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LIGAND EFFECTS ON OXIDATIVE ADDITION REACTIONS OF d^8 METAL COMPLEXES. PREPARATION AND OXIDATIVE ADDITION REACTIONS OF COMPLEXES OF THE TYPE *trans*-[Rh(CO)L_2Cl] (L = S$(C_2H_5)_2$, Se$(C_2H_5)_2$, Te$(C_2H_5)_2$)

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SUMMARY

The preparation and properties of the new complexes *trans*-[Rh(CO)L_2Cl], where L = S$(C_2H_5)_2$, Se$(C_2H_5)_2$, Te$(C_2H_5)_2$ are described. These halocarbonylrhodium(I) derivatives very readily undergo oxidative addition. The reactions of these new compounds with Cl_2, Br_2, I_2, HCl, CH_3I, $C_6H_5SO_2Cl$ are described, and their behaviour is compared with that of the analogous compounds containing ligands with Group V donor elements.

The complexes [Rh(CO)$(CH_3)L_2$ClI] have been shown to undergo CO insertion into the Rh–CH_3 bond.

The versatility of the new complexes for various oxidative additions is attributed to a balance of σ and π factors, the former being dominant in the case of the ligands considered.

INTRODUCTION

Studies of four-coordinate d^8 complexes indicate that the tendency to undergo oxidative addition depends markedly upon the nature of the central metal ion as well as upon the nature of the ligands[1]. Additions to Ir^I complexes generally occur more readily than those to analogous Rh^I complexes, because of the difference in promotional energies for $M^I \rightarrow M^{III}$, but there is little information in the literature on the effects of the ligands on these reactions. We now describe the preparation of new compounds of the type *trans*-[Rh(CO)L_2Cl], where L is a ligand containing Group VI element as donor, and their reactions with covalent molecules.

EXPERIMENTAL

μ-Dichlorobis[dicarbonylrhodium(I)] was prepared as previously described[2]. All other chemicals were reagent grade materials. Infrared spectra were recorded on a Perkin–Elmer model 457 spectrometer. Operations involving free diethyl selenide or diethyl telluride were carried out under nitrogen. All reactions were followed by IR spectroscopy. Elemental analyses were by Alfred Bernhardt, Microanalytisches Laboratorium, Mülheim, Germany.

trans-Chlorocarbonylbis(diethyl sulphide)rhodium(I), $\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$

An excess of diethyl sulphide was added to a solution of $[Rh(CO)_2Cl]_2$ in pentane. The reaction mixture was refluxed for 6 h, and the resulting solution filtered, concentrated to a small volume and cooled to −80°. The yellow product, which separated, was crystallized at −80° from methylene chloride/pentane. This compound is liquid at room temperature.

trans-Chlorocarbonylbis(diethyl selenide)rhodium(I), $\{Rh(CO)[Se(C_2H_5)_2]_2Cl\}$

$[Rh(CO)_2Cl]_2$ in pentane was similarly treated with $Se(C_2H_5)_2$. Working up as above, *trans*-$\{Rh(CO)[Se(C_2H_5)_2]_2Cl\}$ is formed as a yellow liquid.

trans-Chlorocarbonylbis(diethyl telluride)rhodium(I), $\{Rh(CO)[Te(C_2H_5)_2]_2Cl\}$

Diethyl telluride in excess was added to $[Rh(CO)_2Cl]_2$ in pentane. After 2 h at room temperature, the solution was filtered and concentrated to a small volume. Cooling to −80° gave yellow-brown crystals, which were filtered off, and washed with pentane; m.p. 30°. (Found: C, 19.90; H, 3.69; Cl, 6.22. $C_9H_{20}ClORhTe_2$ calcd.: C, 20.1; H, 3.74; Cl, 6.60%.)

Addition of halogen to trans-$[Rh(CO)L_2Cl]$ *complexes*

Addition of chlorine. A solution in pentane of *trans*-$\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$ was added with vigorous stirring to a saturated solution of chlorine in pentane. After 5 min the resulting orange solution was concentrated to a small volume on a rotary evaporator. On cooling, *trans*-$\{Rh(CO)[S(C_2H_5)_2]_2Cl_3\}$ was precipitated as orange crystals, which were filtered off and washed several times with pentane: m.p. 76–78°. (Found: C, 25.91; H, 4.65; Cl, 25.8; S, 15.7. $C_9H_{20}Cl_3ORhS_2$ calcd.: C, 25.8; H, 4.81; Cl, 25.4; S, 15.3%.)

The yellow-orange solids $\{Rh(CO)[Se(C_2H_5)_2]_2Cl_3\}$ m.p. 51° decomp. (Found: C, 20.97; H, 4.04; Cl, 20.32. $C_9H_{20}Cl_3ORhSe_2$ calcd.: C, 21.13; H, 3.95; Cl, 20.82%.), and $\{Rh(CO)[Te(C_2H_5)_2]_2Cl_3\}$, decomp. 64–75° (Found: C, 18.03; H, 3.51; Cl, 17.3. $C_9H_{20}Cl_3ORhTe_2$ calcd.: C, 17.7; H, 3.30; Cl, 17.41%.) were similarly obtained on treating *trans*-$[Rh(CO)L_2Cl]$ $[L=Se(C_2H_5)_2$ or $Te(C_2H_5)_2]$ with chlorine in pentane.

Addition of bromine. *trans*-$\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$ in pentane was slowly treated, with vigorous stirring, with a solution of bromine in pentane. After 10 min the solution was concentrated; the yellow-orange solid was filtered off and washed several times with pentane; m.p. 103–105°. (Found: C, 21.59; H, 3.91; S, 12.8. $C_9H_{20}Br_2ClORhS_2$ calcd.: C, 21.34; H, 3.98; S, 12.6%.)

$\{Rh(CO)[Se(C_2H_5)_2]_2ClBr_2\}$, m.p. 82–84°, was similarly obtained as an orange solid by treating *trans*-$\{Rh(CO)[Se(C_2H_5)_2]_2Cl\}$ in pentane with bromine in the same solvent. (Found: C, 18.11; H, 3.35; Br, 26.58; Cl, 5.94. $C_9H_{20}Br_2ClORhSe_2$ calcd.: C, 18.00; H, 3.36; Br, 26.62; Cl, 5.90%.)

Bromine in pentane was added to *trans*-$\{Rh(CO)[Te(C_2H_5)_2]_2Cl\}$ in the same solvent. After evaporation, a red-brown oil was obtained, which was extracted with CCl_4. Pentane was added to the CCl_4 extract to give $\{Rh(CO)[Te(C_2H_5)_2]_2ClBr_2\}$ as yellow solid, decomp. >30°. (Found: C, 15.8; H, 2.99. $C_9H_{20}Br_2ClORhTe_2$ calcd.: C, 15.5; H, 2.99%.)

Addition of iodine. To *trans*-$\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$ in methylene chloride, iodine in pentane was added dropwise with vigorous stirring. After about 15 min, the red-brown solution was concentrated to a small volume. Addition of pentane gave the red-brown $\{Rh(CO)[S(C_2H_5)_2]_2ClI_2\}$, which was filtered off, washed with pentane and dried at 45° *in vacuo*, m.p. 96–98°. (Found: C, 18.26; H, 3.18; S, 10.71. $C_9H_{20}ClI_2ORhS_2$ calcd.; C, 18.01; H, 3.35; S, 10.68%.)

The red-brown $\{Rh(CO)[Se(C_2H_5)_2]_2ClI_2\}$, m.p. 89–92° (Found: C, 15.05; H, 2.87. $C_9H_{20}ClI_2ORhSe_2$ calcd.: C, 15.57; H, 2.88%.) and $\{Rh(CO)[Te(C_2H_5)_2]_2ClI_2\}$, m.p. 62–65°. (Found: C, 12.44; H, 2.46; I, 32.42. $C_9H_{20}ClI_2ORhTe_2$ calcd.: C, 12.32; H, 2.58; I, 32.55%.) were similarly obtained by adding iodine in pentane to a solution of *trans*-$[Rh(CO)L_2Cl]$ $[L=Se(C_2H_5)_2$ or $Te(C_2H_5)_2]$ in methylene chloride.

Action of dry hydrogen chloride on trans-$[Rh(CO)L_2Cl]$ complexes

When dry hydrogen chloride was bubbled through a solution of *trans*-$[Rh(CO)L_2Cl]$ in pentane, a yellow-orange precipitate slowly formed. This was filtered off and washed with pentane and shown to be the corresponding *trans*-$[Rh(CO)L_2Cl_3]$ complex, which has been previously described.

Reactions of trans-$[Rh(CO)L_2Cl]$ complexes with methyl iodide

A mixture of *trans*-$\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$ and methyl iodide (2 ml) was allowed to stand for about 10 min under nitrogen. The resulting red-brown solution was concentrated on a rotary evaporator and pentane was added. The red-brown oil obtained by evaporating to dryness the solution was washed with diethyl ether. The ethereal solution was concentrated and cooled to give $\{Rh(CH_3)(CO)[S(C_2H_5)_2]_2ClI\}$ as a red-brown solid, decomp. >41°. (Found: C, 20.81; H, 4.67; S, 13.08. $C_{10}H_{23}ClIORhS_2$ calcd.: C, 20.63; H, 4.74; S, 13.12%.)

$\{Rh(CH_3)(CO)[Se(C_2H_5)_2]_2ClI\}$, m.p. 63–70° decomp. (Found: C, 20.98; H, 3.91; Cl, 6.10; I, 21.01. $C_{10}H_{23}ClIORhSe_2$ calcd.: C, 20.65; H, 3.81; Cl, 6.10; I, 21.82%.) and $\{Rh(CH_3)(CO)[Te(C_2H_5)_2]_2ClI\}$, decomp. 71–78° (Found: C, 17.85; H, 3.55; I, 18.79. $C_{10}H_{23}ClIORhTe_2$ calcd.: C, 17.67; H, 3.41; I, 18.67%.) were similarly obtained as red-brown crystals from the *trans*-$[Rh(CO)L_2Cl]$ $[L=Se(C_2H_5)_2$ or $Te(C_2H_5)_2]$.

Action of carbon monoxide on $[Rh(CH_3)(CO)L_2ClI]$ complexes

Carbon monoxide was bubbled through a solution of $\{Rh(CO)(CH_3)[S(C_2H_5)_2]_2ClI\}$ in methylene chloride for about 15 min. The solution was evaporated to dryness and the crude product was crystallized from diethyl ether as red-brown powder, m.p. 61–63° decomp. (Found: C, 25.37; H, 4.42; S, 12.31. $C_{11}H_{23}ClIO_2RhS_2$ calcd.: C, 25.57; H, 4.48; S, 12.41%.)

$\{Rh(CO)(CH_3CO)[Se(C_2H_5)_2]_2ClI\}$, decomp. >38° was similarly obtained from $\{Rh(CO)(CH_3)[Se(C_2H_5)_2]_2ClI\}$ (Found: C, 21.24; H, 3.65. $C_{11}H_{23}ClIO_2RhSe_2$ calcd.: C, 21.64; H, 3.79%.)

The same procedure with $\{Rh(CO)(CH_3)[Te(C_2H_5)_2]_2ClI\}$ gave a red-brown oil, which could not be crystallized.

Reactions of trans-$[Rh(CO)L_2Cl]$ complexes with benzenesulphonyl chloride

trans-$\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$ in pentane was treated dropwise under nitrogen with benzene sulphonylchloride in the same solvent. A yellow precipitate was slowly formed and after 9 h it was filtered off and washed several times with pentane; m.p. 119–120°. (Found: C, 34.21; H, 4.66; Cl, 13.11. $C_{15}H_{25}Cl_2O_3RhS_3$ calcd.: C, 34.42; H, 4.81; Cl, 13.54%.)

The yellow solids $\{Rh(CO)(C_6H_5SO_2)[Se(C_2H_5)_2]_2Cl_2\}$, m.p. 103–106° decomp. (Found: C, 28.89; H, 4.38; Cl, 10.98. $C_{15}H_{25}Cl_2O_3RhSSe_2$ calcd.: C, 29.19; H, 4.08; Cl, 11.49%.) and $\{Rh(CO)(C_6H_5SO_2)[Te(C_2H_5)_2]_2Cl_2\}$, decomp. >71° (found: C, 25.03; H, 3.39; Cl, 9.73. $C_{15}H_{25}Cl_2O_3RhSTe_2$ calcd.: C, 25.21; H, 3.52; Cl, 9.92%) were similarly obtained from *trans*-$[Rh(CO)L_2Cl]$ $[L=Se(C_2H_5)_2, Te(C_2H_5)_2]$ but with a reaction time of only 2 h.

Action of molecular hydrogen on trans-$[Rh(CO)L_2Cl]$ *complexes*

Attempts to activate molecular hydrogen by *trans*-$[Rh(CO)L_2Cl]$ complexes were unsuccessful.

RESULTS AND DISCUSSION

The halogen bridges in μ-dichlorobis[dicarbonylrhodium(I)], $[Rh(CO)_2Cl]_2$, are split by $S(C_2H_5)_2$, $Se(C_2H_5)_2$ and $Te(C_2H_5)_2$ to give mononuclear complexes of the type *trans*-$[Rh(CO)L_2Cl]$.

When a small excess of the ligand was added to a solution of $[Rh(CO)_2Cl]_2$ in pentane, the IR spectrum indicated the rapid disappearance of the $[Rh(CO)_2Cl]_2$ carbonyl stretching band and the formation of two equally intense strong terminal carbonyl stretching bands in the range 2005–2090 cm^{-1}; analogous bands were observed on treating $[Rh(CO)_2Cl]_2$ with $P(C_6H_5)_3$ (molar ratio 1/2) at $-10°$, and were attributed to an intermediate thermodynamically unstable *cis*-$\{Rh(CO)_2[P(C_6H_5)_3]Cl\}$[3]. All our attempts to isolate this intermediate failed, even when low ligand concentrations were used at 0°. It seems that an equilibrium is operating between the labile intermediate, tentatively formulated as *cis*-$[Rh(CO)_2LCl]$, and the *trans*-$[Rh(CO)L_2Cl]$ complex.

The complexes *trans*-$\{Rh(CO)[S(C_2H_5)_2]_2Cl\}$ and *trans*-$\{Rh(CO)[Se(C_2H_5)_2]_2Cl\}$ are liquid at room temperature; their compositions and configurations were established from the analogy between their IR spectra and that of the *trans*-$\{Rh(CO)[Te(C_2H_5)_2]_2Cl\}$, which is a yellow-brown solid for which satisfactory elemental analysis was obtained. The IR spectra of the $[Rh(CO)L_2Cl]$ complexes show a single terminal carbonyl stretching band in the range 1955–1965 cm^{-1} and one band $\nu(Rh–Cl)$ in the range 299–304 cm^{-1}. This is consistent with a chlorine *trans* to a CO group in a Rh^I complex[4].

The formation of trihalorhodium(III) carbonyl complexes of the type $[Rh(CO)L_2X_3]$ $[L=P(C_6H_5)_3, As(C_6H_5)_3$ or $Sb(C_6H_5)_3]$ by halogenation of the corresponding rhodium monohalide was first reported by Vallarino[5]; chlorine and iodine both added satisfactorily, but no compounds containing bromine could be prepared even when the reaction was carried out at $-80°$.

Heck[6] reported that bis(tri-n-butylphosphine) derivatives add bromine as well as chlorine and iodine.

The complexes *trans*-$[Rh(CO)L_2Cl]$ $[L=S(C_2H_5)_2, Se(C_2H_5)_2$ or $Te(C_2H_5)_2]$ undergo fast and quantitative oxidative addition reactions when treated with halogens forming the corresponding Rh^{III} adducts, $[Rh(CO)L_2ClY_2]$ (Y=Cl, Br or I). It is known that the metal–chlorine stretching frequencies in the IR spectra of octahedral complexes are primarily dependent on the nature of the ligand *trans* to chlorine[7], and this enabled us to assign configurations to the adducts derived from *trans*-$[Rh(CO)L_2Cl]$ complexes.

Addition of chlorine, bromine, or iodine to the chloro derivatives $[Rh(CO)L_2Cl]$ afforded octahedral complexes, apparently by *trans* addition (Table 1). The *trans* disposition of the L ligands in similar octahedral adducts in which L is diphenylmethylphosphine[8,9] was also indicated by the NMR spectra.

TABLE 1

SELECTED INFRARED BANDS (cm^{-1})

Compound	ν(CO) (nujol)	ν(CO) ($CHCl_3$)	ν(Rh–Cl)
trans-$Rh(CO)[S(C_2H_5)_2]_2Cl$	1965 vs	1973 vs	304 s
trans-$Rh(CO)[Se(C_2H_5)_2]_2Cl$	1961 vs	1964 vs	302 s
trans-$Rh(CO)[Te(C_2H_5)_2]_2Cl$	1955 vs	1953 vs	299 s
$Rh(CO)[S(C_2H_5)_2]_2Cl_3$	2098 s	2103 vs	345 vs 322 s
$Rh(CO)[Se(C_2H_5)_2]_2Cl_3$	2069 s	2092 vs	343 vs 319 s
$Rh(CO)[Te(C_2H_5)_2]_2Cl_3$	2060 s	2078 vs	332 s
$Rh(CO)[S(C_2H_5)_2]_2ClBr_2$	2090 s	2094 vs	322 s
$Rh(CO)[Se(C_2H_5)_2]_2ClBr_2$	2076 vs	2083 vs	318 s
$Rh(CO)[Te(C_2H_5)_2]_2ClBr_2$	2056 vs	2072 vs	314 m
$Rh(CO)[S(C_2H_5)_2]_2ClI_2$	2073 vs	2079 vs	318 s
$Rh(CO)[Se(C_2H_5)_2]_2ClI_2$	2061 s	2065 s	
$Rh(CO)[Te(C_2H_5)_2]_2ClI_2$	2043 s	2060 vs	328 s
$Rh(CO)[S(C_2H_5)_2]_2(CH_3)ClI$	2052 s	2065 vs	340 m(br)
$Rh(CO)[Se(C_2H_5)_2]_2(CH_3)ClI$	2034 m	2051 s	319 m
$Rh(CO)[Te(C_2H_5)_2]_2(CH_3)ClI$	2030 m	2040 s	321 m
$Rh(CO)[S(C_2H_5)_2]_2(CH_3CO)ClI$	2062 s 1708 vs	2072 vs 1720 vs	325 m(br)
$Rh(CO)[Se(C_2H_5)_2]_2(CH_3CO)ClI$	2055 s 1704 vs	2064 vs 1715 vs	
$Rh(CO)[Te(C_2H_5)_2]_2(CH_3CO)ClI$		2060 vs 1713 vs	
$Rh(CO)[S(C_2H_5)_2]_2(C_6H_5SO_2)Cl_2$	2097 vs	2105 vs	335 s 294 vs
$Rh(CO)[Se(C_2H_5)_2]_2(C_6H_5SO_2)Cl_2$	2086 vs	2096 vs	331 s 290 vs
$Rh(CO)[Te(C_2H_5)_2]_2(C_6H_5SO_2)Cl_2$	2064 vs	2087 vs	320 s 292 vs

Gaseous hydrogen chloride in pentane oxidizes *trans*-$[Rh(CO)L_2Cl]$ complexes to the corresponding rhodium(III) derivatives $[RhCl_3(CO)L_2]$. Similar behaviour was noted for analogous rhodium–carbonyl derivatives containing tertiary phosphines[3,10]. Examples of cleavages of the metal–hydride bond by acids are known[11,12], and it seems reasonable to assume that an intermediate with a direct Rh–H bond is formed, but even for reactions at 0° no spectroscopic evidence for the probable intermediate $[Rh(CO)L_2HCl_2]$ was obtained. It is noteworthy that the only relatively stable Rh^{III} adducts with HCl are given by the RhL_3Cl complexes having $L=P(C_6H_5)_3$, $As(C_6H_5)_3$ or $Sb(C_6H_5)_3$, which activate hydrogen[13,14].

The chlorocarbonylrhodium(I) derivatives, $[Rh(CO)L_2Cl]$ $[L=S(C_2H_5)_2$, $Se(C_2H_5)_2$ or $Te(C_2H_5)_2]$ react readily with an excess of CH_3I in the absence of solvent, and the IR spectrum in methylene chloride solution shows that the reaction is complete in short time. The complexes formed, $[Rh(CH_3)(CO)L_2ClI]$, react readily with carbon monoxide to give the acyl derivatives $[Rh(CO)(COCH_3)L_2ClI]$. The IR spectra of these acylrhodium carbonyl complexes, in $CHCl_3$, show a strong band due to the metal carbonyl and another due to acyl group (Table 1); the far-infrared spectra indicate that there are no variations in the stereochemistry of the complexes.

Reactions of d^8 complexes with alkyl halides seem to be uncommon. Few five-coordinated d^8 complexes have been alkylated, and studies of four-coordinated d^8 complexes clearly indicate that the nature of the ligands has a dramatic effect on the tendency of the complex to undergo alkylation[1]. Addition of methyl iodide occurs to Wilkinson's complex[15], but not to the similar $\{Rh(CO)[P(C_6H_5)_3]_2Cl\}$ complex. The only halocarbonylrhodium(I) complexes which give stable rhodium(III) adducts with alkyl halides are those containing ligands such as $P(n\text{-}C_4H_9)_3$ or $P(CH_3)_2(C_6H_5)$[6,17]. It is noteworthy that CO insertion in the Rh^{III} adducts with the latter ligands is slow.

The complexes *trans*-$[Rh(CO)L_2Cl]$ easily add benzenesulphonyl chloride to give new compounds formulated as rhodium(III) derivatives; the IR spectra of these new complexes exhibit two strong bands at about 1235 and 1065 cm^{-1}, ascribed to the asymmetric and symmetric stretching modes of the $-SO_2-$ group bound to the metal through sulphur[16]. Strong d_π–d_π back-bonding from rhodium to the sulphonyl group is inducted by the $\nu_{as}(SO_2)$ and $\nu_s(SO)_2$ values and confirmed by the low $\nu(Rh-Cl)$ ascribed to chloro *trans* to sulphonyl group (assuming *trans*-addition for the benzenesulphonyl chloride). Similar alkane- or arenesulphonyl chloride adducts of the type $[Rh(CO)(C_6H_5SO_2)L_2Cl_2]$ [where $L=P(CH_3)_2(C_6H_5)$ or $As(CH_3)_2(C_6H_5)$] have been prepared by Deeming and Shaw[17].

The IR spectra of complexes $[Rh(CO)L_2Cl]$ [where $L=S(C_2H_5)_2$, $Se(C_2H_5)_2$ and $Te(C_2H_5)_2$] show a strong band due to a CO stretching mode in the range 1955–1965 cm^{-1}. In the corresponding rhodium(III) complexes they are at least 100 cm^{-1} higher (Table 1). The increase in frequency on going from rhodium(I) to rhodium(III) complexes is interpreted as resulting from a diminished back-donation from the metal to the antibonding π^* orbitals of the CO group and from a synergic decrease in the σ donation from the CO to the central atom. In a series of adducts of the same oxidation state which differ only in the nature of the ligands L, the $\nu(CO)$ can be considered as measure of the electronic density on the metal, which clearly depends upon the nature of L. The comparison of CO stretching frequencies for the adducts $[Rh(CO)L_2ClXY]$ ($XY=Cl_2$, Br_2, I_2, CH_3I, $C_6H_5SO_2Cl$) shows that the $\nu(CO)$ frequency decreases in the order $L=S(C_2H_5)_2 > Se(C_2H_5)_2 > Te(C_2H_5)_2$. This is consistent with the order of the ability of ligands to facilitate electron release to metal[18].

The main factor controlling the ease of the oxidation $M(d^8) \rightarrow M(d^6)$ is the promotional energy value of the metal in the complex[19,20], which depends markedly upon the properties of the ligand. Ligands which withdraw electrons from the metal increase the promotional energy and reduce the tendency to undergo oxidative additions; correspondingly, ligands of lower π-acidity and higher polarizability stabilize the metal in the +3 oxidation state.

From our results we can conclude that the $S(C_2H_5)_2$, $Se(C_2H_5)_2$ or $Te(C_2H_5)_2$ ligands affect differently the promotion energy for the rhodium(III) oxidation state. The strong tendency of the complexes *trans*-[Rh(CO)L_2Cl] to undergo oxidative addition can be attributed to a balance of σ and π factors in the Rh–L bond, with the σ factor dominant.

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