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Equilibrium between CO-bridged and non-bridged forms of $[(\eta^5\text{-}C_5H_5]Ru(CO)_2]_2$ and selective photoreactivity of the non-bridged form

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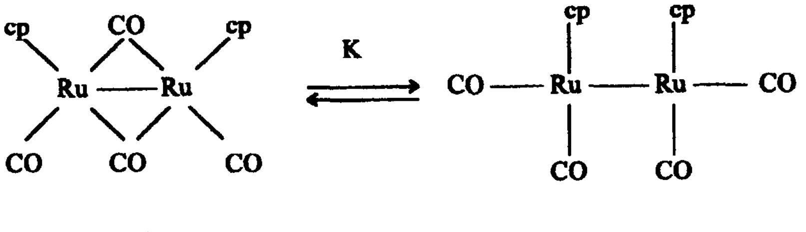
Abstract—The reaction volumes, $\Delta \bar{V}$ for the equilibrium between CO-bridged and non-bridged forms of the $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ complex in isooctane, isopropanol and acetonitrile were determined spectrophotometrically. The values of $\Delta \bar{V}$ show that an increase in pressure facilitates formation of the CO-bridged form. The effect of pressure is discussed and compared to that of temperature and solvent polarity. Selective photolysis of the non-bridged form in toluene induces the symmetrical cleavage of the Ru—Ru bond to give two $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^{\cdot}$ radicals. EPR experiments with nitrosodurene spin trap indicate that the ruthenium organometallic radicals activate the C—H bond and abstract an H atom from toluene. © 1997 Elsevier Science Ltd

Keywords: bis[dicarbonylcyclopentadienyloruthenium(I)]; solvent effect; temperature effect; pressure effect; reaction volume; photochemistry.

There are a number of structurally well characterized dinuclear organometallic complexes having direct metal-metal bonds. The chemistry of both CO-bridged and non-bridged complexes is dominated by cleavage of the metal-metal bond [1].

It has been shown that the $[(\eta^5\text{-}C_5H_5)M(CO)_2]_2$ complexes (where M = Fe or Ru) have bridged dinuclear structures in the solid state [2]. However, in solution they behave differently: the iron complex exists for the most part (>99%) in its CO-bridged dinuclear form, whereas the ruthenium complex is known to exist in the equilibrium of the CO-bridged (I) and non-bridged (II) forms (eq. 1, cp = $\eta^5\text{-}C_5H_5$) [3–9].



(1)

(I) (II)

The equilibrium (1) was found to be both temperature and solvent dependent [3–9]. The present work reports on pressure dependence of equilibrium

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constant K and compares it with temperature and solvent dependences studied by us and by other authors. The results of this study also shed new light on the selective photoreactivity of the non-bridged form (II).

EXPERIMENTAL

$[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ was purchased from Strem Chemicals and used as received. All solvents for spectroscopic studies were dried and distilled under argon.

UV–vis absorption spectra were recorded using a Shimadzu UV-2101 PC spectrophotometer. A standard quartz cuvette and a pillbox cell combined with high pressure equipment [10] were used under ambient conditions and under high pressure (up to 180 MPa), respectively. In both cases, temperature of sample solution was controlled to within ±0.1 K. IR spectra were recorded on a Bruker IFS 48 spectrometer in 0.4 or 1 mm NaCl cells.

Reaction enthalpy (ΔH°) and reaction volume ($\Delta \bar{V}$) for eq. (1) were calculated from the changes of $K = c_{nb}/c_b$ with temperature and pressure. Because the knowledge of absolute values of K is not necessary for these calculations, the concentration ratio c_{nb}/c_b was replaced by the proportional ratio $A_{nb}/A_b = \alpha K$, where A_{nb}, A_b are maximum absorbances of the UV–vis bands $\lambda_{nb} = 330$ nm and $\lambda_b = 265$ nm, characteristic of the non-bridged and bridged forms, respectively.

EPR experiments were carried out using a Bruker ER 200 D spectrometer. Solutions containing 0.005 M nitrosodurene spin trap (2,3,5,6-tetramethylnitrosobenzene, ND) and 0.01 M $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ were used. The reaction mixture was carefully deoxygenated. A quartz flat cell attached to an H-shaped mixing chamber was used. Photolysis was carried out inside the cavity of the EPR spectrometer using a 500 W ORIEL mercury lamp equipped with f/3.4 Applied Photophysics monochromator.

RESULTS

Effect of solvent polarity

The typical UV–vis spectra of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (eq. (1)) in five different solvents are presented in Fig. 1. The spectra are characterized by two intense bands at 265 and 330 nm. The former was assigned to the $\sigma_b \rightarrow \sigma_b^*$ excitation of the CO-bridged Ru species (I) and the latter to the $\sigma_{nb} \rightarrow \sigma_{nb}^*$ excitation of the non-bridged form (II) [1,9]. The considerable changes in the relative intensity of both the bands (A_{nb}/A_b) in various solvents reflect shifts in the equilibrium (1). The values of αK were found to increase within the series:

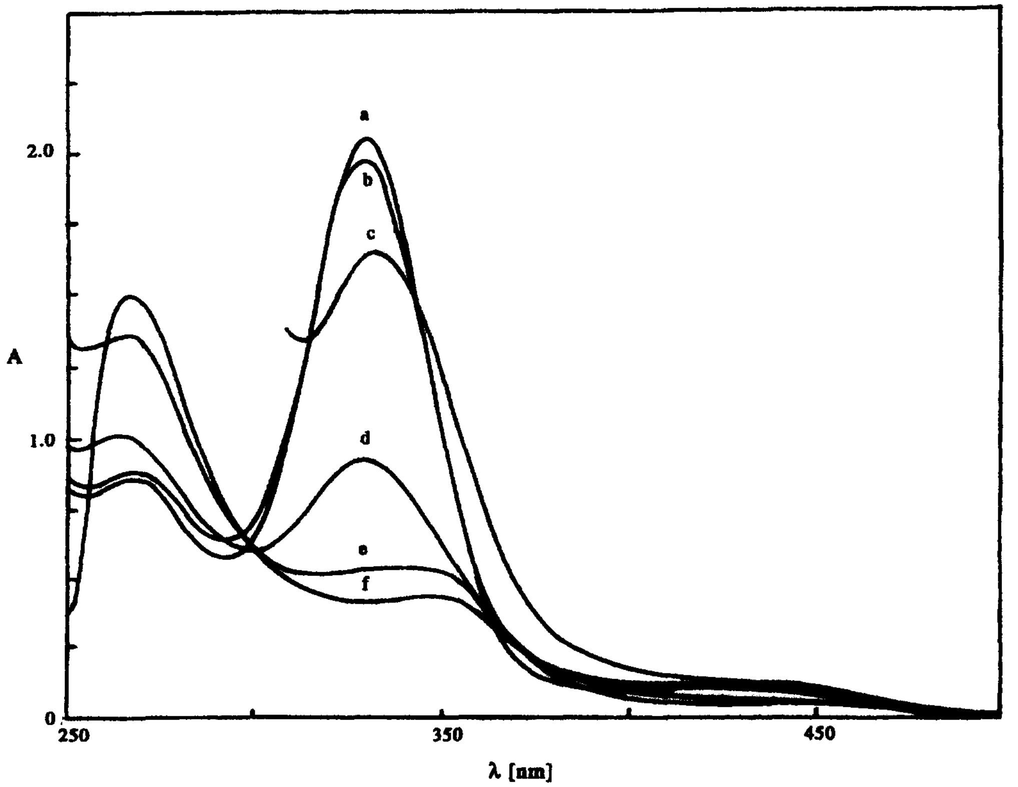

Fig. 1. Electronic absorption spectra of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ complex in *n*-heptane (a), isooctane (b), toluene (c), isopropanol (d), acetonitrile (e), dimethylsulphoxide (f).

$$\text{dimethylsulphoxide} < \text{acetonitrile} < \text{isopropanol} < \text{toluene} < \text{isooctane} \sim n\text{-heptane} \quad (2)$$

and to correlate well with the solvent polarity characterized by its dielectric constant (Table 1), or by its dipole moment.

IR spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$ consist of several peaks which could also be used to evaluate the equilibrium constant (eq. 1) [3,5,6]. Based on changes of two IR bands: 1785 cm^{-1} and 1938 cm^{-1} assigned to the CO-bridged and non-bridged form, respectively, Noack [4] estimated thermodynamic data for the equilibrium (1) in carbon disulphide. In the solvents studied in this work, however, the IR spectra appeared not to be suitable for the quantitative analysis due to the overlap of peaks originating both from the different complex forms and from the solvents. Therefore, our thermodynamic characteristics were based mainly on the analysis of electronic spectra. Nevertheless, analysis of IR spectra in different solvents leads to the same series (2) as that derived from the UV–vis spectra.

Effect of temperature

The spectra of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$ in acetonitrile were recorded within the temperature range 278–313 K. The well-defined spectral changes reflect the shift of equilibrium (1) towards the non-bridged form (II) with an increase in temperature. These results are consistent with those cited in the literature [1,3,4,9]. From the temperature dependence of αK the reaction enthalpy and the reaction entropy were determined in the usual way (see Table 1). The obtained ΔH° and ΔS° values are comparable with those found by Noack for the solution of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$ in CS_2 [4].

Effect of pressure

The pressure effect on equilibrium (1) was studied at 298 K for three solvents (isooctane, isopropanol, acetonitrile) within the pressure range 0.1–180 MPa. The spectra show that an increase in pressure leads to an increase in the concentration of the CO-bridged form (I), i.e. equilibrium (1) is shifted to the left as pressure increases (Fig. 2). The spectral changes with pressure were used to calculate the reaction volume $\Delta \bar{V}$.

$$\left(\frac{\partial \ln(\alpha K)}{\partial p}\right)_T = -\frac{\Delta \bar{V}}{\mathrm{R}T}$$

The plots of $\ln(\alpha K)$ against pressure for equilibrium (1) are linear (Fig. 3) within experimental error. $\Delta \bar{V}$ values calculated from the slopes of the above plots are presented in Table 1.

Selective photolysis of the non-bridged form (II)

Thermodynamic parameters describing eq. (1) are of importance for interpretation of thermal and photochemical reactivity of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$. Photochemistry of this complex is complicated; the literature data suggest two different photolytic behaviours: CO dissociation leading to formation of $[(\eta^5\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_3]$, and cleavage of the Ru—Ru bond leading to formation of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]^\bullet$ radicals [9,11,12]. To distinguish between the two behaviours the photolysis of $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$ in toluene at $\lambda = 336$ nm in the presence of nitrosodurene (ND) as a spin trap was carried out. In toluene the non-bridged form (II) of the complex $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$ is the dominant species (see Table 1). By irradiating the system at $\lambda = 336$ nm the non-bridged

Table 1. Solvent polarity, temperature and pressure effects on the equilibrium: CO-bridged $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2 \rightleftarrows$ non-bridged $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru(CO)}_2]_2$

Solvent	$\varepsilon_{0.1\text{MPa}}/\varepsilon_{200\text{MPa}}$ (298 K)	$\varepsilon_{283\text{K}}/\varepsilon_{313\text{K}}$ (0.1 MPa)	$A_{\text{nb}}/A_{\text{b}}$ [a]	ΔH° [kJ mol^{-1}]	ΔS° [J K^{-1} mol^{-1}]	$\Delta \bar{V}$ [b] [cm^3 mol^{-1}]
n-heptane	1.94/2.02[c,d]		2.32			
isooctane		1.957/1.914[c]	2.17			2.1 ± 0.1
toluene		2.385/2.347[c]	~1.72[e]			
isopropanol	18.8/~21.1[c]	21.2/16.7[c]	0.83			2.7 ± 0.1
acetonitrile	36.1/41.45[f]	38.9/33.3[f]	0.39	6.1 ± 0.1	17.6 ± 0.3	3.1 ± 0.2
DMSO		~55[c,g]	$\leqslant 0.30$			
CS_2		2.64[c,g]		6.5[h]	23.0[h]	

[a] 298 K; 0.1 MPa.
[b] Data at 298 K.
[c] Ref. [17].
[d] The data at 291 K for the range 0.1–80 MPa.
[e] Estimated from the $A_{\text{nb}}/A_{\text{b}}$ vs dipole moment correlation.
[f] Ref. [18].
[g] Data at 293 K.
[h] Ref. [4].

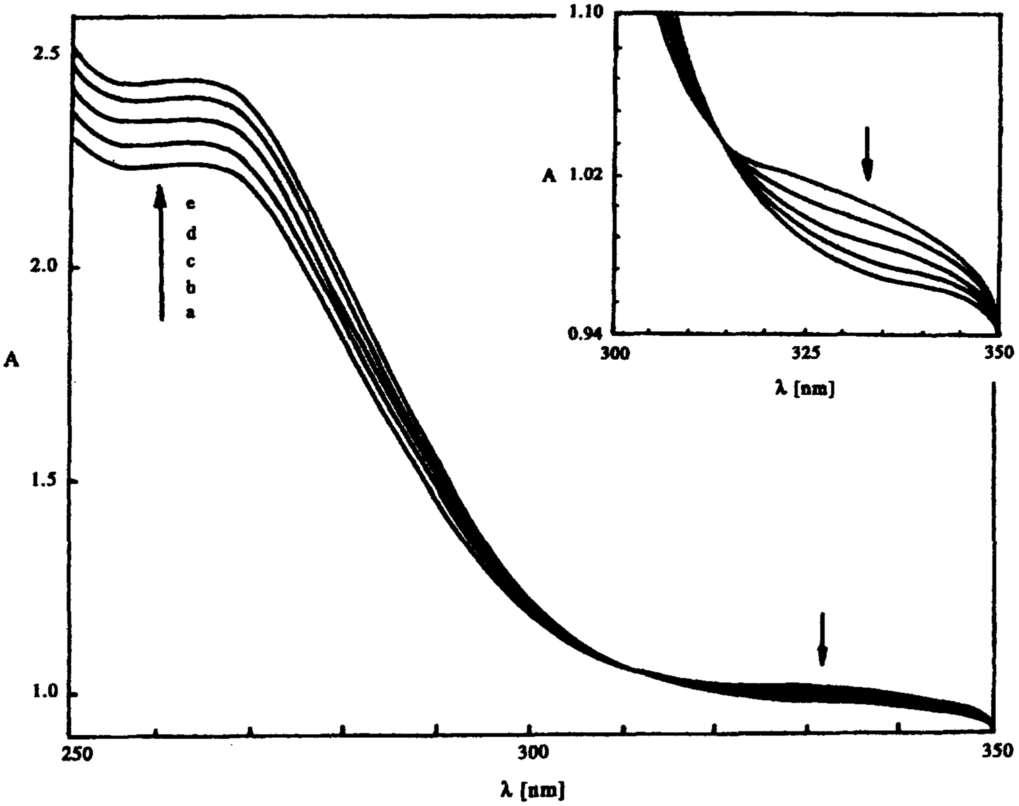

Fig. 2. Pressure effect on the absorption spectra of the $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ complex in acetonitrile. Experimental conditions: total concentration of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2 \approx 1 \times 10^{-4}$ M, optical path length = 2 cm, $T = 298$ K, pressure [MPa]: 5 (a), 30 (b), 60 (c), 90 (d), 120 (e).

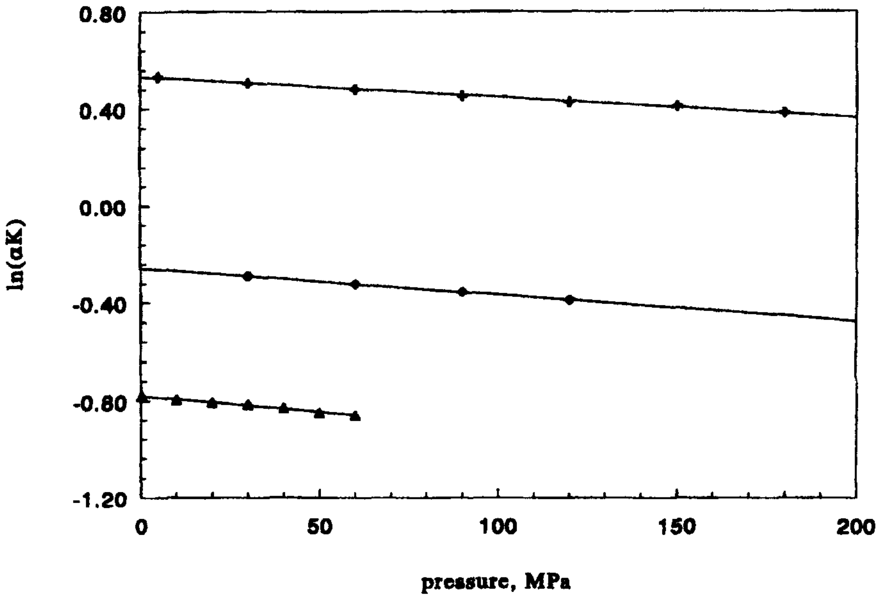

Fig. 3. Pressure dependence of ln (αK) for the equilibrium (1) in isooctane (+), isopropanol (◆) and acetonitrile (▲).

form was selectively excited. Two EPR signals were observed: one was assigned to the $\{(\eta^5\text{-}C_5H_5)Ru(CO)_2\cdot ND\}$ adduct ($g = 2.0078$, $a_N = 1.705$ mT, $a_{Ru(99)} = 0.504$ mT, $a_{Ru(101)} = 0.570$ mT), and the other to the $\{ND\cdot CH_2C_6H_5\}$ adduct [$g = 2.0061$, $a_N = 1.35$ mT, $a_H = 0.780$ mT, (2H)]. These results imply that the radicals $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^{\cdot}$ are the primary photoproducts. The secondary thermal reaction of the Rucentred radicals with toluene is likely to occur giving rise to $C_6H_5CH_2^{\cdot}$ radicals and to the formation of $[(\eta^5\text{-}C_5H_5)Ru(H)(CO)_2]$ hydride as a reactive intermediate [13]. This suggests that abstraction of an H atom from the solvent effectively competes with the 17-electron radical $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^{\cdot}$ dimerization [14]. The experimental evidence supporting this scheme is as follows: (i) Photolysis ($\lambda = 336$ nm) of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ in toluene-d_8 in the presence of nitrosodurene gave EPR signals of the $\{ND\cdot CD_2C_6D_5\}$ adducts ($a_N = 1.35 \pm 0.01$ mT, $a_D = 0.11 \pm 0.01$ mT, $g = 2.0061 \pm 0.0008$); (ii) A photolyzed reaction mixture of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ and CH_3I showed the formation of the anticipated product $[(\eta^5\text{-}C_5H_5)Ru(CO)_2I]$ [1,12]. EPR monitoring of the photoreaction revealed the presence of $\{ND\cdot CH_3\}$ spin adducts ($a_N = 1.37 \pm 0.08$ mT, $a_H = 1.24 \pm 0.08$ mT (3H)). EPR signals of $\{ND\cdot CD_2C_6D_5\}$ adduct were not present; (iii) On the other hand, photolysis ($\lambda = 336$ nm) of the $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$, ND and PPh_3 mixture in toluene neither generated EPR signals other than those described above, nor did it result in the formation of the $[(\eta^5\text{-}C_5H_5)_2Ru_2(CO)_3(PPh_3)]$ complex. These observations exclude the photoinduced Ru—CO cleavage in the non-bridged form [12].

DISCUSSION

The equilibrium between the CO-bridged (I) and non-bridged (II) forms of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]_2$ (eq. 1) was found to depend on solvent polarity, temperature and pressure. An increase in pressure and solvent polarity and also a decrease in temperature favour formation of the bridged form (I). As predicted on the basis of UV–vis spectral characteristics, the obtained ΔH° values indicate that the energy difference between the two forms is very low. Also the reaction volume and reaction entropy for eq. (1) were found to be small positive and slightly dependent on the solvent nature. Among studied parameters (i.e. solvent polarity, temperature and pressure) solvent polarity appeared to exert the predominant influence on eq. (1). In this study solvent polarity was changed not only by using different solvents but also by changing temperature and pressure for the same solvent. Temperature and pressure effects on solvent polarity strongly depend on the solvent nature. For the non-polar solvents the effect is relatively small (e.g. isooctane, *cf* Table 1), whereas for the polar solvents it can be quite significant (e.g. CH_3CN, *cf* Table 1). The reaction volume for eq. (1) found for the studied solvents (Table 1) must be considered as the sum of intrinsic ($\Delta \bar{V}_i$) and solvational ($\Delta \bar{V}_{solv}$) components. The solvational component in this study mainly results from the changes in solvent polarity. The rough estimation based on the dielectric constants showed that in agreement with predictions, the contribution of $\Delta \bar{V}_{solv}$ to the measured $\Delta \bar{V}$ increases in the series: isooctane, isopropanol, acetonitrile. For non-polar isooctane the contribution is so small that it can be neglected, but for acetonitrile it has to be taken into account. This manifests itself in increasing $\Delta \bar{V}$ values along the same series of solvents (Table 1). The other thermodynamic parameters ($\Delta H^\circ, \Delta S^\circ$) must also be considered as the sum of intrinsic and solvational components due to temperature effect on the dielectric constant.

The strong effect of the solvent polarity seems to be highly surprising in view of the lack of charge or strongly polar bonds in the case of the ruthenium dimeric complexes. However, both isomers were reported to exist mostly in *cis*- forms [5], which should result in their dipole moments $\mu \neq 0$. One likely possibility would be stabilization of the CO-bridged form by the dipole-dipole interaction; another possibility is behaviour of the polar solvent molecule as ligating the non-bridged form which facilitates its conversion into the CO-bridged isomer. The latter hypothesis is supported by increased donor numbers [15] along the series (2).

In toluene the non-bridged species can be selectively excited. This excitation leads to formation of the $[(\eta^5\text{-}C_5H_5)Ru(CO)_2]^{\cdot}$ radicals which, in turn, activate the C—H bond of toluene. Production of $[(\eta^5\text{-}C_5H_5)Ru(CO)_2(H)]$ as an intermediate species seems to be justified. A detailed photochemical study of the CO-bridged form in comparison to the non-bridged isomer has been published elsewhere [16].

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