A New Charge Transfer Complex Involving $ReH_5(PPh_3)_3$

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Introduction

Growing interest in second-sphere coordination of transition metal complexes[1] has prompted us to study their intermolecular interactions both in solution and in the solid state. We have primarily focused on hydrogen bonding and the resulting solvatochromism observed in rhenium polyhydrides,[2] but we now show that a polyhydride complex can also act as an unconventional donor in an intermolecular charge transfer (CT) complex. We report here the spectroscopic solution characterization of a CT complex formed from $ReH_5(PPh_3)_3$ (**1**) and *p*-chloranil (CHL), where the Re complex acts as the electron donor and the hydroquinone form of CHL (tetrachloro-*p*-hydroquinone, $CHLH_2$) as the acceptor. The hydroquinone is formed by reduction of CHL by some of the excess hydride. We report the formation constants and thermodynamic parameters for the interaction. Charge transfer interactions involving π acceptors such as CHL are well-known,[3] but no work appears to have been done with metal hydride complexes as donors.[4]

Results and Discussion

We previously reported[2e,5] that $ReH_5(PPh_3)_2(py)$ (py = pyridine, **2**) shows a solvatochromic intramolecular $n \rightarrow \pi^*$ metal-to-ligand charge transfer (MLCT) band in the UV−visible spectrum. In order to observe an intermolecular CT band, we needed to avoid possible overlap by eliminating the intramolecular CT transition. This suggested study of a related polyhydride complex lacking an intramolecular MLCT. We therefore selected $ReH_5(PPh_3)_3$ (**1**) for this study, a phosphine being a much poorer intramolecular CT acceptor ligand than pyridine. For the intermolecular studies the following series of conventional CT acceptors were examined: I_2, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ), tetracyanoethylene (TCNE), and *p*-chloranil (CHL). Although we observed CT complexation in solution between **1** and all four of these acceptors, we found that, for I_2, DDQ, and TCNE, CT complex formation was followed by an irreversible chemical reaction involving loss of the metal hydrides to give as yet uncharacterized materials.[6] However, in the case of CHL, a π-acceptor of considerably lower electron affinity, not only was a stable CT complex of $CHLH_2$ observed in solution but it could also be isolated in the solid state. The lack of chemical reaction between **1** and $CHLH_2$ allowed further characterization of the outer-sphere interaction in this case.

Unexpected Stability of 1 in Mixed Solvents. Although **1** is very soluble in pure CH_2Cl_2, the complex steadily decomposes in solution over a period of hours. However, **1** was essentially insoluble in nonpolar solvents like *n*-hexanes. We now find that we can dissolve **1** in a mixed-solvent solution of CH_2Cl_2−n-hexanes (5:95 v/v) so that the solubility is entirely adequate for our purposes yet the complex does not decompose at a significant rate. Figure 1 shows the great difference in stability of **1** both in pure CH_2Cl_2 and in mixed CH_2Cl_2−n-hexane (5:95 v/v) solvents as a function of time.

This rather surprising result is probably explained as follows. The CH_2Cl_2 molecules may associate sufficiently with **1** to provide adequate solubility, yet the decomposition is inhibited by the low polarity of the solvent mixture—presumably the first step of the decomposition involves a charge transfer step and the initially formed ions require a polar solvent for stability. In practice, **1** was first dissolved in CH_2Cl_2 and then carefully diluted with *n*-hexanes to give a 5:95 solution. A stock of this mixed-solvent solution was used during all the UV−vis experiments.

UV−Vis Study of the CT Complex between 1 and $CHLH_2$. A 4:1 mixture of **1** and *p*-chloranil in a 5:95 CH_2Cl_2−n-hexanes solution exhibits two new UV−vis bands at 305 and 420 nm, not present in the spectrum of either starting material. In the UV−vis studies, the donor in the same concentration was used in the reference beam to cancel any donor absorption. The 305 nm band increases in intensity with time, while the 420 nm band decreases. We assign the intense band at 305 nm to an intermolecular CT transition resulting from donation from the rhenium center to $CHLH_2$ and assign the 420 nm band to a partially reduced intermediate, e.g., a semihydroquinone. Rhenium polyhydrides like **1** are well-known to transfer H to electrophiles,[7] but we have not yet been able to determine the fate of the oxidized rhenium complex.

Using the continuous variation method (Job's method), we determined that the stoichiometry of the CT complex in solution is 1:1 (Figure 2), but elemental analysis of the solid CT complex indicates a 2:3 ratio of **1**:$CHLH_2$ in the solid state. It is not unusual for the stoichiometry to change on crystallization as a result of the packing being better in a non-1:1 ratio. Redissolving the solid complex results in the reappearance of the intense band at 305 nm in the UV−vis spectrum but not the band at 420 nm.

The ^1H and $^{31}P\{^1H\}$ NMR spectra of the dissolved solid CT complex indicate that no chemical transformation of **1** has

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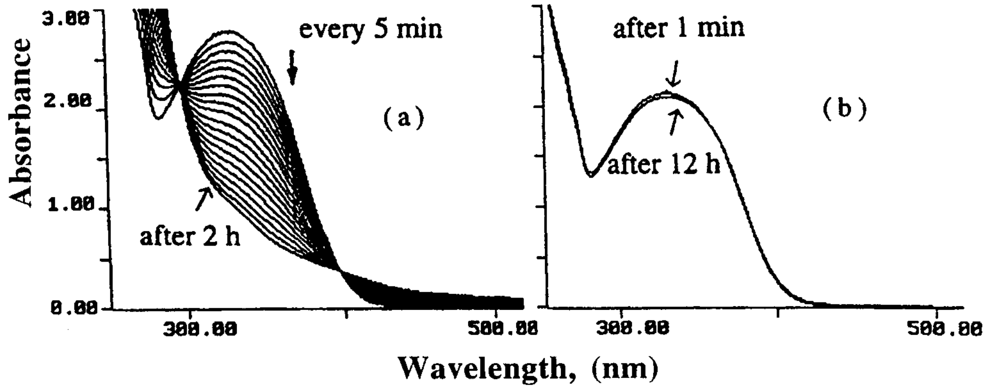

Figure 1. Effect of time on the elctronic absorption spectra of **1**. [**1**] = 4.0 × 10^{-4} mol dm^{-3} (a) in pure CH_2Cl_2 and (b) in CH_2Cl_2−n-hexanes (5:95 v/v).

Table 1. λ_{max} (nm), E_{CT} (eV), Formation Constants (K_{CT}), and Molar Extinction Coefficient (ϵ_{CT}) Values for the CT Molecular Complex of **1** with $CHLH_2$ in CH_2Cl_2−*n*-hexanes (5:95) Mixed Solvent

		K_{CT} (dm^3 mol^{-1})				
λ_{max} (nm)	E_{CT} (eV)	10 °C	15 °C	20 °C	25 °C	$\epsilon_{CT}{}^a$ (dm^3 mol^{-1} cm^{-1})
305	4.05	2700 ± 300	2300 ± 400	1900 ± 500	1600 ± 200	10000 ± 1000

[a] ϵ_{CT} was calculated at 25 °C.

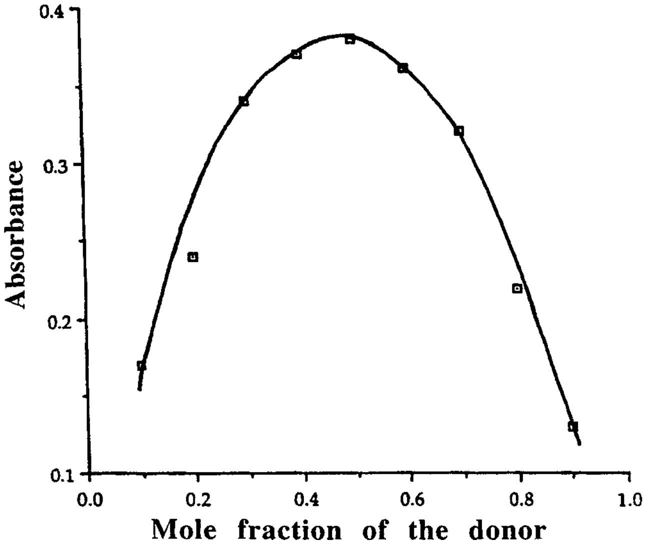

Figure 2. Continuous-variation method for the CT complex between **1** and $CHLH_2$ in CH_2Cl_2−n-hexanes (5:95 v/v). Total concentration = 2.0 × 10^{-4} mol dm^{-3} (λ_{max} = 305 nm).

Table 2. Ionization Potential (IP) of **1** and the Thermodynamic Parameters for the CT Molecular Complex with $CHLH_2$

λ_{max} (nm)	IP (eV)	$-\Delta H°$ (kJ mol^{-1})	$-\Delta S°$ (J mol^{-1})	$-\Delta G°$ (kJ mol^{-1})	$(b/a)^2$
305	10.02	25.8 ± 0.7	25 ± 2	18 ± 2	0.06

occurred. In addition, the main band at 305 nm, observed for the CT complex in solution, does not correspond to the reported wavelengths for the anion radical of CHL, so the latter is not present.[8]

Effect of Time on CT Complexation. It was previously shown that CT complexation can be slow, taking minutes to hours to go to completion.[9] We find here that the formation of the observed CT band at 305 nm for **1**·acceptor displays a time dependency; equilibrium is only reached after 90 min. Conversion from the solvent-separated to the contact donor−acceptor state of CT complexation is often assumed[9] to be responsible, but in our case we looked at the IR spectra of the solid complex and found that the usual CHL carbonyl band at 1680 cm^{-1} was absent and that there was a new OH band at 3400 cm^{-1}. We believe that because we work with excess polyhydride, reduction of the CHL to the $CHLH_2$ hydroquinone form precedes formation of the final CT adduct, accounting for the time dependency for CT complexation, and that the resulting hydroquinone is the true acceptor. IR and NMR data show that complete conversion to the $CHLH_2$ form has taken place after 90 min. In the IR spectrum, complete loss of the ν(CO) bands occurs along with the appearance of a ν(OH) band, while in the proton NMR, an OH resonance appears. This could explain the slow formation of presumed CHL CT complexes seen earlier, because many reductants can reduce CHL to $CHLH_2$.[9e]

Formation Constants and Thermodynamic Parameters for CT Complexation. Tables 1 and 2 show the formation constants and thermodynamic parameters calculated for CT complexation in the temperature range 10−25 °C. Formation constants were calculated using the Benesi−Hildebrand equation.[10]

Typical absorption spectra at 25 °C for the CT complex formed between **1** and $CHLH_2$, recorded 90 min after mixing for varying concentrations of CHL and scanned against the same donor concentration as in the test solutions, are shown in Figure 3. The absence of CHL anion bands supports our belief that we are dealing with a CT complex without ionization, and the formation constants (cf. Table 1) indicate that the CT complexation is strong. The $\Delta H°$ and $\Delta S°$ values calculated from a van't Hoff plot are consistent with strong CT complexation.

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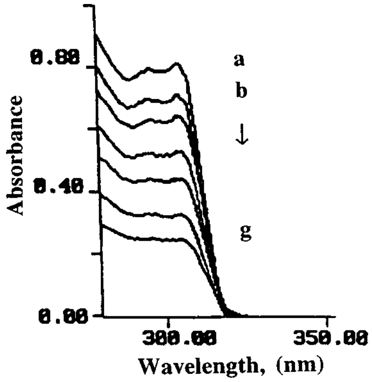

Figure 3. Electronic absorption spectra of the CT complex between **1** and $CHLH_2$ in CH_2Cl_2−n-hexanes (5:95 v/v) at 25 °C. [**1**] = 4.0×10^{-4} mol dm^{-3} (constant); 10^4 [CHL] = (a) 1.6, (b) 1.4, (c) 1.2, (d) 1.0, (e) 0.8, (f) 0.6, (g) 0.4 mol dm^{-3}.

We also find that using the proposed equation[11a] (eq 1) allows

$$(b/a)^2 = -\Delta H°/h\nu \qquad (1)$$

us to estimate Mulliken's ratio (b/a) between the coefficients of the dative bond to the nonbond wave functions ($\Psi_{D^+A^-}$ and Ψ_{D-A}, respectively). The value found is comparable to those previously seen[11] for cases with strong CT complexation. The ionization potential of the donor (**1**) was estimated as 10.02 eV from the energy of the CT transition, using the empirical relation of Aloisi and Pignataro.[12] The value of the ionization potential of **1** is similar to those of amines, which supports the strong CT complexation between **1** and $CHLH_2$.

Conclusion

Although donor−acceptor CT complexes are well recognized with organic donors, we find here that metal hydride complexes are also very effective; the thermodynamic data observed for **1**·$CHLH_2$ indicate strong complexation. CHL reduction is proposed to account for the slow rate of CT complex formation, the resulting hydroquinone being the true acceptor, supported by UV, IR, and NMR spectroscopy. Reduction of the acceptor may need to be considered in other cases[9] of slow ($t_{1/2}$ = h) CT complex formation in the literature.

Experimental Section

General Procedures. $ReH_5(PPh_3)_3$ was prepared according to literature methods.[13] Chloranil was purchased from Aldrich and used without further purification. All solvents were of spectroscopic grade (J. T. Baker). ^1H and ^{31}P NMR spectra were recorded on a GE-Omega 300 MHz spectrometer (121.8 MHz for ^{31}P) and were referenced to an internal residual solvent peak (^1H) and external 85% phosphoric acid (^{31}P). UV−vis spectra were recorded on a Cary 3E Varian spectrophotometer with a temperature-controlled cell holder. IR spectra were recorded on a Midac M1200 FT-IR spectrometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA.

Preparation of the Solid CT Complex between 1 and *p*-Chloranil. Equimolar amounts (0.5 mmol) of **1** and the *p*-chloranil were dissolved separately in a minimum volume of CH_2Cl_2. A 10-fold volume of *n*-hexane was added carefully to each solution, and the two solutions were combined and refluxed for 1 h, during which the solution changed from yellow to brown and a brown precipitate formed, which was filtered off and washed with copious amounts of *n*-hexanes. The brown solid was recrystallized from CH_2Cl_2−*n*-hexane and dried in vacuo (yield 20−40%). ^1H NMR (25 °C, CD_2Cl_2): −5.32 ppm (q, 5H), 6.1 ppm (br s, 2H), 6.8−8.5 ppm (br m, 45H). $^{31}P\{^1H\}$ NMR (25 °C, CD_2Cl_2): 33.9 ppm. FT-IR (Nujol, cm^{-1}): ν(OH) 3394, ν(Re−H) 1913. Elemental analysis indicates a **1**:$CHLH_2$ ratio of 2:3. Anal. Calcd (found) for $C_{63}H_{53}P_3O_3Cl_6Re$: C, 55.99 (55.25); H, 3.92 (3.96); Cl, 15.78 (15.15).

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