# Non-Luminescent 1,2-Diiminetricarbonylrhenium(I) Chloride Complexes – Synthesis, Electrochemical and Spectroscopic Properties of Re(DIAN)(CO)$_3$Cl with DIAN = *p*-Substituted Bis(arylimino)acenaphthene

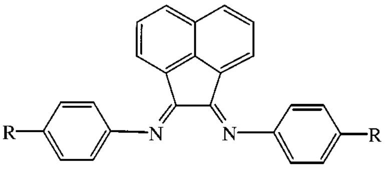
**Günther Knör,*[a] Markus Leirer,[a] Tia E. Keyes,[b] Johannes G. Vos,[c] and Arnd Vogler*[a]**

**Keywords:** Rhenium / Diimine ligands / Charge transfer / Solvatochromism / Substituent effects

Re(1,2-diimine)(CO)$_3$Cl compounds containing the *p*-substituted bis(arylimino)acenaphthene derivatives DIAN-R with R = H, Me, OMe, Br, and Cl were prepared and characterized. The diimine ligands of this series provide unoccupied orbitals at rather low energies and display a pronounced π-accepting strength. This feature determines the electrochemical and spectroscopic properties of the Re(DIAN-R)(CO)$_3$Cl complexes. All compounds show rhenium(I) to π*(diimine) metal-to-ligand charge transfer (MLCT) absorptions in the visible spectral region. The maxima of these CT bands systematically shift upon modification of the substituents R and are sensitive to variations of the solvent polarity (negative solvatochromism). Re(DIAN-R)(CO)$_3$Cl complexes are non-luminescent both in fluid solution at 298 K and in solvent glass at 77 K.

## Introduction

Electronic spectra of complexes of the composition Re$^I$(1,2-diimine)(CO)$_3$(L) with L = e.g. halide, CO, phosphane or amine have been studied extensively in recent years.[1,2] These efforts were stimulated by the luminescence behaviour of such compounds, which are characterized by long-lived $^3$MLCT (triplet metal-to-ligand charge transfer) states. The excited state properties can be utilized for a variety of different purposes such as electron transfer, energy transfer, photochemical CO$_2$ reduction and the development of optical sensors.[1–4] While mainly polypyridines have been used as 1,2-diimines, ligands with imino groups that are not part of a heterocyclic aromatic system were largely neglected. Since the latter ligands provide π* orbitals at rather low energies,[5–7] the corresponding MLCT absorptions are shifted to much longer wavelengths. Although such complexes may be no longer luminescent owing to the low energy of the MLCT states (energy gap law[8]), they nevertheless could show other useful properties. For example, the charge transfer behaviour might be exploited for nonlinear optical (NLO) devices.[9] For several other applications (e.g. NIR absorbers) photochemical stability is a desireable feature. On the contrary, long-lived excited states tend to participate in bimolecular processes such as the generation of singlet oxygen, which promote photochemical decomposition. It follows that the absence of luminescence from Re$^I$(1,2-diimine)(CO)$_3$(L) complexes may present advantages in certain applications. We explored this possibility and selected substituted bis(arylimino)acenaphthenes (DIAN-R)[10] as ligands for the present study (Scheme 1).



Scheme 1. Structural formula of the DIAN-R ligands

These compounds are accessible by standard organic synthesis and can be systematically modified by a variation of the substituents R at the *para* position of their phenyl groups. Owing to the terminal imino groups, the π* energies of these ligands should be rather low. Moreover, since the diimine function is attached to the larger delocalized π-electron system of the acenaphthene moiety, it may be expected to display a high π-accepting strength.

## Results and Discussion

The complexes Re$^I$(DIAN-R)(CO)$_3$Cl with R = H, Me, OMe, Br, and Cl have been prepared and characterized by elemental analysis and a variety of spectroscopic techniques. All results are consistent with a pseudooctahedral structure of the compounds and a facial (*fac*) coordination of the carbonyl ligands in agreement with previous studies of other complexes of this type.[1,2]

The absorption spectra of Re$^I$(DIAN-R)(CO)$_3$Cl show various bands below 400 nm and a pronounced absorption in the visible spectral region (Figure 1, Table 1). The shorter wavelength bands include certainly intraligand (IL) transitions of the diimines, which absorb as free ligands in the same spectral region. The longer-wavelength band dominating the visible spectrum is assigned to the MLCT transition from rhenium(I) to the π* orbitals of DIAN-R. The charge

---

[a] Institut für Anorganische Chemie, Universität Regensburg, 93040 Regensburg, Germany
[b] School of Chemistry, Dublin Institute of Technology, Kevin Street, Dublin 8, Ireland
[c] School of Chemical Sciences, Dublin City University, Glasnevin, Dublin 9, Ireland

© WILEY-VCH Verlag GmbH, D-69451 Weinheim, 2000 1434–1948/00/0404–0749 $ 17.50+.50/0

transfer character of this transition is supported by the fact that the corresponding absorption maxima of all complexes shift to higher energies with increasing solvent polarity (negative solvatochromism). This effect can be evaluated quantitatively by applying different solvent polarity scales such as the empirical $E_T$ parameters[11] or the $E^*_{MLCT}$ values[12] (Figure 2). Generally a linear correlation is observed, although smaller deviations are noticed as previously reported for related complexes.[12] The substituent R of the DIAN-R ligands should also affect the MLCT energy. However, the $\pi^*$ energy of the ligands is only slightly dependent on the nature of R because the phenyl groups at the nitrogen atoms are not coplanar with the diimine moiety.[10] Indeed, a Hammett plot (Figure 3) shows a linear correlation of the $\sigma_p$-parameter with the MLCT energies, but the slope (930 $cm^{-1}$) is rather small. A much stronger dependence on *p*-substituents has been observed for *meso*-tetraphenylporphyrins.[13] In this case the phenyl groups at the *meso* positions are also not coplanar with the porphyrin plane, but the $\pi\pi^*$ transitions are more significantly shifted.

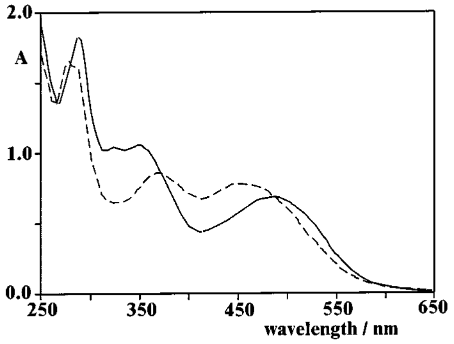


Figure 1. Electronic absorption spectra of Re(DIAN-R)$(CO)_3$Cl with R = OMe (– – –) and R = Cl (—) in acetonitrile solution; $c = 1.3 \cdot 10^{-4}$ M, 1-cm cells

Table 1. UV-VIS spectroscopic data of the Re(DIAN-R)$(CO)_3$Cl complexes in acetonitrile solution at 298 K

| R | $\lambda_{max}$ [nm] (ε [L/(mol·cm)]) | | | | |
|---|---|---|---|---|---|
| H | 474 (5100) | 348 (7600) | 320 (8000) | 286 (13400) | 223 (44800) |
| Me | 470 (5700) | 355 (8400) | 322 (7400) | 286 (14200) | 219 (57100) |
| OMe | 451 (6600) | 370 (7200) | – | 285 (13500) | 223 (51200) |
| Br | 481 (5600) | 350 (8600) | 323 (8400) | 288 (14800) | 223 (65400) |
| Cl | 481 (5100) | 349 (7700) | 324 (7600) | 288 (13300) | 224 (54200) |

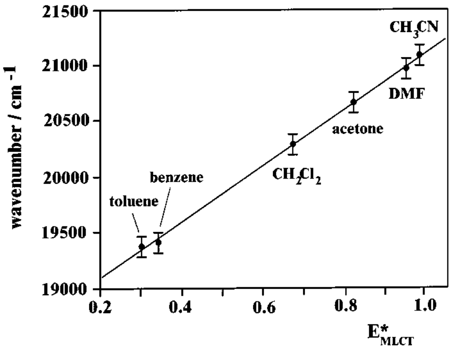


Figure 2. Correlation between the energy of the charge transfer transition of Re(DIAN-H)$(CO)_3$Cl and the solvent parameter $E^*_{MLCT}$ [12]

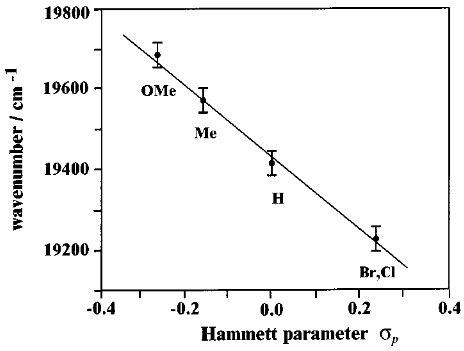


Figure 3. Substituent effects on the MLCT absorption maxima of Re(DIAN-R)$(CO)_3$Cl complexes in benzene at 298 K

To obtain further information about the π-acceptor properties of the bis(arylimino)acenaphthene ligands, electrochemical and spectroelectrochemical experiments were performed with the unsubstituted derivative $Re^I$(DIAN-H)$(CO)_3$Cl. The first reduction of this compound occurs in cyclic voltammetry as a reversible one-electron step at a redox potential of −0.65 V vs SCE at 298 K in dry DMF containing 0.1 M tetraethylammonium tetrafluoroborate. The reversible spectral changes associated with this process suggest that the first reduction takes place at the DIAN-H ligand. An approximate value of +1.4 V vs SCE can be estimated for the corresponding reaction in the MLCT excited state. These redox potentials reflect the much higher π-acceptor strength of bis(phenylimino)acenaphthene compared to many other frequently used diimine ligands. For example, the compound $Re^I$(bpy)$(CO)_3$Cl (bpy = 2,2-bipyridyine) displays its first ligand based reduction at the rather negative potential of −1.64 V vs SCE (−1.74 V vs ferrocene/ferrocenium[14]) in the electronic ground state. With exception of the initial reduction wave, the voltammetric response obtained for $Re^I$(DIAN-H)$(CO)_3$Cl between 1.7 and −2.0 V vs SCE indicates the occurrence of chemical reactions coupled to the heterogeneous electron transfers. Recently, a complex sequence of fragmentation and dimerization steps has been proposed for a related $Re^I$(1,2-diimine)$(CO)_3$Cl species under similar conditions.[15] A detailed investigation of such processes, however, was not attempted in the present study.

The complexes $Re^I$(DIAN-R)$(CO)_3$Cl do not show any luminescence at 298 K or 77 K. In general, the emission quantum yields of $Re^I$(1,2-diimine)$(CO)_3$(L) decrease with decreasing energy of the emitting MLCT state. This behaviour has been attributed to the energy gap law.[1,2,5,8] The same explanation may also apply to the absence of emission from the $Re^I$(DIAN-R)$(CO)_3$Cl series, since these compounds show their MLCT absorption at distinctly longer wavelength compared to corresponding complexes with polypyridyls as diimine ligands. However, it is surprising that $Re^I$(DIAN-R)$(CO)_3$Cl complexes do not emit at all, while $[Os(bpy)_3]^{2+}$ and some of its derivatives are luminescent, although their MLCT absorptions appear at similar or longer wavelengths[2] than those of $Re^I$(DIAN-R)$(CO)_3$Cl. Therefore it cannot be excluded that other effects contribute to the lack of emission from $Re^I$(DIAN-R)$(CO)_3$Cl.

A decrease of the π* energy of the diimine ligand usually is accompanied by a red-shift of the MLCT absorption. Moreover, a large contribution of the N atomic orbitals to the π* acceptor orbital causes a large overlap stabilization and may lead to an increased mixing of rhenium dπ and ligand Lπ* orbitals.[6] Indeed, the solvatochromism of the $Re^I$(DIAN-R)$(CO)_3Cl$ complexes (average slope = 2860 $cm^{-1}$) is significantly smaller than that of complexes with polypyridyl ligands[2] [e.g. $Re^I(bpy)(CO)_3Cl$, slope = 3120 $cm^{-1}$], since the "MLCT" transition of the DIAN complexes has less CT character owing to an enhanced delocalization of the participating orbitals. In contrast to polypyridyl complexes, the MLCT transitions of DIAN complexes occur then between strongly bonding dπ and antibonding Lπ* orbitals. The concomittant geometrical changes and the associated skeletal vibrations could facilitate an efficient nonradiative decay.[5,6]

Moreover, a further effect may account for the absence of luminescence from $Re^I$(DIAN-R)$(CO)_3Cl$. The increased back-bonding results in a stabilization of the dπ orbitals, which may drop below the π-orbitals of the chloride ligand.[16] The $Cl^- \rightarrow L\pi^*$ diimine LLCT (ligand-to-ligand charge transfer) and MLCT transitions could now be of comparable energies. If the LLCT state is not emissive, its population might provide a new efficient channel for radiationless deactivation.

## Experimental Section

**Materials and Instrumentation:** All starting materials were commercially available and used without further purification. The bis(arylimino)acenaphthene ligands were obtained from acenaphthene quinone and the corresponding *p*-substituted anilines.[10] – Electronic absorption spectra were recorded on a Kontron Uvikon 932 double-beam spectrophotometer and a Shimadzu 3100 UV-VIS/NIR spectrophotometer. – Emission properties were investigated with a Hitachi 850 spectrofluorometer equipped with a Hamamatsu 928 photomultiplier. – The electrochemistry was conducted at a teflon shrouded glassy carbon electrode with SCE reference and platinum mesh auxillary electrode in dry DMF containing 0.1 M tetraethyltetrafluoroborate as electrolyte. – Spectroelectrochemical measurements were carried out with equipment described elsewhere.[17] – IR spectra were measured on a Beckman Acculab 6 spectrometer. – Mass spectra were obtained using Finnigan MAT 95 and Varian MAT 311 instruments. – $^1$H-NMR data were recorded with a Bruker AC 250 (250 MHz) spectrometer with TMS added as internal standard.

**Preparation of the Complexes Re(DIAN-R)$(CO)_3Cl$:** A suspension of 181 mg (0.50 mmol) of $Re(CO)_5Cl$ and the equimolar amount of the corresponding bis(arylimino)acenaphthene in 10 mL of toluene was refluxed for 30 min. After cooling the reaction mixture to room temperature and addition of *n*-hexane, the products were obtained as red microcristalline precipitates. The compounds with R = Br and Cl were further purified by chromatography on silica gel using dichloromethane as eluent.

**Re(DIAN-H)$(CO)_3$Cl:** Yield 289 mg (0.45 mmol, 91%). – IR (KBr): $\tilde{\nu}$ = 3050 $cm^{-1}$ (CH), 2020, 1915, 1890 (CO), 1580 (aromatic rings). – $^1$H NMR ($CDCl_3$): δ = 8.06 (d, 2 H), 7.00 (d, 2 H), 7.74–7.36 (m, 12 H). – MS ($FD^+$, $CHCl_3$): *m/z* (%): 638 (100) [$M^+$]. – $C_{27}H_{16}ClN_2O_3Re$ (638.10): calcd. C 50.82, H 2.53, N 4.39; found: C 50.35, H 2.82, N 4.11.

**Re(DIAN-Me)$(CO)_3$Cl:** Yield 306 mg (0.46 mmol, 92%). – IR (KBr): $\tilde{\nu}$ = 3030, 2920 $cm^{-1}$ (CH), 2040, 1930, 1890 (CO), 1630, 1600 (aromatic rings). – $^1$H NMR ($CDCl_3$): δ = 8.09 (d, 2 H), 7.09 (d, 2 H), 7.56–7.28 (m, 10 H), 2.52 (s, 6 H). – MS ($FD^+$, $CHCl_3$): *m/z* (%): 666.0 (100) [$M^+$]. – $C_{29}H_{20}ClN_2O_3Re$ (666.15): calcd. C 52.29, H 3.03, N 4.20;. found: C 52.34, H 3.33, N 4.12.

**Re(DIAN-OMe)$(CO)_3$Cl:** Yield 289 mg (0.45 mmol, 91%). – IR (KBr): $\tilde{\nu}$ = 3070, 3015, 2980, 2850 $cm^{-1}$(CH), 2040, 1920, 1890 (CO), 1630, 1600 (aromatic rings). – $^1$H NMR ($CDCl_3$): δ = 8.06 (d, 2 H), 7.17 (d, 2 H), 7.90–7.36 (m, 8 H), 7.19–7.10 (m, 2 H), 3.94 (s, 6H). – MS ($FD^+$, $CHCl_3$): *m/z* (.%): 698.0 (100) [$M^+$]. – $C_{29}H_{20}ClN_2O_5Re$ (698.15): calcd. C 49.89, H 2.89, N 4.01; found: C 48.73, H, 2.96, N, 3.81.

**Re(DIAN-Br)$(CO)_3$Cl:** Yield 111 mg (0.14 mmol, 28%). – IR (KBr): $\tilde{\nu}$ = 2020, 1915, 1885 $cm^{-1}$ (CO). – $^1$H NMR ($CDCl_3$): δ = 8.11 (dd, 2 H), 7.10 (dd, 2 H), 7.78–7.23 (m, 10 H). – MS ($FD^+$, $CHCl_3$): *m/z* (%): 796.0 (100) [$M^+$]. – $C_{27}H_{14}Br_2ClN_2O_3Re$ (795.89): calcd. C 40.75, H 1.77, N 3.52; found: C 40.78, H 2.36, N, 3.20.

**Re(DIAN-Cl)$(CO)_3$Cl:** Yield 312 mg (0.44 mmol, 88%). – IR (KBr): $\tilde{\nu}$ = 3050, 2960, 2920 $cm^{-1}$ (CH), 2030, 1920, 1890 (CO), 1620, 1595 (aromatic rings). – $^1$H NMR ($CDCl_3$): δ = 8.06 (dd, 2 H), 7.10 (dd, 2 H), 7.70–7.31 (m, 10 H). – MS ($FD^+$, $CHCl_3$): *m/z* (%): 706.0 (100) [$M^+$]. – $C_{27}H_{14}Cl_3N_2O_5Re$ (706.98 ): calcd. C 45.87, H 2.00, N 3.96; found: C 46.12, H 2.78, N 3.48.

## Acknowledgments

Support for this research by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. A. L. Spek is acknowledged for supplementary material on the structures of the DIAN-R ligands.

---

[1] D. J. Stufkens, A. Vlcek, Jr., *Coord. Chem. Rev.* **1998**, *177*, 127–179.

[2] [2a] D. M. Roundhill, *Photochemistry and Photophysics of Metal Complexes*, Plenum Press, New York, **1994**. – [2b] K. Kalyanasundaram, *Photochemistry of Polypyridine and Porphyrin Complexes*, Academic Press, London, **1992**.

[3] H. Hori, F. P. A. Johnson, K. Koike, O. Ishitani, T. Ibusuki, *J. Photochem. Photobiol. A: Chem.* **1996**, *96*, 171–174.

[4] I. Klimant, P. Belser, O. S. Wolfbeis, *Talanta* **1994**, *41*, 985–991.

[5] A. J. Lees, *Chem. Rev.* **1987**, *87*, 711–743.

[6] D. J. Stufkens, *Coord. Chem. Rev.* **1990**, *104*, 39–112.

[7] J. Reinhold, R. Benedix, P. Birner, H. Hennig, *Inorg. Chim. Acta* **1979**, *33*, 209–213.

[8] J. V. Caspar, T. J. Meyer, *J. Phys. Chem.* **1983**, *87*, 952–957.

[9] [9a] B. J. Coe, S. Houbrechts, I. Asselberghs, A. Persoons, *Angew. Chem.* **1999**, *111*, 377–380; *Angew. Chem. Int. Ed.* **1999**, *38,* 366–369. – [9b] F. W. Vance, J. T. Hupp, *J. Am. Chem. Soc.* **1999**, *121*, 4047–4053.

[10] R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88–98.

[11] C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319–2358.

[12] D. M. Manuta, A. J. Lees, *Inorg. Chem.* **1983**, *22*, 3825–3828.

[13] A. Ghosh, *J. Molec. Struct. (Theochem)* **1996**, *388*, 359–363.

[14] S. Berger, A. Klein, W. Kaim, J. Fiedler, *Inorg. Chem.* **1998**, *37*, 5664–5671.

[15] G. J. Stor, F. Hartl, J. W. M. van Outersterp, D. J. Stufkens, *Organometallics* **1995**, *14*, 1115–1131.

[16] G. J. Stor, D. J. Stufkens, A. Oskam, *Inorg. Chem.* **1992**, *31*, 1318–1319.

[17] T. E. Keyes, R. J. Forster, M. J. Pradeep, C. G. Coates, J. J. McGarvey, J. G. Vos, *Inorg. Chem.* **1998**, *37*, 5925–5932.

Received August 19, 1999
[I99310]