptafluorobutyrate) (**1c**) in Fluorolube) (100 °C), Rh(I) (dicarbonylrhodium(I) 3-(trifluoroacetyl)-(1*R*)-camphorate (**2d**) in squalane) (50 °C), and Ag(I) (silver nitrate (**3**) in ethylene glycol)[8] (40 °C). $K_{rel}((Z)$-2-butene) = 1.00.

Chart II. Relative Stability Constants of Cis Olefins vs. Trans Olefins with Rh(II), Rh(I), and Ag(I) (Data from Table II)[a]

Rh(II)	1.00	0.60	0.53	0.09	0.42
Rh(I)	1.00	1.69	1.38	2.04	2.60
Ag(I)	1.00	0.80	0.57	0.57	0.72

Rh(II)	0.22	0.11	0.13	0.04	0.08
Rh(I)	0.49	0.59	0.60	0.43	0.73
Ag(I)	0.26	0.20	0.15	0.13	0.18

[a] $K_{rel}((Z)$-2-butene) = 1.00.

The higher stability of complexes formed with cis olefins as compared to trans isomers may be due to two effects:

(i) The free cis olefin is more strained than the trans isomer, and this strain is partially relieved upon π-complexation to a metal ion by virtue of the lengthening of the double bond and of rehybridization. This effect is obviously important for Rh(I) (vide supra).

(ii) The bond formed between cis olefins and the metal ion is stronger than for trans olefins. This effect may arise from the

Table III. Influence of the Carboxyl Residue of **1** on Selectivity (Related to (*Z*)-2-Butene) of Olefin Coordination at 50 °C

| olefin	**1a**[a]	**1c**[b]	**1d**[b]
2-methylpropene	0.73	0.89	0.84
1-butene	0.26	0.26	0.18
(*E*)-2-butene	0.23	0.22	0.26
(*Z*)-2-butene	1.00	1.00	1.00
3-methyl-1-butene	0.11	0.09	0.11
2-methyl-1-butene	0.38	0.46	0.56
2-methyl-2-butene	0.59	0.72	0.92

[a] In squalane. [b] In Fluorolube.

Table IV. Relative Stability Constants of C_2–C_4 Olefin Coordination with Dicarbonylrhodium(I) 3-Acyl-(1*R*)-camphorates (**2**) in Squalane at 25 °C[a]

olefin	**2a**	**2b**	**2c**	**2d**	**2e**
ethene	37	30	28	23	22
propene	3.9	2.3	3.2	3.3	3.1
1-butene	4.5	4.4	4.2	3.7	3.8
(*Z*)-2-butene	1.00	1.00	1.00	1.00	1.00
(*E*)-2-butene	0.43	0.34	0.34	0.43	0.47
2-methylpropene	0.12	0.07	0.08	0.13	0.12

[a] $K_{rel}((Z)$-2-butene) = 1.00.

different mode of distortions necessary to minimize nonbonded repulsions.[21] Steric interactions between disubstituted ethenes and **1**, which possesses a unique coordination face of D_{4h} symmetry, may be reduced by (a) rotation around the olefin-bonding axis for cis olefins ((*Z*)-2-butene), (b) rotation around the olefin–metal–metal axis for trans olefins ((*E*)-2-butene), and (c) rotation around an axis aligned perpendicular to the previous axes for *gem*-disubstituted olefins. Although the σ-bond is insensitive to rotation around the olefin–metal–metal axis, the existence of a barrier to rotation[22] may prevent trans-configured olefins from relieving steric interaction by adopting a suitable conformation. This barrier is thought to arise from a four-electron repulsive interaction between the π-orbital of the olefin and the filled metal d_{xy} orbitals in analogy to that predicted for the d^6 ML_5(ethene) system,[23] leading to an equilibrium orientation of the olefin eclipsing the O–Rh–O axis in the Rh(II) cluster **4**.[22] All three ions,

4
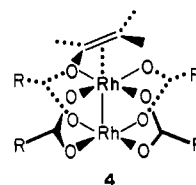
Ag(I), Rh(I), and Rh(II), show the same discrimination in their interaction with cyclic monoolefins of different ring size whereby the six-membered-ring olefin shows the least coordination. The peculiar affinity of Rh(I) for the strained olefin methylenecyclobutane is absent for Rh(II) while the latter is very sensitive to steric hindrance imposed by the alkyl side groups of (*E*)- and (*Z*)-4-methyl-2-pentene. In general, while Rh(I) shows selectivity changes orders of magnitude different in coordination of olefins, the changes with Rh(II) are much less pronounced, spanning factors of less than 30.

It is important to note that changes in the electron-withdrawing properties of the ligands for Rh(I) and Rh(II) do not influence the overall order of olefin coordination; however, slight changes of relative stabilities are discerned for olefins differing in the degree of alkyl substitution at the double bond. Thus, as shown in Tables III–V, electron-rich olefins show a slight increase of interaction

(21) Winter, W.; Koppenhöfer, B.; Schurig, V. *J. Organomet. Chem.* **1978**, *150*, 145; cf. Figure 2.
(22) Personal communication from Professor Roald Hoffmann, Cornell University, 1979.
(23) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801.

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Table V. Relative Stability Constants of C_2–C_4 Olefin Coordination with $(CO)_4Rh_2Cl_2$ (**5**) and Dicarbonylrhodium(I) Acetylacetonates (**6**) in Squalane at 25 °C[a]

olefin	5	6a[b]	6b[c]	6c[d]
ethene	15	33	19	12
propene	2.6	3.7	3.1	2.5
1-butene	3.8	4.8	3.7	3.0
(Z)-2-butene	1.00	1.00	1.00	1.00
(E)-2-butene	0.38	0.38	0.46	0.50
2-methylpropene	0.06	0.11	0.12	0.16

[a] $K_{rel}((Z)\text{-2-butene}) = 1.00$. [b] Dicarbonylrhodium(I) acetylacetonate. [c] Dicarbonylrhodium(I) trifluoroacetylacetonate. [d] Dicarbonylrhodium hexafluoroacetylacetonate.

Table VI. Relative Stability Constants K of Alkynes and Dirhodium(II) tetrakis(heptafluorobutyrate) (**1c**) in Fluorolube (100 °C) in Comparison to Those of Other Substrates

donor substrate	K_{rel}	donor substrate	K_{rel}
(Z)-2-butene	1.00	1-pentyne	0.31
benzene	<0.01	2-pentyne	0.43
isoprene	0.65	1-hexyne	0.30
propyne	0.44	2-hexyne	0.80
1-butyne	0.50	3-hexyne	0.66
2-butyne	1.09		

as compared to poor donors as the acceptor property of the metal ion increases.

It should be mentioned that the selectivity of olefin interaction with Rh(I) (**2d**), as measured by gas chromatography, agrees well with that determined by IR spectroscopy for the exchange reaction of olefins with $(C_2H_4)_2Rh(acac)$.[24] The relative stability data also correlate surprisingly well with differences in the rate constants for the Co(I)- and Rh(I)-catalyzed hydroformylation of olefins, i.e. with selectivity changes due to alkyl substitution at the double bond, alkyl chain length and branching, E/Z ratio, and ring size.[25] It is anticipated that selectivities presented in this work for dirhodium tetracarboxylates **1** may be of relevance to rates of olefin transformations mediated by Rh(II) in a similar way as has been established for molybdenum(VI) reagents, i.e. with the stability data for olefins being directly comparable with rates of alkene epoxidation.[20,26] Some hydrogenation experiments of olefins performed with catalytic amounts of **1c** in DMF, or after induction periods in benzene, were, however, inconclusive in this respect as it could not be ruled out that reduced rhodium species do participate in catalysis. In view of the propensity of **1** to coordinate with olefins, the metal–olefin interaction in the rhodium car-

boxylate catalyzed cyclopropanation of olefins, hitherto discounted,[2] should be further scrutinized.

Dirhodium(II) tetrakis(heptafluorobutyrate) (**1c**) also undergoes coordination with diolefins such as isoprene as well as with alkynes (cf. Table VI). It is noted that the overall strengths of coordination of alkenes and alkynes with **1c** are similar. As with olefins, alkyl substitution at the triple bond increases interaction with Rh(II), which reinforces the concept of pronounced σ-bonding in Rh(II) adduct formation also for alkynes. Although complexation of benzene with dirhodium(II) tetrabutyrate (**1** R = $-C_3H_7$) has been inferred recently to explain the unusual behavior of 1:1 and 1:2 Lewis base adduct formation,[9a] no such evidence could be obtained gas chromatographically with **1c**. Coordination of benzene with **1c**, if any, would be a factor of 10^2 less than that with (Z)-2-butene (cf. Table VI).

The fast and reversible coordination equilibrium of olefins with **1c** or **1d** can also be demonstrated by ^1H NMR spectroscopy via the induced downfield shift of olefin proton resonances ($\Delta\delta = 0.3$ ppm for the olefinic protons of 3-methyl-1-pentene (0.4 M) with added **1c** (0.2 M) in $CDCl_3$). Similar results were recently obtained by Doyle and co-workers.[3] **1c** in conjunction with lanthanide shift reagents such as $Eu(TFA\text{-}Cam)_3$[27] can be used to increase induced shifts for alkenes ($\Delta\delta = 1$ ppm for the olefinic protons of α-methylstyrene (0.2 M) in the presence of **1c** (0.07 M) and $Eu(TFA\text{-}Cam)_3$ (0.06 M) in $CDCl_3$). Note that the ^1H NMR spectra are not affected by **1c** being devoid of protons.

1, containing chiral residues R*,[11] are interesting compounds for enantioselective olefin transformations or for the gas chromatographic resolution of racemic olefins as has been established with Rh(I) (**2d**).[28] Investigations along these aspects are being continued in our laboratory.

(24) Cramer, R. *J. Am. Chem. Soc.* **1967**, *89*, 4621; cf. Table III.
(25) (a) Wender, I.; Mettin, S.; Ergun, S.; Sternberg, H. W.; Greenfield, H. *J. Am. Chem. Soc.* **1956**, *78*, 5401. (b) Evans, D.; Osborn, J. O.; Wilkinson, G. *J. Chem. Soc. A* **1968**, 3133. (c) Heil, B.; Marko, L. *Chem. Ber.* **1969**, *102*, 2238. (d) Pruett, R. L. *Adv. Organomet. Chem.* **1979**, *17*, 1–60. (e) Relative rates (k_{rel}) of hydroformylation with $RhH(CO)(PPh_3)_3$ in olefin/toluene (1:1 v/v) at 100 °C, 80 bar H_2/CO (1:1): (Z)-2-butene, 1; (E)-2-butene, 0.39; 1-butene, very fast; cyclopentene, 0.69; cyclohexene, <0.1 (Personal communication from Dr. Kummer, Ammoniaklaboratorium, BASF, Ludwigshafen, FRG, 1979).
(26) Kagan, H. B.; Mimoun, H.; Mark, C.; Schurig, V. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 485.

(27) Schurig, V. *Tetrahedron Lett.* **1972**, *13*, 3297.
(28) Schurig, V. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 110.