This does not give any clear indication as to how much Ru-Ru bonding may be present. However, the magnetic susceptibility data indicate that there is effectively one unpaired electron on each metal atom, although perhaps these are loosely coupled. Essentially, these III,III molecules are not metal-metal bonded.

Finally, we must comment on the remarkable and characteristic difference between the EPR spectra for the unsymmetric and symmetrical types of II,III compounds. As already noted by Stephenson and co-workers, we have here a very handy criterion for distinguishing between the two classes, although it is not possible in this way (or by CV data) to distinguish between the C_2 and C_{2v} types of $L_2ClRuCl_3RuClL_2$ compounds. The "axial" spectrum given by the $L_3RuCl_3RuCl_2L$ molecule is consistent with the proposed valence trapping since the odd electron is in an approximately axial $Ru^{III}Cl_5L$ environment. For the symmetrical molecules in which there is no symmetry axis of order > 2, the appearance of a rhombic **g** tensor is expected.

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Supplementary Material Available: Tables of anisotropic displacement parameters and additional bond distances and angles (33 pages); listings of calculated and observed structure factors (144 pages). Ordering information is given on any current masthead page.

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Solvent, Temperature, and Pressure Dependence of the Oxidative Addition of Iodomethane to Complexes of the Type Rh^I(β-diketonate)(CO)(PPh_3)

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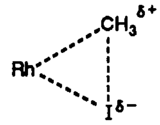
A combined solvent-, temperature-, and pressure-dependence study of the oxidative addition of iodomethane to Rh(Sacac)(CO)(PPh_3) and Rh(cupf)(CO)(PPh_3) was undertaken for a range of solvents covering a large range of ϵ_0 and q_p values. The kinetic data for the thioacetylacetone (Sacac) complex exhibit no significant dependence on the solvent and are interpreted in terms of a concerted three-center transition state. In the case of the cupferron (cupf) complex, a significant solvent effect was observed for the most polar solvents. This observation is interpreted in terms of a linear transition state and the participation of an ion-pair intermediate at least in the case of the polar solvents. The results are discussed in reference to all the data available in the literature for such reactions.

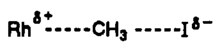
Introduction

Oxidative-addition reactions of alkyl halides to transition-metal complexes are of general importance in terms of the formation of metal alkyl and metal acyl species and their role in catalytic processes.[2-4] We are especially interested in the mechanistic behavior of β-diketone and related complexes of Rh(I) and Ir(I) because of the possibility to support these complexes on a polymer like polystyrene and so heterogenize the potentially homogeneous catalysts.

We have in recent years investigated the kinetics of the oxidative addition of iodomethane to complexes of the type Rh(LL)(CO)(PX_3) and Rh(LL)(PX_3)$_2$, where LL = β-diketones and cupferron and X = phenyl, *p*-chlorophenyl and *p*-methoxyphenyl.[5-10] Solvent and pressure effects[9-11] were studied in order to obtain more information on the nature of the transition state in terms of I (for a concerted three-centered mechanism) or II (for a S_N2 mechanism). For the oxidative addition of CH_3I to



I



II

Ir(Cl)(CO)(PPh_3)$_2$,[11] the volume of activation exhibited a good correlation with the solvent parameter q_p,[12] from which it was concluded that a linear transition state (II) is more in accordance with the measured $\Delta V^{\ddagger}$ data than the concerted three-center state (I).[11] In our earlier studies, some solvent effects were observed,[8-10] but data for a wide range of solvents in terms of ϵ and q_p values were lacking and prevented a detailed interpretation.

In this study, we have now investigated the solvent, temperature, and pressure dependence of reactions 1 and 2 for a series of

$$\mathrm{Rh(Sacac)(CO)(PPh_3) + CH_3I \rightarrow Rh(Sacac)(COCH_3)(I)(PPh_3)} \quad (1)$$

$$\mathrm{Rh(cupf)(CO)(PPh_3) + CH_3I \rightarrow Rh(cupf)(CO)(CH_3)(I)(PPh_3)} \quad (2)$$

solvents, where HSacac = thioacetylacetone, $CH_3C(S)CH_2C(O)CH_3$, and cupf = cupferron, $C_6H_5N(OH)NO$. The product in the case of reaction 1 is the acyl complex, whereas the alkyl

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(12) q_p is the pressure derivative of the solvent parameter $q = (\epsilon - 1)/(2\epsilon + 1)$, i.e. $q_p = [3/(2\epsilon + 1)^2](\partial\epsilon/\partial p)$, where ϵ is the dielectric constant of the solvent.

Table I. k as a Function of Temperature for the Oxidative Addition of CH_3I to $Rh(Sacac)(CO)(PPh_3)$ and $Rh(cupf)(CO)(PPh_3)$ in Various Solvents

solvent	10^4k, M^{-1} s^{-1} T = 288.0 K	T = 298.0 K	T = 308.0 K
Reaction of $Rh(Sacac)(CO)(PPh_3)$			
chloroform	58.3	108	177
chlorobenzene	4.70	9.25	16.5
dichloromethane	55.0	83.1	137
1,2-dichloroethane	37.3	67.4	121
acetone	17.6	36.7	74.6
nitromethane	117	223	355
acetonitrile	56.4	123	221
Reaction of $Rh(cupf)(CO)(PPh_3)$			
chloroform	28.5	50.4	76.6
dichloromethane	24.7	41.2	70.1
1,2-dichloroethane	17.1	30.4	56.1
acetone	10.6	17.3	29.3
acetonitrile	43.9	84.6	150
methanol	15.6	32.8	57.5

Table II. k as a Function of Pressure for the Oxidative Addition of CH_3I to $Rh(Sacac)(CO)(PPh_3)$ and $Rh(cupf)(CO)(PPh_3)$ in Various Solvents at 25.0 °C[a]

Reaction of $Rh(Sacac)(CO)(PPh_3)$

solvent	10^4k, M^{-1} s^{-1} p = 50 bar	p = 250 bar	p = 500 bar	p = 750 bar	p = 1000 bar
chloroform	108 (2)	127 (1)	156 (4)	182 (4)	207 (2)
chlorobenzene	9.3 (3)	10.5 (4)	12.0 (2)	13.6 (2)	15.9 (3)
dichloromethane	83.1 (15)	100 (2)	123 (2)	145 (2)	170 (2)
1,2-dichloroethane	67.4 (4)	77.5 (4)	88.7 (4)	99.1 (10)	114 (1)
acetone	36.7 (1)	41.6 (4)	48.1 (3)	55.1 (3)	67.1 (4)
nitromethane	223 (4)	262 (2)	300 (7)	357 (9)	403 (9)
acetonitrile	124 (3)	138 (2)	155 (2)	179 (2)	215 (3)

Reaction of $Rh(cupf)(CO)(PPh_3)$

solvent	10^4k, M^{-1} s^{-1} p = 50 bar	p = 350 bar	p = 700 bar	p = 1000 bar
chloroform	50.4 (8)	65.1 (10)	81.0 (6)	100 (2)
dichloromethane	41.2 (5)	53.0 (4)	67.4 (9)	81.2 (15)
1,2-dichloroethane	30.4 (8)	37.6 (6)	48.2 (15)	56.8 (18)
acetone	17.3 (3)	21.2 (6)	25.6 (2)	32.2 (3)
acetonitrile	84.6 (12)	116 (2)	171 (3)	225 (4)

[a] The quoted values of k are the mean of at least four determinations for which the standard deviation is given in parentheses.

complex is the product in reaction 2. The solvents were selected in order to cover a wide as possible ϵ and q_p range, so that it would be possible to separate $\Delta V^{\ddagger}$ into $\Delta V^{\ddagger}_{\rm intr}$ and $\Delta V^{\ddagger}_{\rm solv}$, the intrinsic and solvational volumes of activation, respectively.[8-11,13]

Experimental Section

$Rh(Sacac)(CO)(PPh_3)$ and $Rh(cupf)(CO)(PPh_3)$ were synthesized as described before.[8,9] Solvents and chemicals of analytical reagent grade were used throughout this study. The reactions at atmospheric pressure were followed on a Hitachi Model 150-20 spectrophotometer equipped with a thermostated cell holder (±0.1 °C). The high pressure kinetic measurements were performed on a modified (double-beam) Zeiss PMQ II spectrophotometer equipped with a thermostated high-pressure cell.[14] The oxidative-addition reactions were followed at 380 and 402 ± 3 nm for the cupferron and thioacetylacetone complexes, respectively. All reactions were studied under pseudo-first-order conditions with CH_3I in at least a 10-fold excess. Typical experimental conditions were [Rh] = 2×10^{-4} M and [CH_3I] between 0.05 and 0.5 M. At least four concentrations of CH_3I were selected to determine the second-order rate constant. The observed first-order rate constants were calculated from plots of ln $(A_t - A_\infty)$ versus time, where A_t and A_∞ are the absorbances at time t and infinity, respectively. These plots were linear for at least 2-3 half-lives of the reaction.

Results and Discussion

A detailed study of reaction 1 indicated that the final acyl complex is formed via the alkyl intermediate, for which the formation of the latter species is the rate-determining step.[8] In reaction 2, the alkyl complex is formed directly and no evidence for the formation of an intermediate acyl complex was found.[7,8] The investigated reactions and selected conditions are such that the observed first-order rate constant, $k_{\rm obsd}$, depends linearly on the iodomethane concentration, i.e. $k_{\rm obsd} = k[CH_3I]$.[7,8] The values of k as a function of solvent, temperature, and pressure are summarized in Tables I and II, respectively. The activation parameters $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$, and $\Delta V^{\ddagger}$ were calculated from these data by using a least-squares analysis and are summarized along with important solvent parameters in Table III. Plots of ln k versus pressure were linear under all conditions, such that $\Delta V^{\ddagger}$ could be calculated directly from the slope ($=-\Delta V^{\ddagger}/RT$) of such plots. Both reactions 1 and 2 are characterized by significantly negative $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values, which indicate that bond formation and/or charge creation (electrostriction) must play an important role on forming the transition state. The differentiation between these intrinsic and solvational contributions should be possible on the basis of the solvent dependence of the kinetic parameters as employed and suggested before,[8,9,11] especially in terms of the data for $\Delta V^{\ddagger}$.

As pointed out earlier, $\Delta V^{\ddagger}$ may be considered as the sum of two components: $\Delta V^{\ddagger}_{\rm intr}$, which represents the change in volume due to changes in the coordination number, bond lengths, and angles, and $\Delta V^{\ddagger}_{\rm solv}$, which represents the change in volume due to changes in solvation, i.e. electrostriction, on forming the transition state. During oxidative addition, an overall volume decrease is expected because of bond formation with the metal center ($\Delta V^{\ddagger}_{\rm intr}$) and increasing electrostriction ($\Delta V^{\ddagger}_{\rm solv}$) due to a polar transition state involving heterolytic cleavage of the CH_3–I bond as indicated in I and II. This volume decrease may be partially offset by a volume increase due to CH_3–I bond fission. The Kirkwood model can be adopted to account for the solvent dependence of $\Delta V^{\ddagger}_{\rm solv}$ as shown in (3).[15,16] According to this

$$\begin{aligned}\Delta V^{\ddagger} &= \Delta V^{\ddagger}_{\rm intr} + \Delta V^{\ddagger}_{\rm solv} \\ &= \Delta V^{\ddagger}_{\rm intr} - (N_0\Delta\mu^2/r^3)q_p \qquad (3)\end{aligned}$$

equation, $\Delta V^{\ddagger}_{\rm intr}$ can be estimated from a plot of $\Delta V^{\ddagger}$ versus q_p for the investigated solvents as done before for the oxidative addition of CH_3I to $Ir(Cl)(CO)(PPh_3)_2$.[11] The solvents selected in this study are such that the ϵ and q_p values vary by a factor of 10 (see Table III)[17], such that significant effects on $\Delta V^{\ddagger}$ are expected.

Although the data in Table III for the oxidative addition to the Sacac complex indicate some larger values for k at higher solvent polarity, both the $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ values are very constant. This trend indicates that the solvent can in some cases ease charge separation during the formation of the transition state[8] without affecting electrostriction. The $\Delta V^{\ddagger}$ data are in excellent agreement with data reported for the oxidative addition of CH_3I to $Rh(\beta\text{-diketonate})(P(OPh)_3)_2$ in acetone, chloroform, and dichloromethane for β-diketone = acetylacetone, (trifluoroacetyl)acetone, and (trifluorobenzoyl)acetone.[9,10] The latter values also exhibit no significant dependence on q_p. It follows that the observed $\Delta V^{\ddagger}$

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(17) The quoted q_p values were calculated from the given expression[12] and the relationship $(1/\epsilon_0^2)(\partial\epsilon/\partial p) = A'/B'$, where ϵ_0, A', and B' were taken from the literature.[16] It should be noted that the q_p values obtained in this way were divided by 2.303 to take into account that the above equation was obtained by differentiation of the empirical equation $1/\epsilon_0 - 1/\epsilon_p = A' \log [(B' + P)/(B' + P_0)]$. This conversion of the log term to the ln term was not taken into account in the data reported in the literature.[16,18]

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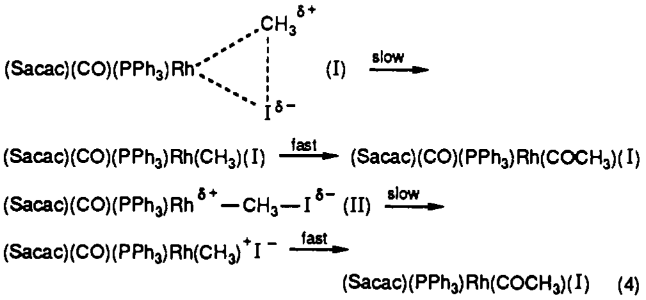
Table III. Rate Constants at 25.0 °C and Activation Parameters for the Oxidative Addition of CH_3I to $Rh(Sacac)(CO)(PPh_3)$ and $Rh(cupf)(CO)(PPh_3)$ in Various Solvents

			$Rh(Sacac)(CO)(PPh_3) + CH_3I$				$Rh(cupf)(CO)(PPh_3) + CH_3I$			
solvent	ϵ_0	$10^6 q_p$	$10^4 k$, $M^{-1}\,s^{-1}$	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}	$10^4 k$, $M^{-1}\,s^{-1}$	$\Delta H^\ddagger$, kJ mol^{-1}	$\Delta S^\ddagger$, J K^{-1} mol^{-1}	$\Delta V^\ddagger$, cm^3 mol^{-1}
chloroform	4.64	16.7	108	37 ± 2	−160 ± 6	−16.9 ± 1.0	50.4	33 ± 3	−180 ± 9	−17.3 ± 0.8
chlorobenzene	5.44	10.2	9.25	43 ± 1	−160 ± 4	−13.6 ± 0.3				
dichloromethane	8.64	11.5	83.1	32 ± 3	−177 ± 8	−18.3 ± 0.9	41.2	37 ± 1	−168 ± 4	−17.4 ± 0.8
1,2-dichloroethane	10.1	12.2	67.4	41 ± 1	−150 ± 2	−13.2 ± 0.5	30.4	42 ± 2	−151 ± 5	−16.1 ± 0.3
acetone	19.7	6.4	36.7	51 ± 1	−122 ± 2	−15.2 ± 0.6	17.3	36 ± 2	−180 ± 5	−15.7 ± 0.7[a]
nitromethane	35.8	1.8	223	36 ± 3	−156 ± 10	−15.2 ± 0.7				
acetonitrile	36.1	1.5	123.5	45 ± 3	−128 ± 10	−13.9 ± 0.7	84.6	42 ± 1	−144 ± 1	−25.4 ± 0.7
methanol	30.8	3.3					32.8	43 ± 3	−147 ± 10	−24.9 ± 0.5[b]

[a] Previously determined value is −17.1 ± 0.8 cm^3 mol^{-1}.[11] [b] Taken from the literature.[11]

for these reactions mainly represents $\Delta V^\ddagger_{intr}$ with an average value of −14.7 ± 1.5 cm^3 mol^{-1} for the Sacac data in Table III. This value is indeed very close to the $\Delta V^\ddagger_{intr}$ value of −17 cm^3 mol^{-1} reported for the oxidative addition to $Ir(Cl)(CO)(PPh_3)_2$.[11] In the present system, the final reaction product is the acyl complex, and two possible reaction routes via transition states I and II have been suggested:[8]



$$(Sacac)(CO)(PPh_3)Rh(CH_3)(I) \xrightarrow{fast} (Sacac)(CO)(PPh_3)Rh(COCH_3)(I)$$

$$(Sacac)(CO)(PPh_3)Rh^{\delta+}{-}CH_3{-}I^{\delta-}\ (II) \xrightarrow{slow}$$

$$(Sacac)(CO)(PPh_3)Rh(CH_3)^+I^- \xrightarrow{fast} (Sacac)(PPh_3)Rh(COCH_3)(I) \qquad (4)$$

On the basis of the solvent-independent $\Delta V^\ddagger$ data, we conclude that the reaction via transition state I is more likely, since a significant solvent dependence is expected for the reaction scheme (II) involving an ion-pair intermediate (see further discussion). The concerted three-center reaction route (I) not only accounts for the solvent independence of $\Delta V^\ddagger$ but can also quantitatively account for the magnitude of $\Delta V^\ddagger$. Substitution reactions of such Rh(I) complexes are typically associative and characterized by $\Delta V^\ddagger$ values of ca. −6 cm^3 mol^{-1}. It should be noted that the volume decrease during the formation of a five-coordinate species is partially offset by the volume increase due to structural changes from tetragonal pyramidal to trigonal bipyramidal, generally observed in substitution reactions of square-planar complexes.[19] It thus follows that the average value of −14.7 ± 1.5 cm^3 mol^{-1} is in line with the simultaneous formation of two bonds between the rhodium center and CH_3I in the concerted three-center mechanism (I).

The data for the cupferron system in Table III indicate no meaningful correlation between k and the polarity of the solvent. Furthermore, $\Delta V^\ddagger$ has a value of −17 cm^3 mol^{-1} for four solvents, but is significantly more negative, ca. −25 cm^3 mol^{-1}, for the more polar solvents acetonitrile and methanol. It follows that the more polar solvents may allow more charge creation, which is accompanied by a large change in dipole moment ($\Delta\mu^2$, see eq 3) in the transition state. The more negative $\Delta V^\ddagger$ values do not correlate with the smaller q_p values for these solvents, such that electrostriction effects cannot account for these observations. However, formation of an ion-pair intermediate will be more favored in more polar solvents, indicating that this oxidative-addition reaction most probably proceeds via the linear transition state II in the most polar solvents. In the case of the less polar solvents the $\Delta V^\ddagger$ value of −17 cm^3 mol^{-1} can either be due to single-bond formation and partial charge creation in the linear transition state II or due to simultaneous formation of two bonds in the three-center mechanism I.

We conclude that large variations in the nature of the solvent, in terms of parameters such as ϵ_0 and q_p, have a minor influence on oxidative addition reactions of most Rh^I(β-diketonate) complexes. So far only in the case of the cupferron complex could a meaningful effect be observed for highly polar solvents, which could indicate the participation of ion-pair intermediates. In all the work performed so far, the inclusion of a sulfur donor atom in the bidentate chelate resulted in the formation of only the acyl complex. This trend could be related to a possible trans-labilization effect of coordinated sulfur. Another property that can be used to determine the stereochemistry of the transition state is the configuration of optically active molecules like ethyl α-bromopropionate during oxidative addition.[20,21] It is however uncertain to what extent the oxidative addition of CH_3I can be compared to the oxidative addition of such a bulky molecule. Since the radii of CH_3 and I are rather similar, the oxidative addition of CH_3I can be rather compared with that of homonuclear molecules like H_2 and I_2, which are known to add in the cis configuration via a concerted three-centered transition state.

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