Preparation and Properties of Alkylbis(dimethylglyoximato)rhodium(III) Complexes☆

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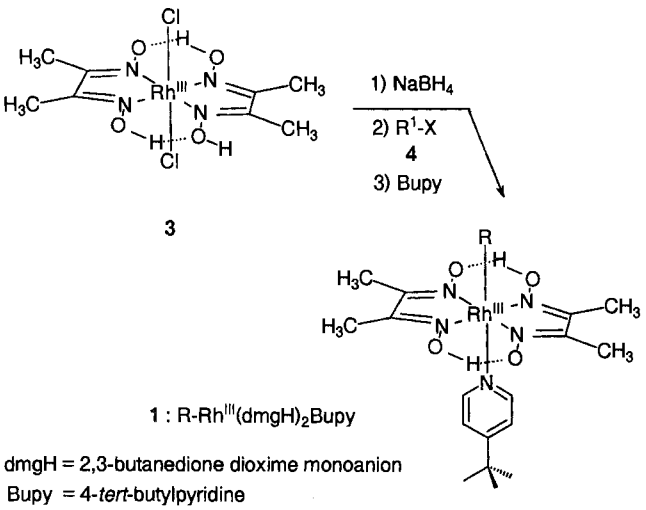
Primary, secondary, and tertiary alkylrhodoximes **1** were prepared from alkyl bromides and tosylates **4** and the *trans*-dichlororhodium complex **3**. X-ray crystallography of the previously unknown *tert*-butylrhodoxime **1k** reveals structural features of this *tert*-σ-alkylrhodium compound. Photochemical homolytic cleavage of the Rh–C bond in alkylrhodoximes **1** only occurs in the presence of efficient radical traps which allow further mechanistic studies.

Butanedione dioxime (dimethylglyoxime) complexes of transition metals play an important role in applied coordination chemistry[1]. For example photolabile alkyl(dimethylglyoxime)cobalt complexes **2** (alkylcobaloximes **2**) are convenient sources of carbon-centered radicals[2], and a technetium dimethylglyoxime complex ([^{99m}Tc]-Teboroxime) is used for imaging regional myocardial perfusion[3].

Alkylcobaloximes **2** have played a major role in elucidating reaction mechanisms of vitamin B_{12} and related alkylcobalamines[4]. 5′-Deoxyadenosylrhodibalamine, the rhodium analog of the cobalamine coenzyme, has been synthesized and tested as a vitamin B_{12} inhibitor in *E. coli* showing an IC_{50} index of 52[5]. As part of our studies of alkylcobaloximes as sources of *free* alkyl radicals in organic synthesis we were interested in photochemical properties of alkylrhodoximes **1** compared to their cobalt analogs **2**. Especially the inhibitory effect of 5′-deoxyadenosylrhodibalamine in enzyme reactions led us to the conclusion that carbon-rhodium bonds could be more stable compared to C–Co bonds. Thus tertiary σ-alkylrhodium complexes could be in synthetic reach.

Alkylrhodoximes **1** were prepared from *trans*-dichloro(dimethylglyoximato)(dimethylglyoxime)rhodium(III) (**3**)[6,7] after $NaBH_4$ reduction, subsequent alkylation and axial ligand exchange in moderate to good yields.

Large differences in yields of structurally similar alkylrhodoximes **1** (Table 1) seem to be paralleled by a change in reaction mechanisms[6a]. 6-Bromo-1-hexene (**4b**) is converted into 5-hexenylrhodoxime **1b** in a clean reaction at room temperature whereas secondary 6-bromo-1-heptene (**4h**) and tertiary 6-bromo-6-methyl-1-heptene (**4i**) are transformed into five-membered ring alkylrhodoximes **1c** and **1i**, respectively. Interesting features in this reaction are the five-membered ring geometries of isomerized alkyl ligands in **1c** and **1i** and the *cis*:*trans* ratio of (2-methylcyclopentyl)rhodoximes **1c** (78:22 as determined by ^{1}H- and ^{13}C-NMR analysis). These findings are reminiscent of the stereochemistry of the 6-hepten-2-yl-to-cyclopentylmethyl radical cyclization at room temperature[8]. Carbon-rhodium bond formation from sterically hindered secondary and tertiary alkyl bromides **4h**, **4i**, or **4e** thus occurs by an electron-transfer reaction and via alkyl radical intermediates[2b,9]. Other syn-



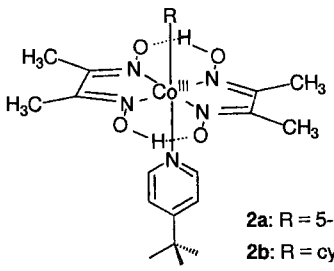


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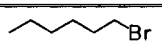
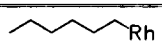
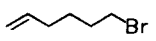
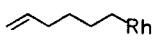
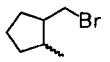
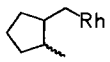
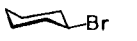
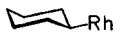
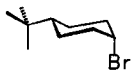
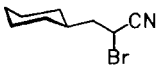
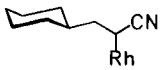
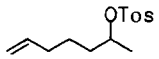
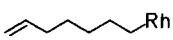
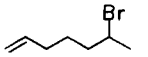
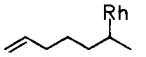
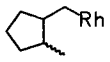
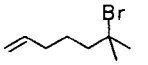
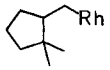
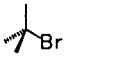
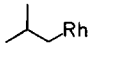
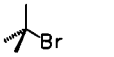
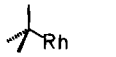
Table 1. Preparation of alkylrhodoximes

No	R^1-X 4	No	R-Rh^{III}(dmgH)$_2$Bupy 1 R-Rh	Reaction temp.[°C]	Yield (%)
a		a		25	80
b		b		25	87
c	 *cis* : *trans* = 74 : 26	c	 *cis* : *trans* = 71 : 29	25	40
d		d		25	74
e		e	 *cis* : *trans* = 55:45	-40	51
f		f		-40	31
g		g		25	31
h		h		80	
		c	 *cis* : *trans* = 78 : 22	: 20 -40	28
i		i		-40	10
j		j		25	61
k		k		-40	63

theses of alkylrhodoximes **1** such as (2-methylpropyl)rhodoxime **1j** and 6-heptenylrhodoxime **1g** proceed by a clean 1,2-migration during carbon-bromine or carbon-oxygen bond cleavages and carbon-rhodium bond formations. Preliminary results of cross experiments rule out a reaction pathway via *free* olefin intermediates.

tert-Butylrhodoxime **1k** certainly is one of the most interesting alkyl rhodoximes **1** prepared in the course of this study. It is a yellow crystalline high-melting solid (m.p. 221 – 222 °C) and seems to owe its stability to a rather strong carbon-rhodium bond. *tert*-Butylcobaloxime has not been synthesized so far. Instability of the latter complex obviously arises from spontaneous Co–C bond homolysis, subsequent β-cleavage and isobutene elimination[10]. Stable tertiary alkylcobaloximes are subject to steric restrictions such as bridgehead positions of C–Co bonds or adjacent locations that would lead to a violation of Bredt's rule in the case of fragmentation of *tert*-alkylcobaloxime into olefin and hydridocobaloxime[11].

X-ray analysis of **1k** (Figure 1) shows a distorted octahedral complex with its center ion lifted 0.2 Å out of the N_4 plane of equatorial dimethylglyoxime ligands towards the alkyl ligand. The carbon-rhodium bond [Rh(1)–C(27) = 2.163(4) Å] is significantly longer than those found in isopropylrhodoxime [2.107(5) Å] and ethylrhodoxime [2.080(2) and 2.077(2) Å][12]. However, the length of the axial rhodium-pyridine nitrogen bond [Rh(1)–N(17) = 2.225(3) Å] is similar to the corresponding distances found in other alkylrhodoximes **1** and seems to be independent of the nature of the alkyl substituent. The *tert*-butyl group is situated almost orthogonal to the N_4 plane N(1)–Rh(1)–C(27) = 93.4(1), N(4)–Rh(1)–C(27) = 90.9(1), N(5)–Rh(1)–C(27) = 90.1(1), N(8)–Rh(1)–C(27) = 92.0(1), N(17)–Rh(1)–C(27) = 78.3(1)°] although deviations from perfect symmetry give rise to an unsymmetrical oxime coordination [O(10)–O(11) = 2.735(6), O(9)–O(12) = 2.674(6) Å]. Bond angles Rh(1)–C(27)–C(28) = 109.8(3), Rh(1)–C(27)–C(29) = 111.4(3), and Rh(1)–C(27)–C(30) = 111.1(3)° are close to the tetrahedral angle for C(27). This fact is surprising because a value for the M–C–C angle of 117° seems to be common in alkylrhodoximes **1** and cobaloximes **2**[13]. No bond angle in the *tert*-butyl group shows a significant distortion: C(28)–C(27)–C(29) = 107.9(4), C(28)–C(27)–C(30) = 108.7(4), and C(29)–C(27)–C(30) = 107.9(4)°. Coordinated 4-*tert*-butylpyridine is oriented towards the oxime bridge hydrogens with respect to its horizontal plane of symmetry. Details of an X-ray analysis of **1k** and the positional parameters are listed in Tables 3 and 4.

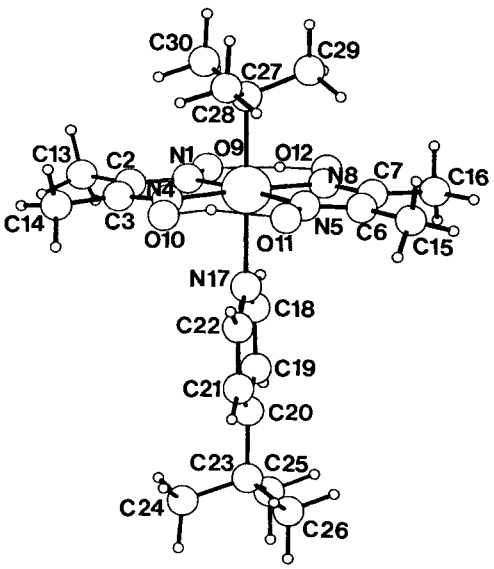


Figure 1. PLUTO plot of *tert*-butylrhodoxime **1k** as determined by X-ray crystallography (labeling scheme for non-hydrogen atoms of **1k**)

Alkylrhodoximes owe their yellow color to a lowest-energy UV/Vis absorption at 402 nm (primary alkylrhodoximes **1a**, **1b**, **1g**) or 407 nm (cyclohexylrhodoxime **1d**), which has been assigned to metal-carbon CT transitions[6,14]. Due to the similarity between the absorption spectra of alkylrhodoximes **1** and alkylcobaloximes[15] interest is focused on photochemical properties of alkylrhodoximes **1**. According to our knowledge no photochemical studies of alkylrho-

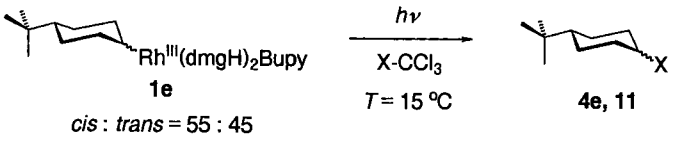
doximes **1** have been reported so far although one example of a thermal decomposition was given[6a].

5-Hexenylcobaloxime **2a** smoothly photorearranges to (cyclopentylmethyl)cobaloxime **2b** by an intermediate 5-hexenyl-to-cyclopentylmethyl radical isomerization[2a,16]. However, 5-hexenylrhodoxime **1b** proved to be much more photoinert and could not be rearranged to (cyclopentylmethyl)rhodoxime **5** even at elevated temperatures and upon prolonged irradiation with incandescent light. The addition of an efficient radical trap CCl_4 to a photolyzed solution of **1b** yields alkyl chlorides **6a**, **7a** and chlororhodoxime **8**. The formation of cyclopentylmethyl chloride (**7a**) points to the intermediate 5-hexenyl radical **9a** and to a homolytic cleavage of the carbon-rhodium bond in **1b** upon irradiation. The radical trap CCl_4 evidently enables the conversion of rhodoxime **1b** to alkyl chlorides **6a** and **7a** by capture of rhodoxime(II) **10** as chlororhodoxime **8** from a photochemical preequilibrium. Due to a more stable Rh–C bond compared to cobalt analogs this equilibrium may be shifted further to the side of the starting rhodoxime **1b**[6a]. Thus, significant photodecomposition of **1b** and presumably other alkylrhodoximes **1** is prevented in the absence of an efficient trap for rhodium radical **10**.

The clean transformation of **1b** to alkyl chlorides **6a** and **7a** was used to estimate the rate constant k_{Cl} of chlorine atom abstraction from CCl_4 by 5-hexenyl radical **9a** generated from **1b**. k_{Cl} was calculated to be $1.1 \cdot 10^4$ l mol^{-1} s^{-1} ($T = 26$ °C). This value matches with the one obtained for free 5-hexenyl radical **9b** ($k_{Cl} = 6.9 \cdot 10^3$ l mol^{-1} s^{-1}) by taking into account experimental uncertainties of ±10%[17].

In order to confirm the *free* radical nature of the intermediates arising from visible-light photolysis of alkylrhodoximes further reactivity and selectivity studies on inter- and intramolecular reactions of **1** were made. Photochemical conversion of 6-hepten-2-ylrhodoxime **1h** in neat tetrachloromethane yields a 2.3:1.0 mixture of open-chain chloride **6b** to cyclopentylmethyl chloride (**7b**)[18]. The *cis:trans* ratio of 1-(chloromethyl)-2-methylcyclopentane (**7b**) is 80:20. This value reflects the stereochemistry of the cyclization of *free* 6-hepten-2-yl radical **9b** to (2-methylcyclopentyl)methyl radical[8].

A useful probe for the stereoselectivity in intermolecular photoreaction of alkylrhodoximes **1** with CCl_4 and $BrCCl_3$ is (4-*tert*-butylcyclohexyl)rhodoxime **1e**. Photochemical conversions of **1e** to secondary halides **4e** and **11** show the same preferential formation of *cis* halides as observed for the *free* 4-*tert*-butylcyclohexyl radical (*cis:trans* = 77:23 for X = Cl and 68:32 for X = Br)[19].



1e *cis* : *trans* = 55 : 45 **4e, 11**

X	*cis*	*trans*
Cl (**11**)	78	22
Br (**4e**)	69	31

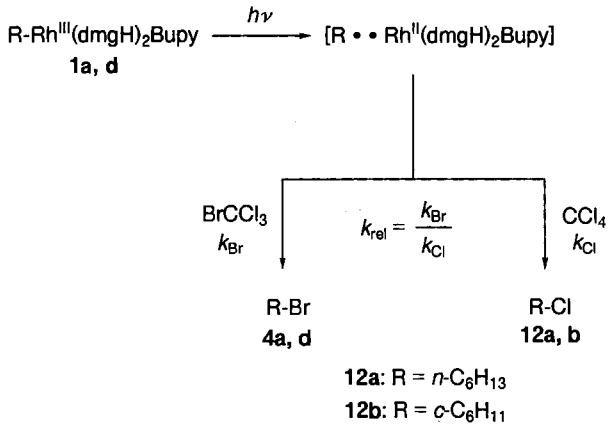
Competition experiments were successfully employed to characterize the *free* radical nature of the reactive intermediates[20]. Thus, a product analysis of the photolyses of *n*-hexylrhodoxime **1a** and cyclohexylrhodoxime **1d** in defined $CCl_4/BrCCl_3$ mixtures at temperatures between 25 and 73 °C yields competition constants k_{rel} and corresponding $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values[21]. The results are given in Table 2. Compared to *free* cyclohexyl radicals, the k_{rel} values and differences in activation parameters match exactly with

Table 2. Relative rate constants for the formation of alkyl bromides **4a, d** versus alkyl chlorides **12a, b** from photoreactions of alkylrhodoximes **1a, d** in $CCl_4/BrCCl_3$

T [°C]	*n*-Hexylrhodoxime **1a**	Cyclohexylrhodoxime **1d**
	k_{rel}	k_{rel}
25	12350	4950
41	8200	3650
51	5850	2700
61	4600	-
71	3600	1600
$\Delta\Delta H^{\neq}$[a]	23 kJ mol^{-1} (12 kJ mol^{-1})	21 kJmol^{-1} (20 kJ mol^{-1})
$\Delta\Delta S^{\neq}$[a]	0 J mol^{-1} K^{-1} (-24 J mol^{-1}K^{-1})	0 J mol^{-1} K^{-1} (-2 J mol^{-1}K^{-1})

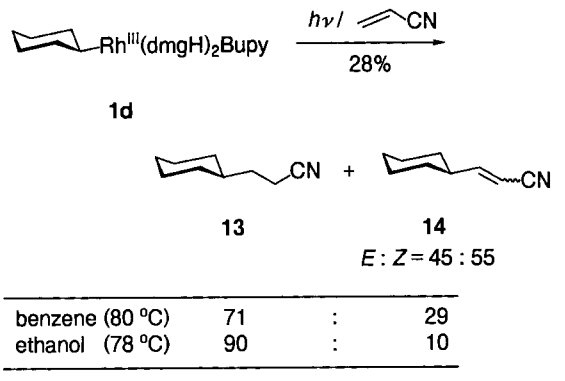
[a] Estimated error: ±10% in $\Delta\Delta H^{\neq}$ and ±20% in $\Delta\Delta S^{\neq}$. Reference data for corresponding *free* alkyl radicals are taken from ref.[21] and given in parentheses.

the photolysis of **1d** in $CCl_4/BrCCl_3$[21]. These data together with the findings from stereochemical experiments lead to the conclusion that the carbon-rhodium bond in secondary alkylrhodoximes **1** is cleaved homolytically in the presence of efficient radical traps to yield *free* alkyl radicals as reactive intermediates.

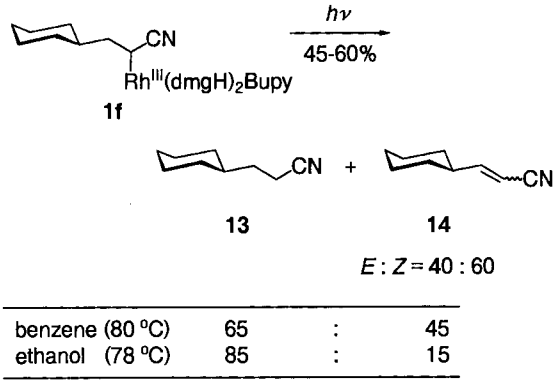


Results from photoreactions of 5-hexenylrhodoxime **1b** in CCl_4 indicate the formation of the *free* 5-hexenyl radical **9a**. However, competition experiments with *n*-hexylrhodoxime **1a** in $CCl_4/BrCCl_3$ show unexpected results which will be the subject of further investigations. k_{rel} values are almost three times as high as those found in free *n*-hexyl radical reactions and differences in $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ values are significant[21–23].

Cyclohexylrhodoxime **1d** can be used in C–C bond forming reactions. Photolysis of **1d** in the presence of acrylonitrile in either benzene or ethanol solvent yields 3-cyclohexylpropanenitrile (**13**) and 3-cyclohexylacrylonitrile (*E*:*Z* mixture) (**14**). Although the process is not very efficient yet and polymerization seems to compare selective 1:1 adduct formation from **1d** and acrylonitrile, it is an interesting reaction from a mechanistic point of view. Unsaturated product **14** arises from photodecomposition of the intermediate rhodoxime **1f** as could be shown by an independent synthesis and photodecomposition of **1f**. The product distribution of unsaturated versus saturated adducts is paralleled by the proton-donating ability of the solvent. Thus, carbanionic cleavage of **1f** and protonation could lead to more saturated product **13**, very similar to the photoreaction of alkylcobaloximes **2** with olefins[2a,b]. *tert*-Butyl radicals can be generated from *tert*-butylrhodoxime **1k**. Until now yields of 1:1 adducts in C–C bond forming reactions are low but work is in progress to optimize these reactions.



benzene (80 °C)	71	:	29
ethanol (78 °C)	90	:	10



benzene (80 °C)	65	:	45
ethanol (78 °C)	85	:	15

Thus, alkylrhodoximes **1** enrich the sources of alkyl radical precursors which could be of interest especially for the generation of tertiary alkyl radicals.

This work was generously supported by the *Volkswagen-Stiftung* and the *Swiss National Science Foundation.*

Experimental

NMR: Bruker WM 300, Bruker AC 300 (TMS as internal standard). – MS: Finnigan MAT. – UV/Vis: Beckman UV 5240 and DK2A. – IR: Perkin Elmer 325. – Gas-liquid chromatography: Carlo Erba GC 6000 (Vega Series). FID connected to Spectra Physics integrator 4290; nitrogen at a flow rate of 3 ml/min (equals 120 kPa pressure) was used as carrier gas; injector and detector temperature 250°C; OV 17/01 and SE 30 capillary column from Macherey & Nagel. – X-ray: Intensity data for crystal structure of **1k** were collected at room temperature by using graphite-monochromated Mo-K_α radiation ($\mu = 6.73$ cm^{-1}) on a Stoe Stadi 4 single-crystal diffractometer. The structures were solved by conventional Patterson and Fourier methods. Anisotropic refinements were obtained by LSQ calculations, difference Fourier synthesis, SHELX 76 and SHELXS 86[30,31]. – Preparative column chromatography: Merck silica gel 60 (0.063–0.200 mm). – Purification of solvents: Benzene was distilled from sodium benzophenone under nitrogen directly before use. *n*-Hexane was refluxed for several hours with calcium hydride, distilled under nitrogen and stored over molecular sieves (4 Å). Tetrachloromethane was refluxed for 4 h with calcium oxide. The center cut of the distillation was collected, refluxed with potassium permangante for 4 h, distilled under nitrogen and stored in dark bottles over molecular sieves (4 Å) for periods not exceeding one week.

The following compounds were prepared according to literature procedures: 6-Hepten-2-yl *p*-toluenesulfonate (**4g**)[24], 6-bromo-1-heptene (**4h**)[24], 4-*tert*-butylcyclohexyl chloride (**11**)[25], 4-*tert*-butylcyclohexyl bromide (**4e**)[26], 1-(bromomethyl)-2-methylcyclopentane (**4c**)[29], 2-bromo-3-cyclohexylpropionitrile (**4f**)[2a], (4-*tert*-butylpyridine)chlororhodoxime **8**[7], 6-chloro-1-hexene (**6a**)[24], (chloromethyl)cyclopentane (**7a**)[27], 6-chloro-1-heptene (**6b**)[24], 1-(chloromethyl)-2-methylcyclopentane (**7b**)[28], 3-cyclohexylacrylonitrile (*E*/*Z* mixture) (**14**)[2a].

1. *Syntheses of Alkyl(4-tert-butylpyridine)rhodoximes* **1**: All alkylrhodoximes **1** containing the axial ligand 4-*tert*-butylpyridine are new compounds. Cyclohexyl(pyridine)rhodoxime has been prepared previously[6a].

trans-Dichloro(dimethylglyoximato)(dimethylglyoxime)rhodium(III) (**3**): A hot solution of 5.31 g (45.6 mmol) of 2,3-butanedione dioxime (dimethylglyoxime) in 50 ml of 95% aqueous hot ethanol is added to a boiling purple suspension of 3.00 g (11.4 mmol) of rhodium(III) chloride trihydrate. The reaction mixture immediately brightens to yellow and is refluxed for 1 min. After cooling to 0°C yellow crystals of **3** are collected on a Buchner funnel and dried to yield 4.00 g (96%) of the desired product which is used for the following reactions without further purification.

Alkyl(4-tert-butylpyridine)rhodoximes **1**: In a typical procedure 2.00 g (4.9 mmol) of **3** is suspended in 300 ml of degassed methanol. The suspension is treated with 50 ml of a 50% aqueous potassium hydroxide solution at room temp. followed by a solution of 0.19 g (5.0 mmol) $NaBH_4$ (Fluka, purum, p.a.-grade) in 5 ml of methanol. An immediate change in the color from yellow to black indicates reduction of the rhodium(III) to the rhodium(I) complex. After 30 min 10.0 mmol of alkyl bromide or tosylate **4** is added at room temp. or at −40°C (neat or dissolved in acetone). After complete decolorization the clear yellow reaction mixture is stirred for 30 min at 25°C, treated with 0.7 ml (4.9 mmol) of 4-*tert*-butylpyridine and stirred for a further 30 min at ambient temp. The solvent is removed in vacuo. The remaining yellow oil is dissolved in 50 ml of chloroform and the solution extracted with water after neutralization with 5% aqueous hydrochloric acid. The organic layer is separated, dried ($MgSO_4$), concentrated in vacuo and the resulting yellow oily product further purified by column chromatography (ethyl acetate, $R_f = 0.4$) to yield alkyl(4-*tert*-butylpyridine)rhodoximes **1** as yellow crystals.

1.1. *Alkylation of Rhodoxime(I) at Ambient Temp.*

(4-tert-Butylpyridine)bis(dimethylglyoximato)-1-hexylrhodium(III) (**1a**): Yield 2.17 g (80%), m.p. 177−178°C. − ^{1}H NMR ($CDCl_3$): δ = 12.45 (s, 2H, OH), 8.31 (dd, J = 1.5/5.0 Hz, 2H, Bupy), 7.25 (dd, J = 1.5/5.0 Hz, 2H, Bupy), 2.15 (s, 12H, CH_3), 1.27 (s, 9H, CH_3), 1.22−0.88 (m, 10H), 0.84−0.81 (m, 3H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 11.85, 14.13, 21.93 (d, $J_{Rh,C}$ = 23.8 Hz), 22.74, 29.70, 30.26, 31.71, 34.87, 122.49, 148.91, 149.04, 161.78. − MS (FD), *m/z*: 554/553 [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 402 nm (971), 318 (7700), 283 (13200), 258 (9610). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 2985, 2930, 2880, 2860, 2500, 2400, 1720, 1660, 1610, 1520, 1495, 1480, 1460, 1420, 1390, 1370, 1360, 1330, 1250, 1165.

$C_{23}H_{40}N_5O_4Rh$ (553.5) Calcd. C 49.91 H 7.28 N 12.65
Found C 49.89 H 7.27 N 12.76

(4-tert-Butylpyridine)bis(dimethylglyoximato)-5-hexenylrhodium(III) (**1b**): Yield 2.35 g (87%), m.p. 173−174°C. − ^{1}H NMR ($CDCl_3$): δ = 12.14 (s, 2H, OH), 8.29 (dd, J = 1.1/5.2 Hz, 2H, Bupy), 7.27 (dd, J = 1.1/5.2 Hz, 2H, Bupy), 5.76 (ddt, J = 7.1/10.5/17.3 Hz, 1H, 5-H), 4.88−4.81 (m, 2H, 6-, 6′-H), 2.15 (s, 12H, CH_3), 1.95 (q, J = 7.1 Hz, 2H, 4-H), 1.32−1.16 (m, 2H), 1.27 (s, 9H, CH_3), 1.16−0.96 (m, 4H). − ^{13}C NMR ($CDCl_3$): δ = 11.67, 21.30 (d, $J_{Rh,C}$ = 22.9 Hz), 29.11, 30.39, 31.00, 33.60, 34.68, 113.61, 121.54, 139.65, 149.12, 149.69, 161.61. − MS (FD), *m/z*: 552/551 [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 401 nm (965), 317 (7820), 282 (13300), 258 (9760). − IR (KBr): $\tilde{\nu}$ = 3100 cm^{-1}, 2990, 2920, 2860, 2490, 2395, 1620, 1515, 1410, 1255.

$C_{23}H_{38}N_5O_4Rh$ (551.5) Calcd. C 50.07 H 6.95 N 12.70
Found C 50.13 H 7.03 N 12.47

(4-tert-Butylpyridine)bis(dimethylglyoximato)[cis- and trans(2-methylcyclopentyl)methyl]rhodium(III) (**1c**): Yield 1.11 g (40%); *cis:trans* ratio 71:29; m.p. of this mixture 185−189°C. − MS (FD), *m/z*: 566/565 [M^+].

$C_{24}H_{40}N_5O_4Rh$ (565.5) Calcd. C 50.97 H 7.13 N 12.38
Found C 50.99 H 7.14 N 12.25

(4-tert-Butylpyridine)bis(dimethylglyoximato)[cis-(2-methylcyclopentyl)methyl]rhodium(III): ^{1}H NMR ($CDCl_3$): δ = 11.84 (s, 2H, OH), 8.30 (dd, J = 1.3/5.2 Hz, 2H, Bupy), 7.26 (dd, J = 1.3/5.2 Hz, 2H, Bupy), 2.14 (s, 12H, CH_3), 1.80−0.82 (m, 10H), 1.26 (s, 9H, CH_3), 0.62 (d, J = 7.0 Hz, 3H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 11.87, 14.58, 22.34, 22.59 (d, $J_{Rh,C}$ = 23.5 Hz), 30.25, 32.00, 33.77, 34.84, 37.96, 44.11, 122.50, 148.85, 149.15, 161.72.

(4-tert-Butylpyridine)bis(dimethylglyoximato)[trans-(2-methylcyclopentyl)methyl]rhodium(III): ^{1}H NMR ($CDCl_3$): δ = 11.84 (s, 2H, OH), 8.30 (dd, J = 1.3/5.2 Hz, 2H, Bupy), 7.26 (dd, J = 1.3/5.2 Hz, 2H, Bupy), 2.14 (s, 12H, CH_3), 1.80−0.82 (m, 10H), 1.26 (s, 9H, CH_3), 0.78 (d, J = 6.4 Hz, 3H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 11.87, 18.88, 24.08, 27.88 (d, $J_{Rh,C}$ = 23.4 Hz), 30.25, 34.54, 34.64, 34.84, 43.36, 48.51, 122.50, 148.85, 149.15, 161.72.

(4-tert-Butylpyridine)cyclohexylbis(dimethylglyoximato)rhodium(III) (**1d**): Yield 2.00 g (74%), m.p. 230−235°C (dec). − ^{1}H NMR ($CDCl_3$): δ = 12.75 (s, 2H, OH), 8.27 (dd, J = 1.5/5.1 Hz, 2H, Bupy), 7.24 (dd, J = 1.5/5.1 Hz, 2H, Bupy), 2.16 (s, 12H, CH_3), 1.90−1.80 (m, 2H, 2-H_{eq}), 1.59−1.45 (m, 3H, 3-H_{eq}, 4-H_{eq}), 1.33 (tq, J = 3.0/11.7 Hz, 1H, 1-H_{ax}), 1.26 (s, 9H, CH_3), 1.21−0.86 (m, 5H). − ^{13}C NMR ($CDCl_3$): δ = 11.97, 27.27, 29.58, 30.24, 34.62, 35.77, 40.33 (d, $J_{Rh,C}$ = 23.2 Hz), 122.41, 148.76, 149.00, 161.58. − MS (FD), *m/z*: 552/551 [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 407 nm (920), 319 (7670), 284 (13400). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3050, 2920, 2860, 2490, 1610, 1510, 1410, 1250, 1130.

$C_{23}H_{38}N_5O_4Rh$ (551.5) Calcd. C 50.07 H 6.95 N 12.70
Found C 50.05 H 6.93 N 12.70

(4-tert-Butylpyridine)bis(dimethylglyoximato)-6-heptenylrhodium(III) (**1g**): Yield 0.86 g (31%), m.p. 145−146°C. − ^{1}H NMR ($CDCl_3$): δ = 12.95 (s, 2H, OH), 8.30 (dd, J = 1.5/5.1 Hz, 2H, Bupy), 7.26 (dd, J = 1.5/5.1 Hz, 2H, Bupy), 5.76 (ddt, J = 6.7/10.2/17.0 Hz, 1H, 6-H), 4.96−4.80 (m, 2H, 7-, 7′-H), 2.15 (s, 12H, CH_3), 1.93 (q, J = 6.8 Hz, 2H, 5-H), 1.27 (s, 9H, CH_3), 1.24−0.99 (m, 8H). − ^{13}C NMR ($CDCl_3$): δ = 11.87, 21.64 (d, $J_{Rh,C}$ = 22.9 Hz), 28.67, 29.50, 30.23, 31.54, 33.90, 34.86, 113.80, 122.51, 139.47, 148.85, 149.06, 161.77. − MS (FD), *m/z*: 566/565 [M^+]. − UV/Vis (CH_2Cl_2): λ_{max} (ε) = 402 nm (1002), 317 (7980), 282 (13500). − IR (KBr): $\tilde{\nu}$ = 3080 cm^{-1}, 3060, 2960, 2930, 2860, 2820, 2460, 2370, 1960, 1630, 1610, 1530, 1500, 1470, 1460, 1440, 1420, 1380, 1370, 1330, 1250.

$RhC_{24}H_{40}N_5O_4$ (565.5) Calcd. C 50.97 H 7.13 N 12.38
Found C 50.85 H 7.07 N 12.31

(4-tert-Butylpyridine)bis(dimethylglyoximato)(2-methylpropyl)-rhodium(III) (**1j**): Yield 1.57 g (61%), m.p. 223−225°C (dec.). − ^{1}H NMR ($CDCl_3$): δ = 12.96 (s, 2H, OH), 8.31 (dd, J = 1.5/5.1 Hz, 2H, Bupy), 7.26 (dd, J = 1.5/5.1 Hz, 2H, Bupy), 2.15 (s, 12H, CH_3), 1.27 (s, 9H, CH_3), 1.09−1.23 (m, 3H, 1-, 2-H), 0.75 (d, J = 6.2 Hz, 6H, CH_3). − ^{13}C NMR ($CDCl_3$): δ = 11.86, 25.50, 28.59, 30.25, 31.83 (d, $J_{Rh,C}$ = 23.5 Hz), 34.84, 122.50, 148.80, 149.14, 161.75. − MS (FD), *m/z*: 526/525 [M^+]. − IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2960, 2480, 2390, 1610, 1520, 1420, 1250, 1120.

$C_{21}H_{36}N_5O_4Rh$ (525.5) Calcd. C 48.00 H 6.91 N 13.33
Found C 47.94 H 7.04 N 13.09

1.2. *Alkylation of Rhodoxime(I) at −40°C*

(cis- and trans-4-tert-Butylcyclohexyl)(4-tert-butylpyridine)bis-(dimethylglyoximato)rhodium(III) (**1e**): Yield 1.52 g (51%); *cis:trans* ratio 56:44. − MS (FD), *m/z*: 608/607 [M^+].

$C_{27}H_{46}N_5O_4Rh$ (607.6) Calcd. C 53.37 H 7.63 N 11.53
Found C 53.34 H 7.38 N 11.47

(cis-4-tert-Butylcyclohexyl)(4-tert-butylpyridine)bis(dimethylglyoximato)rhodium(III): ^{1}H NMR ($CDCl_3$): δ = 12.50 (s, 2H, OH),

8.28 (m, 2H, Bupy), 7.24 (m, 2H), 2.13 (s, 12H, CH_3), 1.26 (s, 9H, CH_3), 1.97–0.70 (m, 10H), 0.76 (s, 9H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.96, 25.54, 27.82, 30.25, 32.66, 34.02, 34.82, 35.11 (d, $J_{Rh,C}$ = 23.2 Hz), 47.22, 122.42, 148.54, 149.58, 161.59.

(trans-4-tert-Butylcyclohexyl)(4-tert-butylpyridine)bis(dimethylglyoximato)rhodium(III): ^1H NMR ($CDCl_3$): δ = 12.50 (s, 2H, OH), 8.28 (m, 2H, Bupy), 7.24 (m, 2H), 2.15 (s, 12H, CH_3), 1.26 (s, 9H, CH_3), 1.97–0.70 (m, 10H), 0.75 (s, 9H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.96, 27.54, 30.08, 30.25, 32.24, 34.82, 35.75, 40.05 (d, $J_{Rh,C}$ = 23.8 Hz), 48.42, 122.42, 148.79, 149.14, 161.59.

(4-tert-Butylpyridine)(1-cyano-2-cyclohexylethyl)bis(dimethylglyoximato)rhodium(III) (**1f**): Yield 0.92 g (31%), m.p. 228–229°C (dec). – ^1H NMR ($CDCl_3$): δ = 12.98 (s, 2H, OH), 8.32 (dd, J = 1.4/5.3 Hz, 2H, Bupy), 7.31 (dd, J = 1.4/5.3 Hz, 2H, Bupy), 2.22 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 1.29 (s, 9H, CH_3), 2.08–0.47 (m, 14H). – ^{13}C NMR ($CDCl_3$): δ = 5.14 (d, $J_{Rh,C}$ = 25.9 Hz), 12.34, 12.52, 25.84, 26.16, 26.62, 30.18, 31.44, 34.30, 35.02, 37.05, 38.03, 123.04, 127.04, 149.10, 150.46, 151.10, 162.84. – MS (FD), *m/z*: 605/604 [M^+]. – IR (KBr): $\tilde{\nu}$ = 3095 cm^{-1}, 2925, 2490, 2380, 2200, 1610.

$C_{26}H_{41}N_6O_4Rh$ (604.6) Calcd. C 51.66 H 6.84 N 13.90
Found C 51.49 H 6.88 N 13.65

(4-tert-Butylpyridine)bis(dimethylglyoximato)-6-hepten-2-ylrhodium(III) (**1h**): Yield 0.61 g (22%). – ^1H NMR ($CDCl_3$): δ = 12.25 (s, 2H, OH), 8.29 (dd, J = 1.5/4.9 Hz, 2H, Bupy), 7.24 (dd, J = 1.5/4.9 Hz, 2H, Bupy), 5.77 (ddt, J = 6.8/10.1/17.1 Hz, 1H, 6-H), 4.96–4.84 (m, 2H, 7-, 7'-H), 2.14 (s, 12H, CH_3), 2.02–1.82 (m, 2H, 5-H), 1.72–1.64 (m, 1H, 2-H), 1.64–0.90 (m, 4H), 1.26 (s, 9H, CH_3), 0.76 (d, J = 6.7 Hz, 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.90, 21.19, 27.77, 30.27, 33.22 (d, $J_{Rh,C}$ = 24.2 Hz), 33.77, 34.84, 37.67, 113.55, 122.44, 139.77, 149.15, 149.16, 161.62. – MS (FD), *m/z*: 566/565 [M^+].

$C_{24}H_{40}N_5O_4Rh$ (565.5) Calcd. C 50.97 H 7.13 N 12.38
Found C 50.89 H 7.22 N 12.32

(4-tert-Butylpyridine)[(2,2-dimethylcyclopentyl)methyl]bis(dimethylglyoximato)rhodium(III) (**1i**): Yield 0.28 g (10%), m.p. 222–225°C (dec.). – ^1H NMR ($CDCl_3$): δ = 12.80 (s, 2H, OH), 8.30 (dd, J = 1.3/5.1 Hz, 2H, Bupy), 7.25 (dd, J = 1.3/5.1 Hz, 2H, Bupy), 2.14 (s, 6H, CH_3), 2.13 (s, 6H, CH_3), 1.81–1.65 (m, 1H), 1.55–1.32 (m, 4H), 1.27 (s, 9H, CH_3), 1.09–0.78 (m, 4H), 0.72 (s, 3H, 8-CH_3), 0.59 (s, 3H, 7-CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.67, 20.52, 21.36, 22.73 (d, $J_{Rh,C}$ = 23.0 Hz), 27.37, 30.28, 32.56, 34.87, 41.62, 42.20, 49.84, 122.49, 148.92, 149.20, 161.75. – MS (FD), *m/z*: 580/579 [M^+]. – IR (KBr): $\tilde{\nu}$ = 2960 cm^{-1}, 2920, 2870, 2480, 2390, 1730, 1605, 1525, 1470, 1460, 1420, 1380, 1360, 1325, 1250.

$C_{25}H_{42}N_5O_4Rh$ (579.5) Calcd. C 51.81 H 7.31 N 12.08
Found C 51.49 H 7.37 N 11.67

tert-Butyl(4-tert-butylpyridine)bis(dimethylglyoximato)rhodium(III) (**1k**): Yield 1.62 g (63%), m.p. 221–222°C (dec). – ^1H NMR ($CDCl_3$): δ = 13.11 (s, 2H, OH), 8.27 (dd, J = 1.5/5.0 Hz, 2H, Bupy), 7.22 (dd, J = 1.5/5.0 Hz, 2H, Bupy), 2.11 (s, 12H, CH_3), 1.26 (s, 9H, CH_3), 0.64 (s, 9H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 11.82, 30.18, 31.88 (d, $J_{Rh,C}$ = 24.8 Hz), 33.54, 34.74, 122.29, 148.53, 149.44, 161.56. – MS (FD), *m/z*: 526/525 [M^+]. – IR (KBr): $\tilde{\nu}$ = 3040 cm^{-1}, 2965, 2840, 2480, 2390, 1605, 1520, 1420, 1250, 1140.

$C_{21}H_{36}N_5O_4Rh$ (525.5) Calcd. C 48.00 H 6.91 N 13.33
Found C 47.93 H 6.84 N 13.34

Table 3. Crystallographic data and data-collection details of **1k**[31]

Formula $C_{21}H_{36}N_5O_4Rh$ (yellow plates); mol. mass 525.46; crystal size 0.70 × 0.50 × 0.55 mm; space group $P\bar{1}$; Z = 2; a = 12.185(5), b = 11.401(5), c = 9.530(4) Å; α = 85.05(1), β = 72.47(1), γ = 87.94(1)°; V = 1257.66 · 10^{-30} m^3; ϱ_{calcd} = 1.387 g · cm^{-3}; μ = 6.73 cm^{-1}; radiation: Mo-K_α = 0.71069 Å; temperature 296 K; no of measured reflections 4612; no. of unique reflections ($R_{int.}$ = 0.012) 3282; no. of indep. reflections $F > 2\sigma(F)$ 3121; $F(000)$ = 548; refined parameters 318; R = 0.30; R_w = 0.035

Table 4. Atomic positional parameters and equivalent isotropic thermal displacement parameters U(EQ) for *tert*-butylrhodoxime **1k**. U(EQ) is defined as one third of the orthogonized U_{ij} tensor

Atom	X/A	Y/B	Z/C	U(EQ)
Rh(1)	0.17752(2)	0.26746(2)	0.15105(2)	0.043(0)
N(1)	0.1903(2)	0.0929(2)	0.1670(3)	0.053(2)
C(2)	0.1785(3)	0.0390(3)	0.0577(5)	0.064(2)
C(3)	0.1592(3)	0.1201(3)	-0.0630(4)	0.062(2)
N(4)	0.1573(2)	0.2286(2)	-0.0375(3)	0.054(2)
N(5)	0.1548(3)	0.4415(2)	0.1417(3)	0.054(2)
C(6)	0.1522(4)	0.4928(3)	0.2599(5)	0.067(2)
C(7)	0.1735(3)	0.4105(3)	0.3787(4)	0.067(2)
N(8)	0.1892(3)	0.3041(2)	0.3445(3)	0.057(2)
O(9)	0.2063(2)	0.0360(2)	0.2860(3)	0.068(2)
O(10)	0.1325(3)	0.3134(2)	-0.1363(3)	0.071(2)
O(11)	0.1351(2)	0.4986(2)	0.0270(3)	0.070(2)
O(12)	0.2101(3)	0.2175(2)	0.4443(3)	0.075(2)
C(13)	0.1897(5)	-0.0903(4)	0.0531(6)	0.098(4)
C(14)	0.1404(5)	0.0803(5)	-0.1996(5)	0.096(3)
C(15)	0.1340(5)	0.6210(4)	0.2709(7)	0.102(4)
C(16)	0.1792(5)	0.4494(5)	0.5222(5)	0.101(4)
N(17)	-0.0114(2)	0.2495(2)	0.2555(3)	0.045(1)
C(18)	-0.0555(3)	0.1811(3)	0.3792(3)	0.049(1)
C(19)	-0.1726(3)	0.1698(3)	0.4484(4)	0.054(2)
C(20)	-0.2499(3)	0.2307(3)	0.3886(3)	0.049(2)
C(21)	-0.2027(3)	0.3013(3)	0.2574(4)	0.057(2)
C(22)	-0.0855(3)	0.3077(3)	0.1964(3)	0.050(2)
C(23)	-0.3812(3)	0.2189(4)	0.4556(5)	0.067(2)
C(24)	-0.4273(4)	0.1497(5)	0.3564(6)	0.105(4)
C(25)	-0.4123(4)	0.1541(6)	0.6096(6)	0.106(3)
C(26)	-0.4399(4)	0.3404(4)	0.4667(6)	0.092(3)
C(27)	0.3604(3)	0.2903(4)	0.0478(4)	0.067(2)
C(28)	0.3817(4)	0.3587(5)	-0.1028(5)	0.088(3)
C(29)	0.4129(4)	0.3585(5)	0.1399(6)	0.096(3)
C(30)	0.4225(4)	0.1721(4)	0.0265(6)	0.087(3)

2. *Photoreactions of Alkylrhodoximes* **1** *in the Presence of Radical Traps*

2.1. *Visible-Light Photolysis of Alkyl Rhodoximes* **1** *in the CCl_4/$BrCCl_3$ Competition System:* 0.2 mmol of alkylrhodoxime **1** and 2–4 mmol of $BrCCl_3$ are dissolved in about 7 mol of degassed CCl_4, and the solution is photolyzed under argon for 15 h at temperatures between 27 and 73°C (incandescent light: Osram Concentra®, R 95 Natura, 300 W PAR 56). Rhodium complexes **1** and **8** are removed by adsorptive filtration on a short silica gel column. Alkyl halides are eluted with 50 ml of *n*-hexane, and the clear, colorless eluate obtained is subjected to GC analysis using a SE 30 column (T = 50°C for hexyl halides or 60°C for cyclohexyl halides). Results at highest and lowest reaction temperatures are checked by three independent runs. Competition constants are calculated from the ratio of alkyl chloride to alkyl bromide according to ref.[21] Isolate yields: 1-chlorohexane (**12a**) 72%, 1-bromohexane (**4a**) 78%, chlorocyclohexane (**12b**) 76%, bromocyclohexane (**4d**) 84%.

2.2. *Photolysis of 5-Hexenylrhodoxime* **1b** *in Tetrachloromethane:* Solutions of 0.2 mmol of **1b** in about 200 ml of degassed anhydrous solvent (either neat CCl_4 or definite CCl_4/benzene mixtures) containing 0.4 mmol of triphenylmethane are photolyzed at 26°C for

48 h, then worked up and analyzed by GC ($T = 65°C$, OV 17/01 column) as mentioned above. Total yield of alkyl chlorides **6a** and **7a**: 21%, chlororhodoxime **8** is detected by TLC.

2.3. *Irradiation of 6-Hepten-2-ylrhodoxime* **1h** *in* CCl_4: 0.2 mmol of **1h** is dissolved in 25 ml of CCl_4 and converted by visible-light photolysis at 15°C to 6-chloro-1-heptene (**6b**) and 1-(chloromethyl)-2-methylcyclopentane (**7b**) (*cis*:*trans* = 80:20). Product analysis is performed on the rhodium-free reaction mixture by GC ($T = 65°C$, OV 17/01 column).

2.4. *Photolysis of (4-tert-Butylcyclohexyl)rhodoxime* **1e** *in the Presence of* CCl_4 *or* $BrCCl_3$: A solution of 0.2 mmol of **1e** in 25 ml of anhydrous solvent (either neat CCl_4 or 2.0 mmol of $BrCCl_3$ dissolved in benzene) is irradiated for 5 h at 15°C. The rhodium-free reaction mixture is subjected to GC analysis [$T = 100°C$ for 4-*tert*-butylcyclohexyl chlorides (**11**) and 110°C for 4-*tert*-butylcyclohexyl bromides (**4e**), OV 17/01 column].

2.5. *Photolysis of Cyclohexylrhodoxime* **1d** *in the Presence of Acrylonitrile*: 0.2 mmol of **1d**, 20.0 mmol of acrylonitrile, and 0.05 mmol nonadecane are dissolved in 10 ml of oxygen-free solvent (either benzene or 95% aqueous ethanol), and the mixture is photolyzed (Osram Power Star HQI/D discharge lamp, visible light) for 48 h at 15°C. The progress of the reaction is monitored by GC [nonadecane as internal standard, SE 30, $T = 80°C$ (5 min), 10°C/min → 150°C, 20°C/min → 250°C]. After complete consumption of **1d** the solvent is removed in vacuo. Diethyl ether (40 ml) is added to the residue and all soluble products are extracted by stirring the mixture at room temp. for 30 min. The reaction mixture is dried (Na_2SO_4), concentrated in vacuo and the residure subjected to either NMR or GC-MS analysis. Yields: (A) photolysis in benzene: 3-cyclohexylpropionitrile (**13**) 20%, (*E*)-3-cyclohexylacrylonitrile (**14**) 5%, (*Z*)-3-cyclohexylacrylonitrile (**14**) 4%. (B) photolysis in ethanol: **13** 34%, (*E*)-3-cyclohexylacrylonitrile (**14**) 3%, (*Z*)-3-cyclohexylacrylonitrile (**14**) 2%.

Likewise, photodecomposition products from (4-*tert*-butylpyridine)(1-cyano-2-cyclohexylethyl)bis(dimethylglyoximato)-rhodium(III) (**1f**) are isolated and analyzed. Yields: (A) photolysis in benzene: **13** 39%, (*E*)-3-cyclohexylacrylonitrile (**14**) 12%, (*Z*)-3-cyclohexylacrylonitrile (**14**) 8%. (B) photolysis in ethanol: **13** 38%, (*E*)-3-cyclohexylacrylonitrile (**14**) 4%, (*Z*)-3-cyclohexylacrylonitrile (**14**) 3%.

☆ Dedicated to Professor Dr. *Klaus Hafner* on the occasion of his 65th birthday.

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$$k_{rel} = \frac{k_{Br}}{k_{Cl}} = \frac{[R{-}Br][CCl_4]}{[R{-}Cl][BrCCl_3]}; \quad (1)$$

$$\ln k_{rel} = \frac{\Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}}{RT} - \frac{\Delta S^{\ddagger}_{Cl} - \Delta S^{\ddagger}_{Br}}{R} \quad (2)$$

$$\Delta\Delta H^{\ddagger} = \Delta H^{\ddagger}_{Cl} - \Delta H^{\ddagger}_{Br}; \qquad \Delta\Delta S^{\ddagger} = \Delta S^{\ddagger}_{Cl} - \Delta S^{\ddagger}_{Br}.$$

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[23] *n*-Hexyl radical: $\Delta\Delta H^{\ddagger} = 12$ kJ mol^{-1}, $\Delta\Delta S^{\ddagger} = -24$ J mol^{-1} K^{-1}; errors are estimated to be $\pm 10\%$ in $\Delta\Delta H^{\ddagger}$ and ± 5 J mol^{-1} K^{-1} in $\Delta\Delta S^{\ddagger}$ [21].

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[436/92]