# Synthesis and Spectroscopic Properties of 1,2-Diiminetricarbonylrhenium(I)chloride Complexes with Aliphatic Diimines (or 1,4-Diaza-1,3-butadienes) as Ligands

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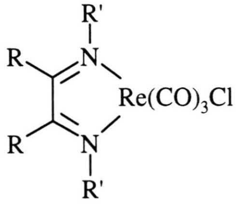
Re(1,2-diimine)$(CO)_3Cl$ complexes with the aliphatic bidentate ligands diiminosuccinodinitrile (DISN), benzilbisanile (BEAN), bisacetylbisanile (BABA), and benzildiimine (BEDIM) are reported. The compounds show Re(I) to $\pi^*$(diimine) metal-to-ligand charge transfer (MLCT) absorptions in the visible spectral region. The energy of these MLCT-transitions decreases in the series BABA > BEDIM > BEAN > DISN, depending on the $\pi^*$ acceptor properties of the coordinated diimine ligands. The maxima of these CT bands undergo a solvent-dependent shift (negative solvatochromism), which indicates a partial charge redistribution in the excited state. The compounds are not photoluminescent at room temperature and 77 K.

## 1. Introduction

In contrast to Re(1,2-diimine)$(CO)_3Cl$ complexes with polypyridyl ligands (e. g. 2,2'-bipyridine) as diimines [1 - 4], the corresponding compounds with delocalized diimines such as substituted acenaphthenequinone diimine [5] or *ortho*-phenylene diimines [6] (*ortho*-benzoquinone diimines) as ligands are characterized by the absence of any luminescence. This lack of emission is apparently related to the low energy of the optical metal-to-ligand charge transfer (MLCT) transition of these complexes. Similar properties could be expected for Re(1,2-diimine)$(CO)_3Cl$ compounds with aliphatic 1,2-diimines (1,4-diaza-1,3-butadienes, DAB) as ligands, because they also provide $\pi^*$ orbitals at rather low energies [7]. We explored this possibility and selected the following complexes for the present study:



| DAB | R | R' |
|---|---|---|
| BABA | $CH_3$ | $C_6H_5$ |
| BEAN | $C_6H_5$ | $C_6H_5$ |
| BEDIM | $C_6H_5$ | H |
| DISN | CN | H |

These compounds are accessible by the reaction of $Re(CO)_5Cl$ with the corresponding 1,2-diimine ligands. In the case of BEDIM, the 1,2-diimine is prepared *in situ* by reaction of benzil-bis-trimethylsilylimine with ethanol. Some data on substituted Re(DAB)$(CO)_3X$ derivatives with DAB = 1,4-diphenyl-2,3-dimethyl-1,4-diaza-1,3-butadiene or 1,4-bis-*p*-tolyl-1,4-diaza-1,3-butadiene and X = Cl, Br or trifluoromethanesulfonate have previously been reported [8].

A variation of the substituents R and R' is expected to modify the MLCT energies. Such effects have been observed for Mo(1,2-diimine)$(CO)_4$ [9] and [Fe(1,2-diimine)$_3$]$^{2+}$ [10] complexes. Since the substituents of previously studied aliphatic 1,2-diimines were mostly alkyl and aryl groups, only moderate effects were found. In contrast to the results for these substituents, we expected to observe a more severe perturbation by introducing R = CN as a strongly electron withdrawing group. Diiminosuccinodinitrile (DISN) was already employed as ligand in other coordination compounds [11].

## 2. Experimental

### 2.1. *Materials and instrumentation*

$Re(CO)_5Cl$ and organic starting compounds were commercially available from Aldrich and used without further purification. All solvents were spectrograde. UV-Vis spectra were recorded on a Kontron Uvikon 860 or 960 absorption spectrophotometer. IR spectra were measured

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on a Beckman Acculab 6 spectrometer. Mass spectra were obtained using a Finnigan MAT 95 and Varian MAT 311 equipment. $^1$H NMR data were recorded on a Bruker AC 250 (250 MHz) spectrometer with TMS as internal standard. For checking out the emission properties, a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier was used.

### *2.2. Synthesis of the Re(DAB)(CO)$_3$Cl complexes*

*Re(DISN)(CO)$_3$Cl:* Diiminosuccinodinitrile (DISN) was synthesized by oxidation of diaminosuccinodinitril (DAMN) with dichlorodicyano-*ortho*-benzoquinone (DDQ) [12]. A suspension of 181 mg (0.5 mmol) of Re(CO)$_5$Cl and the stoichiometric amount of DISN was refluxed for 20 min under argon protection in 10 ml of dry toluene. After cooling down to r. t., 15 ml of *n*-hexane was added. The residue was separated by filtration, washed twice with ether and dried under vacuum. Yield: 140 mg (0.34 mmol, 67%).

Analysis for $C_7H_2ClN_4O_3Re$
Calcd C 20.42 H 0.49 N 13.61%,
Found C 20.02 H 0.65 N 13.96%.

MS (FD$^+$, $CH_2Cl_2$): *m/z*(%): 410 (46.3); 412 (100.0); 414 (19.7). IR(KBr): $\tilde{\nu}$(cm$^{-1}$): 3230 (N-H), 2040, 1950, 1915 (CO-stretch, *fac*-Re(CO)$_3$Cl-fragment).

*Re(BEDIM)(CO)$_3$Cl:* Benzil-bis-trimethylsilylimine was prepared from benzil and sodium-bis-trimethylsilylamide following the literature route [13]. A solution of 160 mg (0.5 mmol) of benzil-bis-trimethylsilylimine in 10 ml of toluene was slowly added to a stirred suspension of 181 mg (0.5 mmol) of Re(CO)$_5$Cl in a mixture of toluene (10 ml) and ethanol (2 ml). When benzil-bis-trimethylsilylimine was completely added, the reaction mixture was heated to reflux for 15 min and then cooled down to r. t. The metal complex was precipitated by addition of 50 ml of *n*-hexane. The crude product was purified by chromatography over silica gel with acetonitrile as eluent. Yield: 188 mg (0.37 mmol, 73%).

Analysis for $C_{17}H_{12}ClN_2O_3Re$
Calcd C 45.35 H 4.36 N 4.07%,
Found C 45.27 H 3.87 N 4.32%.

MS (FD$^+$, $CHCl_3$): *m/z*(%): 612 (46.3); 614 (100.0); 616 (22.2). $^1$H NMR($CDCl_3$): $\delta$ (ppm) 11.04 (2H, s, NH); 7.54-7.29 (10H, m, $C_6H_5$). IR(KBr): $\tilde{\nu}$(cm$^{-1}$): 2025, 1930, 1905 (CO-stretch, *fac*-Re(CO)$_3$Cl-fragment).

*Re(BEAN)(CO)$_3$Cl:* Benzilbisanile was obtained according to published procedures [14]. A suspension of 181 mg (0.5 mmol) of Re(CO)$_5$Cl and 180 mg (0.5 mmol) of BEAN in 10 ml of toluene was heated to reflux for 10 min. After cooling down to r. t., 50 ml of *n*-hexane was added. The brown precipitate was isolated by filtration and dried under reduced pressure. Since Re(BEAN)(CO)$_3$Cl slowly decomposes in most solvents, only freshly prepared solutions were investigated. Yield: 246 mg (0.38 mmol, 74%).

Table I. Absorption data of the Re(DAB)(CO)$_3$Cl complexes in acetonitrile solution at 298 K.

| R | R' | $\lambda_{max}$ [nm] ($\varepsilon$ [l/(mol · cm)]) | | |
|---|---|---|---|---|
| CN | H | 543 (6100) | 296 (6400) | 223 (12000) |
| $C_6H_5$ | H | 463 (6300) | 312 sh (5800) | 251 sh (9400) |
| $C_6H_5$ | $C_6H_5$ | 474 (4400) | 316 sh (4100) | 255 sh (11000) |
| $CH_3$ | $C_6H_5$ | 426 (3700) | 313 sh (2700) | 251 sh (7400) |

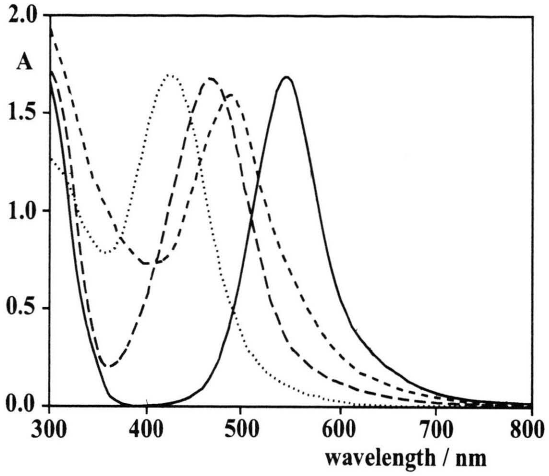

Fig. 1. Electronic absorption spectra of the Re(DAB)-(CO)$_3$Cl complexes in acetonitrile; DISN (—), c = 2.8 × 10$^{-4}$ M; BEDIM (– – –), c = 2.7 × 10$^{-4}$ M; BEAN (- - -), c = 3.6 × 10$^{-4}$ M; BABA (···), c = 4.6 × 10$^{-4}$ M, 1-cm cells.

Analysis for $C_{29}H_{20}ClN_2O_3Re$
Calcd C 52.29 H 3.03 N 4.21%,
Found C 51.54 H 3.40 N 4.07%.

MS (FD$^+$, acetone): *m/z* (%): 664 (43.3); 665 (16.2); 666 (100.0); 667 (22.4); 668 (25.6); 669 (5.6). $^1$H NMR (d$^6$-acetone): $\delta$ (ppm) 7.7 - 7.8 (m, $C_6H_5$). IR(KBr): $\tilde{\nu}$(cm$^{-1}$): 3061 (C-H stretch); 2019, 1927, 1907 (CO strech, *fac*-Re(CO)$_3$Cl-fragment); 1589, 1482 (phenyl rings).

*Re(BABA)(CO)$_3$Cl:* The rhenium bisacetylbisanile complex Re(BABA)(CO)$_3$Cl was obtained according to the literature method [9].

## 3. Results and Discussion

The compounds Re(DAB)(CO)$_3$Cl with DAB = BABA, BEAN, BEDIM, and DISN are characterized by an intense absorption in the visible spectral region (Fig. 1, Table I). Depending on the ligand and the solvent used, a shoulder appears occasionally on the long-wavelength side of this band. In analogy to many other Re(1,2-diimine)$(CO)_3Cl$ complexes, the chromophoric absorption is assigned to a MLCT transition terminating at $\pi^*$ orbitals of the diimine ligand. The MLCT energies of Re(DAB)$(CO)_3Cl$ decrease in the series BABA > BEDIM > BEAN > DISN. This variation can be rationalized by the following considerations: Substitution at the carbon atoms of the imino groups has the strongest influence. The electron-donating nature of $CH_3$ decreases the $\pi$-accepting strength of the diimine. Accordingly, Re(BABA)$(CO)_3Cl$ shows its MLCT absorption at rather short wavelength. On the contrary, the electron-withdrawing nitrile group shifts the MLCT band of Re(DISN)$(CO)_3Cl$ to much longer wavelength. The MLCT absorptions of Re(DAB)$(CO)_3Cl$ with DAB = BEDIM and BEAN, which carry phenyl substituents at the imino carbon atom, appear at intermediate wavelengths. The substitution of hydrogen (BEDIM) at the imino nitrogen by phenyl (BEAN) has a relatively small effect on the MLCT energy. However, these phenyl groups are expected to have a nearly orthogonal orientation to the 1,4-diaza-1,3-butadiene plane. It follows that they do not contribute significantly to the $\pi$-conjugation of the diimine moiety.

Generally, the metal-to-ligand charge transfer (MLCT) absorption of Re(diimine)$(CO)_3Cl$ complexes undergoes a red shift with decreasing solvent polarity. This negative solvatochromism becomes smaller with increasing $\pi$-acceptor strength of the diimine owing to a reduced charge transfer character in the MLCT transition. This is a consequence of stronger mixing of $d\pi$ and $\pi^*$(DAB) orbitals by $\pi$ back bonding. Indeed, the extent of charge transfer in the MLCT transition decreases in the series Re(DAB)$(CO)_3Cl$ with DAB = BABA > BEDIM > BEAN > DISN, as indicated by the variation of the solvatochromic behaviour (Fig. 2, Table II). The slope of the plots displayed in Fig. 2 decreases in the same order from 3430 to 2860, 2500 and 490 $cm^{-1}$, respectively. Since the $d\pi$ donor and $\pi^*$(diimine) acceptor orbitals are apparently almost equally delocalized between metal and ligand, Re(DISN)$(CO)_3Cl$ is only slightly solvatochromic with only minor charge transfer character.

Table II. Solvent dependence of the charge transfer absorption band of the Re(DAB)$(CO)_3Cl$ complexes at 298 K.

| Solvent | $E^*_{MLCT}$ [15] | $\lambda_{max}$ [nm] DISN | BEAN | BEDIM | BABA |
|---|---|---|---|---|---|
| Toluene | 0.30 | — | 509 | 502 | 470 |
| Benzene | 0.34 | 556 | 508 | 502 | 468 |
| Chloroform | 0.42 | 542 | 497 | 497 | 459 |
| THF | 0.59 | 540 | 496 | 474 | 447 |
| Dichloromethane | 0.67 | 543 | 494 | 491 | 425 |
| DMF | 0.95 | — | 462 | 454 | 421 |
| Acetonitrile | 0.98 | 543 | 474 | 463 | 426 |

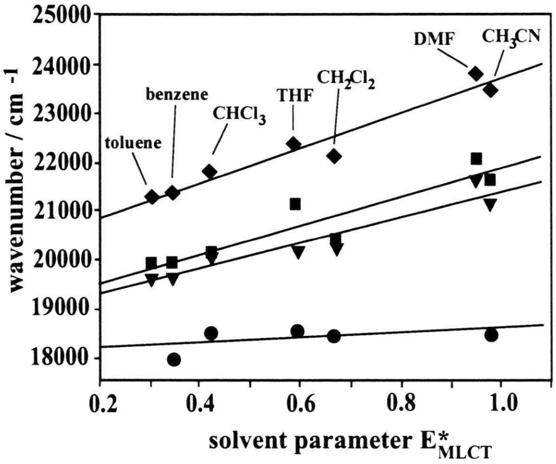

Fig. 2. Correlation between the MLCT energies of the Re(DAB)$(CO)_3Cl$ complexes in different solvents and the $E^*_{MLCT}$ solvent parameter [15] (● DISN, ◆ BABA, ■ BEDIM, ▼ BEAN).

The complexes Re(DAB)$(CO)_3Cl$ with DAB = BABA, BEDIM, BEAN, and DISN are not luminescent in contrast to those containing 2,2'-bipyridyl and related diimine ligands. The reasons for the absence of this luminescence are not quite clear yet, but most probably associated with the low energy of the corresponding MLCT states, which facilitates radiationless deactivation to the electronic ground state [16].

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