Wavelength Dependence of Photocatalytic Cyclohexane Dehydrogenation by Carbonyl- and Thiocarbonyl-(chloro)-phosphine Rhodium(I) Complexes†

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Photocatalytic dehydrogenation of cyclohexane using [RhCl(CS)(PPh$_3$)$_2$] was closely related to photodissociation of the CS ligand, where the effective absorption band was not of the lowest energy but the second lowest, in contrast to the CO analogue. The estimated turnover number of [RhCl(PPh$_3$)$_2$] in the dehydrogenation cycle was 3.8 on the assumption that [RhCl(CS)(PPh$_3$)$_2$] is photodecomposed irreversibly. The wavelength dependence of photocatalysis by these complexes is well interpreted in terms of the molecular-orbital energy levels and orbital interactions.

Dehydrogenation of alkanes by transition-metal complexes is one of the most fascinating and challenging goals for organometallic chemistry as well as for catalytic chemistry. Significant progress has been made in the C–H activation of hydrocarbons by transition-metal complexes.[1] With regard to catalytic functionalization, however, relatively few examples have been reported so far.[2] Catalytic alkane dehydrogenation to yield alkenes was achieved thermally with the aid of 3,3-dimethylbut-1-ene as a hydrogen acceptor[3] and later without it under photoirradiation.[4]

Recent reports on photocatalytic alkane dehydrogenation with carbonyl(chloro)phosphinerhodium complexes have attracted wide attention because of the high turnover frequencies.[5] A reaction mechanism was suggested on the basis of flash photolysis studies, since conclusive evidence was afforded on the photodissociation of the CO ligand from [RhCl(CO)(PR$_3$)$_2$] (R = Ph or Me).[6] The photogenerated three-co-ordinated intermediate [RhCl(PR$_3$)$_2$] is now deemed the key active species for alkane dehydrogenation.[5]

The photochemical behaviour of transition-metal carbonyl complexes has been investigated widely with reference to the wavelength dependence and electronic structure.[7] As for the absorption bands of [RhCl(CO)(PPh$_3$)$_2$], the electronic transition at the longest wavelength was assigned as the metal-to-ligand charge transfer (m.l.c.t.) on the spectroscopic grounds of (*i*) its large molar absorption coefficient, (*ii*) the persistence of its intensity upon cooling and (*iii*) the transition-energy ordering among a series of MA(CO)L$_2$ (M = Ir^I or Rh^I, A = anionic ligand, L = phosphine) compounds.[8]

The yellow colour of [RhCl(CO)(PPh$_3$)$_2$] was unaffected by the ligand substitution of PPh$_3$ using other phosphines.[8a] On the contrary, the influence of co-ordinated CO on the transition energies was so large that an analogous complex [RhCl(CS)(PPh$_3$)$_2$] was orange,[9] suggesting a different absorption spectrum.

In the present work, we attempted to examine the wavelength dependences of cyclohexane dehydrogenation by [RhCl(CO)L$_2$] (L = PPh$_3$, PEtPh$_2$ or PEt$_3$) and [RhCl(CS)(PPh$_3$)$_2$] in terms of a quantum-chemical interpretation of their electronic structures.

Experimental

All manipulations were carried out under a nitrogen atmosphere or *in vacuo*.

A series of Vaska-type rhodium complexes, *i.e.* [RhCl(CO)(PPh$_3$)$_2$],[10] [RhCl(CO)(PEtPh$_2$)$_2$][11] and [RhCl(CO)(PEt$_3$)$_2$],[11] were prepared by the published methods. The complex [RhCl(CS)(PPh$_3$)$_2$] was prepared from PPh$_3$ and [RhCl(PPh$_3$)$_3$] in MeOH–CS$_2$ as the result of a reaction between co-ordinated CS$_2$ and PPh$_3$ to give the CS ligand and SPPh$_3$. The isolated complex was recrystallized from a MeCl–EtOH solution.[9] Cyclohexane of reagent grade (Wako) was dried over molecular sieves and then Na, deaerated, distilled and stored under a nitrogen atmosphere. Ultra-violet spectra were recorded on a UV-365 (Shimazu) spectrometer in CH$_2$Cl$_2$ solution (0.05 mmol dm^{-3}).

Photocatalytic dehydrogenation of cyclohexane was carried out with the rhodium complex using a cylindrical quartz cell (diameter 45 mm, cell length 85 mm), which was irradiated by an external-type Xenon lamp (2 kW, Ushio) through a cut-off filter. Commercial glass cut-off filters, UV-32, UV-34, L-38 and L-42 (Kenko), were used; the UV-32 filter was specified to cut off the shorter-wavelength region of the incident light at 320 nm (within the range of 35 nm), allowing 50% transmittance at 320 nm.

A typical procedure was as follows. After the cyclohexane solution of the rhodium complex (10 μmol per 100 cm^3) had been heated to the boiling point (81 °C), the reaction was started by photoirradiation through a cut-off filter. The amount of gas evolved was measured by a gas burette (20 cm^3). The reaction products were analysed by gas chromatography using active carbon and OV-1 columns for the gas- and liquid-phase products, respectively.

The amount of unchanged [RhCl(CS)(PPh$_3$)$_2$] during the photocatalytic reaction was monitored spectroscopically. After stopping the photoirradiation, the reaction mixture was evaporated to dryness *in vacuo*, the residue dissolved in CH$_2$Cl$_2$ (2.0 cm^3) and transferred to a liquid IR cell (0.2 mm). The peak intensity at ν_{max}(CS) (1305 cm^{-1}) was obtained on an IR spectrometer (JASCO, type A-3).

The UV/VIS spectra of [RhCl(CS)(PPh$_3$)$_2$] were recorded at ambient temperature at appropriate time intervals immediately after the transfer of a small portion of the reaction mixture (4 cm^3) from the photoreaction cell.

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† *Non-SI unit employed:* eV ≈ 1.60 × 10^{-19} J.

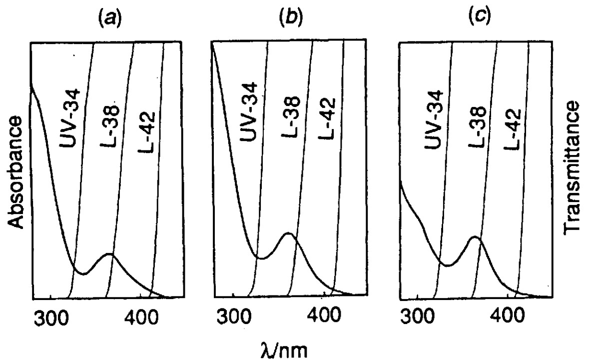


Fig. 1 The UV/VIS spectra of $[RhCl(CO)L_2]$ in CH_2Cl_2 (0.05 mmol dm^{-3}) with reference to the transmission characteristics of the cut-off filters. L = PPh_3 (*a*), $PEtPh_2$ (*b*), or PEt_3 (*c*)

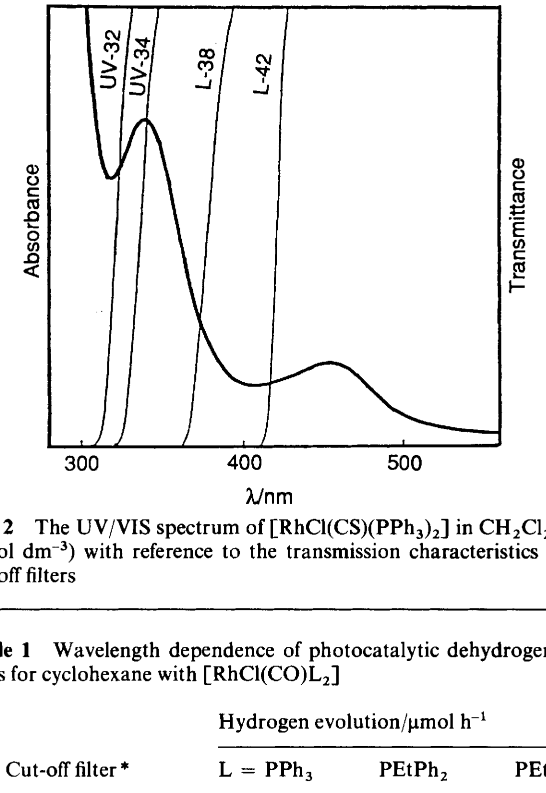


Fig. 2 The UV/VIS spectrum of $[RhCl(CS)(PPh_3)_2]$ in CH_2Cl_2 (0.05 mmol dm^{-3}) with reference to the transmission characteristics of the cut-off filters

Table 1 Wavelength dependence of photocatalytic dehydrogenation rates for cyclohexane with $[RhCl(CO)L_2]$

	Hydrogen evolution/µmol h^{-1}		
Cut-off filter *	L = PPh_3	$PEtPh_2$	PEt_3
UV-34 (340 nm)	50	353	317
L-38 (380 nm)	trace	87	38
L-42 (420 nm)	none	none	none

* Wavelength at 50% transmittance is given in parentheses.

Calculations

Quantum-chemical calculations were performed by the extended-Hückel method. The molecular geometries of $[RhCl(CO)(PPh_3)_2]$, $[RhCl(CS)(PPh_3)_2]$ and $[RhCl(PPh_3)_2]$ were calculated as having C_{2v} symmetry. Various bond lengths were adopted for Rh–C, Rh–Cl, Rh–P, C–O and C–S, including those from the X-ray structures of $[RhCl(CO)(PPh_3)_2]$[12] and $[RhCl(CS)(PPh_3)_2]$.[13] The valence state ionization potential and the Slater exponent for H (1s), C (2s, 2p), O (2s, 2p), Cl (3s, 3p),[14] S (3s, 3p)[15] and Rh [5s, 5p, 4d (double ζ)][16] were taken from the literature.

As for the phosphine ligand, PPh_3 was replaced by PH_3. However, the orbital parameters of hydrogen itself were not adopted for representing the phenyl substituent of phosphine. Both the valence state ionization potential and the Slater exponent of H in PH_3 were chosen here so as to fit best the observed Rh–P NMR spin–spin coupling constants,[17,*] as attempted previously for a series of phosphine rhodium complexes including the PPh_3 ligand within the framework of the Pople–Santry approximation.[18]

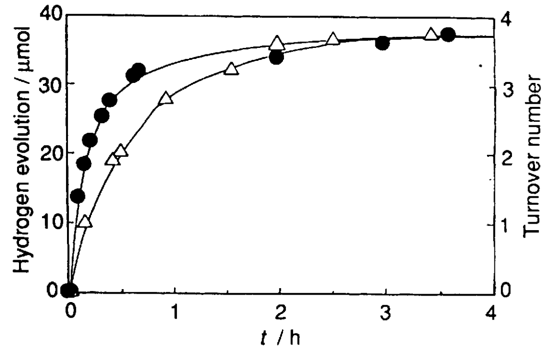
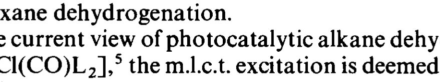


Fig. 3 Time-course plots for photocatalytic dehydrogenation of cyclohexane by $[RhCl(CS)(PPh_3)_2]$ using different cut-off filters: UV-32 (●) and UV-34 (△)

Results and Discussion

Wavelength Dependence of the Photocatalytic Dehydrogenation of Cyclohexane by $[RhCl(CO)L_2]$.—Fig. 1 shows the electronic absorption spectra of $[RhCl(CO)L_2]$ (L = PPh_3, $PEtPh_2$ or PEt_3) together with the transmission characteristics of the cut-off filters used for the photoreactions. The absorption maxima of the single band in the visible–near-UV region appeared at 364, 362 and 362 nm for L = PPh_3, $PEtPh_2$ and PEt_3 respectively.

Photocatalytic reaction rates for cyclohexane dehydrogenation [equation (1)] were analysed from the increasing amount



(1)

of H_2 evolved from the cyclohexane solution of $[RhCl(CO)L_2]$ in 1 h (Table 1). The wavelength dependence of the reaction rates in the order of the optical filters UV-34 > L-38 > L-42 was obtained for the PPh_3, $PEtPh_2$ and PEt_3 complexes. The initial reaction rates using the UV-34 filter were distinctly high, whereas no reaction took place upon photoirradiation through the L-42 filter. These results indicate that photoirradiation of the lowest-energy band of $[RhCl(CO)L_2]$ is effective for cyclohexane dehydrogenation.

In the current view of photocatalytic alkane dehydrogenation by $[RhCl(CO)L_2]$,[5] the m.l.c.t. excitation is deemed essential for generating the three-co-ordinate intermediate $[RhClL_2]$, which is dehydrogenation active and is easily co-ordinated by CO to reproduce the original complex $[RhCl(CO)L_2]$. The present results confirm that photodissociation of the CO ligand is indispensable for catalytic cyclohexane dehydrogenation upon photoirradiation of the lowest-energy band of $[RhCl(CO)L_2]$.

Wavelength Dependence of the Photocatalytic Dehydrogenation of Cyclohexane by $[RhCl(CS)(PPh_3)_2]$.—Fig. 2 shows the electronic absorption spectra of $[RhCl(CS)(PPh_3)_2]$ together with the transmission characteristics of cut-off filters used for the photoreactions. Two absorption bands were found at λ_{max} of 339 and 455 nm in the visible spectral region.

The cyclohexane solution of $[RhCl(CS)(PPh_3)_2]$ yielded hydrogen and cyclohexene upon photoirradiation. The hydrogen evolution rates were dependent on the kind of cut-off filter,

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* Adequacy of the parameters modified for this symbolic H atom is supported by the calculated net charge of Rh in $[RhCl(PPh_3)_2]$, since molecular-orbital parameters of the genuine H atom gave a negative value (−0.164), whereas a reasonable positive value (+0.119) was obtained with the parameters adopted here.

Table 2 Wavelength dependence of photocatalytic dehydrogenation rates for cyclohexane with $[RhCl(CS)(PPh_3)_2]$

Cut-off filter *	Hydrogen evolution/µmol h^{-1}
UV-32 (320 nm)	77
UV-34 (340 nm)	41
L-38 (380 nm)	trace
L-42 (420 nm)	none

* Wavelength at 50% transmittance is given in parentheses.

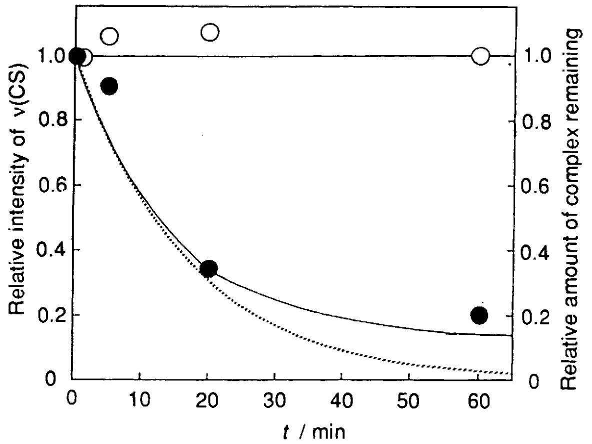

Fig. 4 Time-course plots of IR peak intensity due to $\nu_{max}(CS)$ of $[RhCl(CS)(PPh_3)_2]$ during photocatalytic cyclohexane dehydrogenation using filters UV-32 (●) and L-42 (○). The dotted line determined from the initial reaction rates in Fig. 3 depicts the amount of catalyst left in the solution

as observed for $[RhCl(CO)L_2]$. The time-course plots using the UV-32 and UV-34 filters were shown in Fig. 3, with a common total turnover number of 3.7. The initial reaction rate obtained from the gas-volume increments in the first 30 min (Table 2) was higher upon photoirradiation through filter UV-32 than UV-34. Surprisingly, no reaction occurred upon using the L-42 filter, even though the absorption band at the lowest energy (λ_{max} 455 nm) was photoirradiated.

Photoirradiation of the band at the second lowest energy (λ_{max} 339 nm) was thus indispensable for cyclohexane dehydrogenation, whereas the excitation of the lowest-energy band (λ_{max} 455 nm) was indifferent to the present catalysis.

Wavelength Dependence of Photodissociation of the CS *Ligand from* $[RhCl(CS)(PPh_3)_2]$.—It is plausible that the CS ligand is photodissociated from $[RhCl(CS)(PPh_3)_2]$ in a wavelength-dependent process. The catalyst solution photoirradiated through the L-42 filter neither evolved hydrogen gas nor changed in colour, whereas in the dehydrogenation reaction of cyclohexane a gradual colour change of the solution was observed upon photoirradiation through the UV-34 filter. In order to examine whether the photodissociation of co-ordinated CS is wavelength-dependent or not, the following investigations were made.

In contrast to no UV/VIS spectral changes for the L-42 filter, the absorbance spectrum of the solution photoirradiated through the UV-32 filter increased gradually, with two bands disappearing. Any by-product from the complex would cause the large absorption coefficients.*

The amount of unchanged complex in the solution after photoirradiation was measured using an IR frequency [$\nu_{max}(CS)$ 1305 cm^{-1}] characteristic of CS co-ordination in $[RhCl(CS)(PPh_3)_2]$ (Fig. 4). The contrast of no change and a gradual decrease in $\nu_{max}(CS)$ peak intensity was evident upon photoirradiation through the L-42 and UV-32 filters, respectively.

Let us assume first-order kinetics for the irreversible decomposition of $[RhCl(CS)(PPh_3)_2]$ by excitation of the second lowest-energy band (λ_{max} 339 nm) and photogeneration of $[RhCl(PPh_3)_2]$, which is active for cyclohexane dehydrogenation. Equations (2)–(4) can therefore be derived, where x/µmol is the amount of H_2 evolved during photoirradiation for t min, k/min^{-1} is the rate constant for the decrease in $[RhCl(CS)(PPh_3)_2]$ induced by photodecomposition, n_T is the total turnover number of $[RhCl(CS)(PPh_3)_2]$ throughout the catalyst life, [A]/µmol is the amount of complex remaining in the reactor at the reaction time t, and $[A]_0$/µmol is the amount of complex charged initially (10 µmol). In accordance with equation (4), the

$$dx/dt = kn_T[A] \tag{2}$$

$$n_T[A] = n_T[A]_0 - x \tag{3}$$

$$kt = \ln\{(n_T[A]_0/(n_T[A]_0 - x)\} \tag{4}$$

best fit to the linear relationship $\ln\{n_T[A]_0/(n_T[A]_0 - x)\}$ versus t was obtained for x taken from the time-course plots for hydrogen evolution during the initial 20 min using the UV-32 filter, when $n_T = 3.8$ was adopted. The rate constant k was calculated as 0.059 min^{-1} from the slope. A similar calculation from the data for hydrogen evolution during 1 h using the UV-34 filter gave $n_T = 3.8$.† Almost the same value (3.7) had been obtained experimentally as the total turnover number for the reaction (Fig. 3), suggesting the magnitude of n_T to be reasonable in the present photocatalysis by $[RhCl(CS)(PPh_3)_2]$. Provided that the complex is decomposed without CS co-ordination to regenerate $[RhCl(CS)(PPh_3)_2]$ in the solution, the photogenerated intermediate $[RhCl(PPh_3)_2]$ would be deactivated after 3.8 turnovers of the catalytic cycle of cyclohexane dehydrogenation.

The remaining amount of complex, [A], is depicted as a function of the reaction time t as the dotted line in Fig. 4, adopting $k/\text{min}^{-1} = 0.059$. This coincides well with the gradual decrease in $\nu_{max}(CS)$ peak intensity during the first 30 min. The discrepancy observed between the real and dotted lines in Fig. 4 at longer times would be due to the gradual colour change of the solution, the photons required to be absorbed by $[RhCl(CS)(PPh_3)_2]$ for dehydrogenation being plundered by decomposition products with large absorption coefficients due to an internal filter effect. Bearing in mind this effect, the coincidence between the plots of hydrogen evolution (Fig. 3) and the $\nu_{max}(CS)$ peak intensity (Fig. 4) is quite reasonable.

In summary, the lowest-energy band (λ_{max} 455 nm) of $[RhCl(CS)(PPh_3)_2]$ was indifferent to the CS photodissociation and therefore to cyclohexane dehydrogenation, whereas the second lowest band (λ_{max} 339 nm) was effective in generating the three-co-ordinate intermediate $[RhCl(PPh_3)_2]$, with 3.8 turnovers of the catalytic cycle performed.‡

Quantum-chemical Interpretations for Photodissociation of CO *and* CS *Ligands*.—Photoirradiation of the absorption band with the lowest transition energy in $[RhCl(CO)L_2]$ and the second lowest band in $[RhCl(CS)(PPh_3)_2]$ dissociates the CO and CS ligands, respectively, giving a co-ordinatively unsaturated 14-electron intermediate $[RhCl(PPh_3)_2]$ active for cyclohexane dehydrogenation. Simultaneous decomposition due to photodissociation of the CS ligand occurred for [RhCl-

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* A dimer of the three-co-ordinated intermediate may be mentioned as one possible by-product. Precipitates such as colloidal rhodium formed in the deactivated catalyst solution may also be responsible to some extent.

† The value of k derived for UV-34 as 0.025 min^{-1} is smaller than that for UV-32. It is quite conceivable that part of the incident light effective for CS photodissociation was shielded by using the UV-34 filter.

‡ Thermocatalytic dehydrogenation of cyclooctane, yielding cyclooctene and H_2, was recently revealed with $[RhCl(PPh_3)_3]$ under boiling and refluxing conditions.[19]

Table 3 Occupied and unoccupied molecular orbitals of [RhCl(CO)-$(PPh_3)_2$] and [RhCl(CS)$(PPh_3)_2$]

Complex	Assignment*	Molecular orbital energy/eV
[RhCl(CO)$(PPh_3)_2$]	$3a_2$	−8.0580
	$7b_1$	−8.0724
	$10a_1$	−8.3316
	$5b_2$	−9.6986
	$6b_1$	−11.9487
[RhCl(CS)$(PPh_3)_2$]	$7b_1$	−7.7692
	$3a_2$	−8.0051
	$10a_1$	−8.2727
	$5b_2$	−9.5820
	$6b_1$	−11.6455

* The highest occupied molecular orbitals are assigned to $6b_1$ for both complexes.

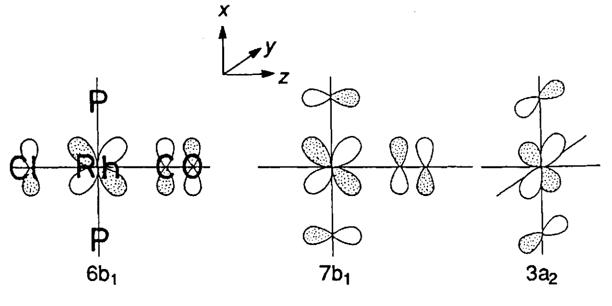

Fig. 5 Molecular orbitals important for electronic transitions in [RhCl(CO)$(PPh_3)_2$]

(CS)$(PPh_3)_2$], as confirmed by IR and UV/VIS spectral analyses. On the contrary, neither the dehydrogenation reaction nor the structural change proceeded upon photoirradiation of the lowest-energy band. We attempted to interpret these different and common features observed for [RhCl(CO)L_2] and [RhCl(CS)$(PPh_3)_2$] by a quantum-chemical method.

The extended-Hückel method has been used as a tool for interpreting chemical phenomena conceptually. We attempted to correlate the ligand photodissociation with the orbital properties of these complexes. The C_{2v} complexes [RhCl-(CO)$(PPh_3)_2$], [RhCl(CS)$(PPh_3)_2$] and [RhCl$(PPh_3)_2$] were modelled with the y axis taken as perpendicular to the molecular plane and z as the C_2 axis, respectively.

Assignment of the electronic spectra of [RhCl(CO)$(PPh_3)_2$] *and* [RhCl(CS)$(PPh_3)_2$]. According to electronic[8a] and magnetic circular dichroism (MCD) spectral[8b] studies, the absorption band at 364 nm of [RhCl(CO)$(PPh_3)_2$] was assigned as the fully allowed m.l.c.t. transition from the occupied rhodium d orbitals to the vacant CO π acceptor orbitals. The excited states of this complex were postulated, however, only by analogy with those of D_{4h} complexes.[8]

We then attempted to assign the absorption bands of both [RhCl(CO)$(PPh_3)_2$] and [RhCl(CS)$(PPh_3)_2$] on the common basis of energy-level differences between the occupied and vacant molecular orbitals and the magnitudes of the transition probabilities. The two low-lying bands of [RhCl(CS)$(PPh_3)_2$] are also ascribed to the allowed m.l.c.t. transitions because of the large molar absorption coefficients (ε_{max} 1450 and 5800 dm^3 mol^{-1} cm^{-1}). Careful attention was paid to the transitions from the highest occupied orbital (HOMO) to unoccupied orbitals for both complexes. The energy levels calculated for the HOMO and lowest unoccupied orbitals (LUMOs) are summarized in Table 3.† These HOMO/LUMO orbital patterns were in good agreement with those of the C_{2v} analogue [RhCl(η^2-P_4)-$(PH_3)_2$].[20,‡]

The HOMO in [RhCl(CO)$(PPh_3)_2$] consisted mainly of Rh(d_{xy}) and CO(π*) orbitals with b_1 symmetry. The transition from HOMO ($6b_1$) to LUMO ($5b_2$) ought to be dipole forbidden, whereas the d–d transition to the second LUMO ($10a_1$) with mixed $d_{x^2-z^2}$ and d_{y^2} orbitals should exhibit low transition probability. Indistinct absorption bands are expected for both. Nevertheless, the transitions from the HOMO ($6b_1$) to the third ($7b_1$) and fourth ($3a_2$) LUMO must be m.l.c.t. and allowed, corresponding to metal-to-carbonyl and metal-to-phosphine charge transfer, respectively. The $7b_1$ and $3a_2$ energy levels spaced closely result in convergence of the transitions from the $6b_1$ orbital into a single band. The longest-wavelength absorption band is therefore assigned to $6b_1 \longrightarrow 7b_1$ and $6b_1 \longrightarrow 3a_2$.

The electronic structure of [RhCl(CS)$(PPh_3)_2$] was almost the same as that of [RhCl(CO)$(PPh_3)_2$] except for the levels $7b_1$ and $3a_2$ (Table 3). Similar reasoning based on transition probabilities indicates that both of these transitions are ascribed to m.l.c.t. excitation. The lowest and the second lowest bands are therefore assigned to the $6b_1 \longrightarrow 3a_2$ and $6b_1 \longrightarrow 7b_1$ transitions, respectively.

Interpretation of the photodissociation of the CO *and* CS *ligands.* As shown in Fig. 5, both the $6b_1$ and $7b_1$ orbitals include the orbital coefficients of Rh(d_{xz}) and CO(π*). The overlapping lobes of Rh(d_{xz}) and C(p_z) of CO(π*) within the molecular plane reflect the bonding interaction between Rh and C in the $6b_1$ orbital. The antibonding interaction between Rh(d_{xz}) and C(p_z) in the $7b_1$ orbital will therefore contribute to dissociate the CO ligand during the $6b_1 \longrightarrow 7b_1$ electronic transition. On the contrary, the $6b_1 \longrightarrow 3a_2$ transition is indifferent to CO dissociation, because the $3a_2$ orbital (Fig. 5) is constituted mainly of Rh(d_{xy}) and P(p_y) and extends perpendicular to the molecular plane.

In order to obtain precise insight into the bonding character, bond orbital populations were analysed for the $7b_1$ orbitals of [RhCl(CO)$(PPh_3)_2$] and [RhCl(CS)$(PPh_3)_2$]. The bonding interactions between the r and s atoms in the molecular orbital $j(j = 7b_1$ in this case) are well represented in terms of $C_{rj}C_{sj}S_{rs}$, where C and S are the molecular-orbital coefficient and the overlap integral, respectively. Table 4 indicates that the atomic orbitals are bonding for Rh(d_{xz})–Cl(p_z) and antibonding for Rh(d_{xz})–C(p_z) and Rh(d_{xz})–P(p_x) in these complexes. Since the extent of antibonding character in the $7b_1$ orbital was larger for Rh–C than for Rh–P in both complexes, the m.l.c.t. transition to $7b_1$ is a plausible cause of the bond cleavage of Rh–CO or Rh–CS, while the Rh–P bond remains intact.

In the case of [RhCl(CS)$(PPh_3)_2$], the lowest-energy band was assigned to the transition to the $3a_2$ orbital with no interaction between Rh–C, whereas the second lowest band was ascribed to the transition to the $7b_1$ orbital, which has antibonding character between Rh and C. The wavelength dependence of the CS dissociation, being photoinduced with not the lowest but the second-lowest band, is thus well understood from the present assignments.

The experimental results on the wavelength dependence of cyclohexane dehydrogenation (Tables 1 and 2) are therefore consistent with these spectral assignments and orbital interpretations.

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† All the examined geometries including the X-ray structures of these complexes gave the order $7b_1 < 3a_2$ for [RhCl(CO)$(PPh_3)_2$] and $3a_2 < 7b_1$ for [RhCl(CS)$(PPh_3)_2$], even though the Rh–C distance was taken as sufficiently short to result in elevation of the $7b_1$ orbital of [RhCl(CO)$(PPh_3)_2$] or the C–S distance long enough to lower the $7b_1$ orbital of [RhCl(CS)$(PPh_3)_2$]. Bond distances of Rh–C (1.740), Rh–Cl (2.333), Rh–P (2.383), C–O (1.110) and C–S (1.650 Å) were adopted, by which the common fragment RhCl$(PPh_3)_2$ was correlated with the ligands CO and CS.

‡ According to Cauletti *et. al.*,[21] the HOMO of [RhCl(CO)$(PMe_3)_2$] is constituted mainly by Rh(d_{y^2}) of a_1 symmetry. Since the lowest-energy band is assigned as the $9a_1$ (HOMO) $\longrightarrow 5b_2$ (LUMO) transition, which brings about an antibonding interaction between Rh(d_{yz}) and C(p_y), CO photodissociation is also well interpreted by this assignment.

Table 4 Mulliken bond orbital populations between the rhodium and ligand atoms of the $7b_1$ orbitals in $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$

Valence orbital	$C_{rj}C_{sj}S_{rs}$	
r *s*	$[RhCl(CO)(PPh_3)_2]$	$[RhCl(CS)(PPh_3)_2]$
$Rh(d_{xz})–C(p_x)$	−0.0602	−0.0562
$Rh(d_{xz})–P(p_z)$	−0.0231	−0.0169
$Rh(d_{xz})–Cl(p_x)$	0.0043	0.0018

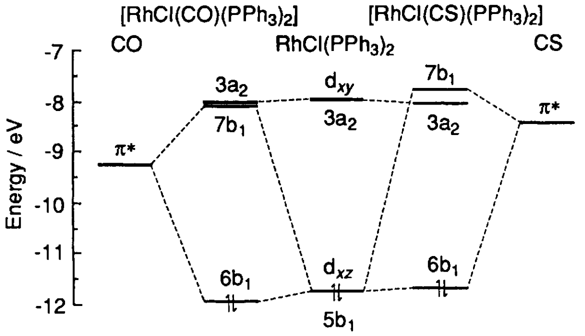

Fig. 6 Interaction diagram of $6b_1$, $3a_2$ and $7b_1$ orbitals important for electronic transitions in $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$

Interpretation of the energy-level difference in $[RhCl(CO)(PPh_3)_2]$ *and* $[RhCl(CS)(PPh_3)_2]$. Fig. 6 shows a simplified EHMO interaction diagram for $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$ built up from the fragments $RhCl(PPh_3)_2$, CO(π*) and CS(π*). The T-shaped $RhCl(PPh_3)_2$ is taken to lie along the *xz* plane. All the $3a_2$ orbitals of $RhCl(PPh_3)_2$, $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$ exhibited almost the same energy, as there was no orbital contribution from CO or CS. On the other hand, the $6b_1$ and $7b_1$ orbitals were greatly affected by CO(π*) or CS(π*) to give different energy levels in $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$. Consequently, the $6b_1 \longrightarrow 7b_1$ and $6b_1 \longrightarrow 3a_2$ transitions in $[RhCl(CO)(PPh_3)_2]$ appeared as a single band, while these two bands were separated in $[RhCl(CS)(PPh_3)_2]$. It is apparent from Fig. 6 that the difference in absorption spectra is caused by the different energy levels of CO(π*) and CS(π*), or originally from the different coulomb integrals of 2p(O) and 3p(S).

In summary, the wavelength dependences of the ligand photodissociation and cyclohexane photodehydrogenation in $[RhCl(CO)(PPh_3)_2]$ and $[RhCl(CS)(PPh_3)_2]$ were well understood by the electronic structures and orbital interactions of these complexes.

Conclusion

The absorption band of $[RhCl(CS)(PPh_3)_2]$ effective for photocatalytic dehydrogenation of cyclohexane was not of the lowest energy (λ_{max} 455 nm) but the second lowest (λ_{max} 339 nm) in contrast to $[RhCl(CO)L_2]$ ($L = PPh_3$, $PEtPh_2$ or PEt_3).

Ligand dissociation of CS from $[RhCl(CS)(PPh_3)_2]$ was confirmed to occur upon photoirradiation of the second lowest band, suggesting that the active species is $[RhCl(PPh_3)_2]$.

On the assumption that $[RhCl(CS)(PPh_3)_2]$ is decomposed irreversibly, $[RhCl(PPh_3)_2]$ was estimated to perform 3.8 turnovers in the catalytic cycle of cyclohexane dehydrogenation.

According to molecular-orbital energy levels and orbital interactions, the lowest band of $[RhCl(CO)(PPh_3)_2]$ and the second lowest band of $[RhCl(CS)(PPh_3)_2]$ were contributed with the $6b_1 \longrightarrow 7b_1$ m.l.c.t. transition, for which Rh–C antibonding character was pointed out, whereas the lowest band of $[RhCl(CS)(PPh_3)_2]$ was assigned to the $6b_1 \longrightarrow 3a_2$ m.l.c.t. transition, being indifferent to the Rh–C interaction.

The observed differences between $[RhCl(CO)L_2]$ and $[RhCl(CS)(PPh_3)_2]$ as regards the absorption spectra and wavelength dependence of photocatalytic activity originate from the energy levels of CO(π*) and CS(π*) or from those of 2p(O) and 3p(S).

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