Available online at www.sciencedirect.com

SCIENCE DIRECT®

Coordination Chemistry Reviews 249 (2005) 1511–1516

COORDINATION CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Review

Excited state properties of organometallics based on interligand interactions between aromatic ligands

Arnd Vogler*, Horst Kunkely

Institut für Anorganische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

Received 20 June 2004
Available online 11 April 2005

Contents

Abstract

Excited state properties of coordination compounds have been studied for many years. Surprisingly, rather little is known about excited states, which are based on intramolecular interligand interactions. There are two types of these interligand excited states. In homoleptic complexes, such as $Mg(C_5H_5)_2$, ligand–ligand interaction creates new low-energy interligand states, which are comparable to intermolecular excimers of aromatic molecules. In heteroleptic complexes of the type $(C_7H_7)M(C_5H_5)$, low-energy ligand-to-ligand charge transfer (LLCT) excited states are available. Various organometallic compounds, which are characterized by such interligand excited states, are discussed in this account.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Absorption spectra; Luminescence; Photochemistry; Metallocenes; Interligand states; LLCT states

1. Introduction

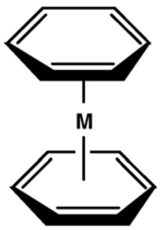
Excited states, which are based on intramolecular interactions between separate ligands of a metal complex, have been investigated to some extent. These studies have been essentially restricted to ligand-to-ligand charge transfer (LLCT) states [1,2]. In this case a donor and an acceptor ligand are coordinated to the same metal, which mediates the electronic coupling between both ligands. In contrast, very little is known about excited states, which are generated by the interaction of identical ligands as they occur in homoleptic complexes. Attractive targets for such investigations should be complexes of the type M(benzene)$_2$ (M = Cr^0, Mo^0 and W^0) which are characterized by a sandwich structure.

---

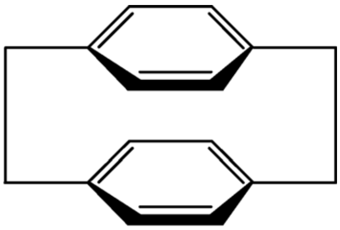
* Corresponding author. Tel.: +49 941 9434485; fax: +49 941 9434488.
E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

0010-8545/$ – see front matter © 2005 Elsevier B.V. All rights reserved.

doi:10.1016/j.ccr.2005.03.008



M^0 $(C_6H_6)_2$



[2.2]paracyclophane

The interaction between both benzene rings of these complexes may be compared with that which takes place in paracyclophanes [3,4]. Another analogy can be drawn to the electronic interaction in arene excimers [4–6]. They are composed of two parallel arene molecules and exist only in the excited state.

$$\text{arene} + h\nu \rightarrow \text{arene}^* \tag{1}$$

$$\text{arene}^* + \text{arene} \rightarrow (\text{arene/arene})^* \tag{2}$$

The formation of the excimer is associated with an emission, which appears at longer wavelength than that of the arene monomer. Unfortunately, $M(C_6H_6)_2$ complexes are hardly suitable for the examination of interligand excited states because the metal (e.g., Cr^0, Mo^0 and W^0) participates in low-energy transitions [7]. In particular, metal-centered ligand field (LF) and metal-to-ligand charge transfer (MLCT) transitions certainly obscure interligand transitions. Accordingly, an appropriate metal complex should not engage in low-energy transitions involving the metal. We explored this possibility and selected the metal centers Mg^{2+}, Gd^{3+}, Hg^{2+} and Rh^{3+} as suitable candidates. Since metals such as Mg^{2+} and Gd^{3+} do not form stable benzene complexes, the cyclopentadienyl anion (Cp^-) was chosen as a substitute. The Cp^- anion is also an aromatic 6π-electron system. Complexes such as $MgCp_2$ or $GdCp_3$ are stabilized to a considerable extent by electrostatic attraction between the metal cation and the ligand anions. As an alternative the benzene ligand may be replaced by the phenyl anion $C_6H_5^-$ which forms M–C σ-bonds. Again, electrostatic attraction between the metal cation and $C_6H_5^-$ as ligands contributes to the stability of complexes such as $Hg^{II}(C_6H_5)_2$. Of course, the interligand interaction in this linear complex is different from that in sandwich-type $M(C_6H_6)_2$ compounds but a ligand–ligand coupling should also exist. Finally, the electronic spectra of the complex $[Rh(Cp^*)(Ch)]^{3+}$ was examined. In this case, the two benzene ligands of $M(C_6H_6)_2$ complexes are replaced by the isoelectronic combination $C_5Me_5^-$ (Cp^{*-}) and $C_7H_7^+$ (Ch^+) which introduces a charge asymmetry into the ligand–ligand interaction.

2. Bis(cyclopentadienyl)magnesium

$MgCp_2$ offers the advantage that Mg^{2+} does not participate in any low-energy electronic transition. Moreover, this compound is well characterized including the crystal structure [8]. The solid contains isolated $MgCp_2$ molecules with the typical metallocene sandwich structure.

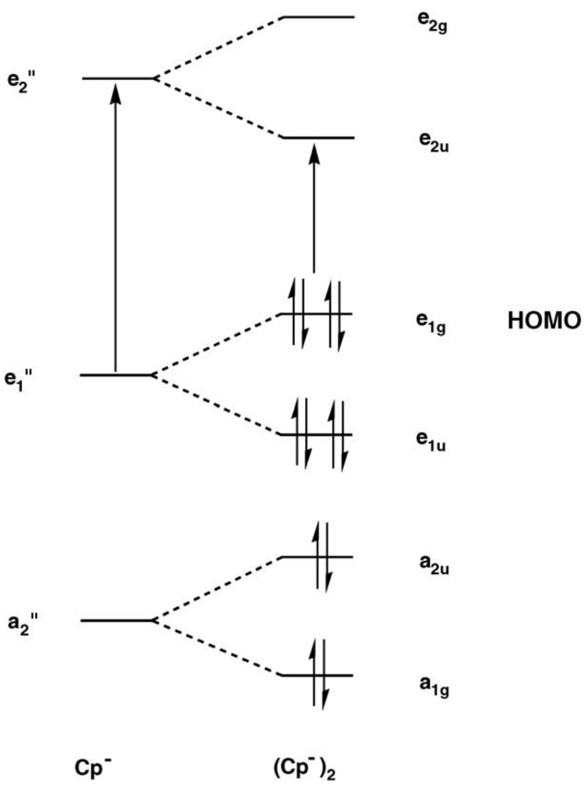
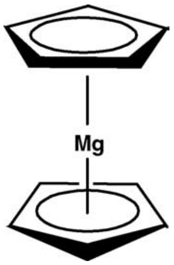


Fig. 1. Qualitative MO scheme for $MgCp_2$ (D_{5d} symmetry) adapted from Ref. [9]. The arrows indicate the lowest-energy π–π* transition.



The electronic structure of $MgCp_2$ should directly reflect the Cp^-/Cp^- interligand interaction which has been previously discussed on the basis of a simple MO model [9] (Fig. 1). The overlap of the π-orbitals of both Cp^- rings causes a splitting which leads to a decrease of the HOMO–LUMO gap. While this effect may be small in the ground state it might become much larger in the excited state since the electronic excitation involves the removal of an antibonding (e_{1g}) electron and the population of a bonding (e_{2u}) orbital. It follows that the interligand excitation is associated with the formation of a formal bond between both ligands. A concomitant reduction of the interligand distance should be indicated by a distinct Stokes shift. Unfortunately, the emission spectra of isolated Cp^- anions are not known. However, for simple aromatic species the Stokes

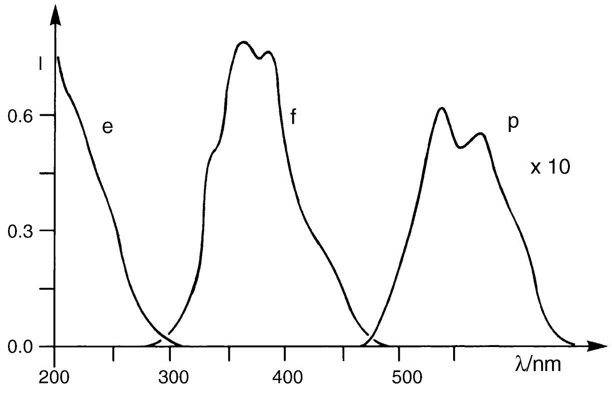
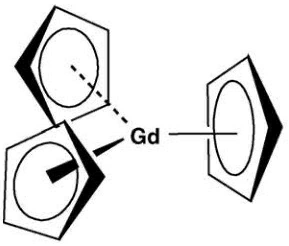


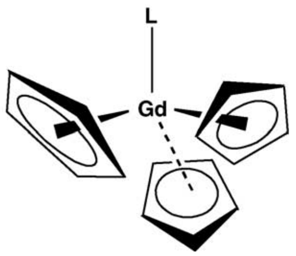
Fig. 2. Electronic excitation (e, $\lambda_{em} = 363$ nm), fluorescence (f, $\lambda_{exc} = 280$ nm) and phosphorescence (p, $\lambda_{exc} = 280$ nm) spectra of solid $MpCp_2$ under argon at room temperature (e and f) and at 77 K (p), intensity in arbitrary units.

shifts are generally rather small [10]. In contrast, the fluorescence spectrum of $MgCp_2$ (Fig. 2) is displaced to much longer wavelength ($\lambda_{max} = 363$ nm) when compared with the excitation spectrum ($\lambda_{max} = 240$ nm, sh) [11]. At 77 K, $MgCp_2$ shows an additional phosphorescence at rather low energies ($\lambda_{max} = 535$ nm). These observations support the assumption that the interligand interaction indeed leads to a contraction of the $MgCp_2$ molecule in the lowest-energy interligand excited state. In this context, it is of interest that various metallocenes of transition metals (e.g., $RuCp_2$ and $OsCp_2$) also exhibit a luminescence [12–18]. However, in these cases, the emissive states are of the charge transfer or metal-centered type.

3. Tris(cyclopentadienyl)gadolinium

The lanthanides including gadolinium form tris(cyclopentadienyl) complexes which in solution exist as discrete $LnCp_3$ molecules or as solvates of the type $LnCp_3L$ with L = solvent [19]. The structure of $LnCp_3$ consists of a regular triangle with the centers of the η^5-coordinated Cp^- planes at the corners and the metal in the middle (D_{3h} symmetry). The $LnCp_3L$ complexes have a pseudotetrahedral structure with a trigonal-pyramidal $LnCp_3$ fragment (C_{3v}).





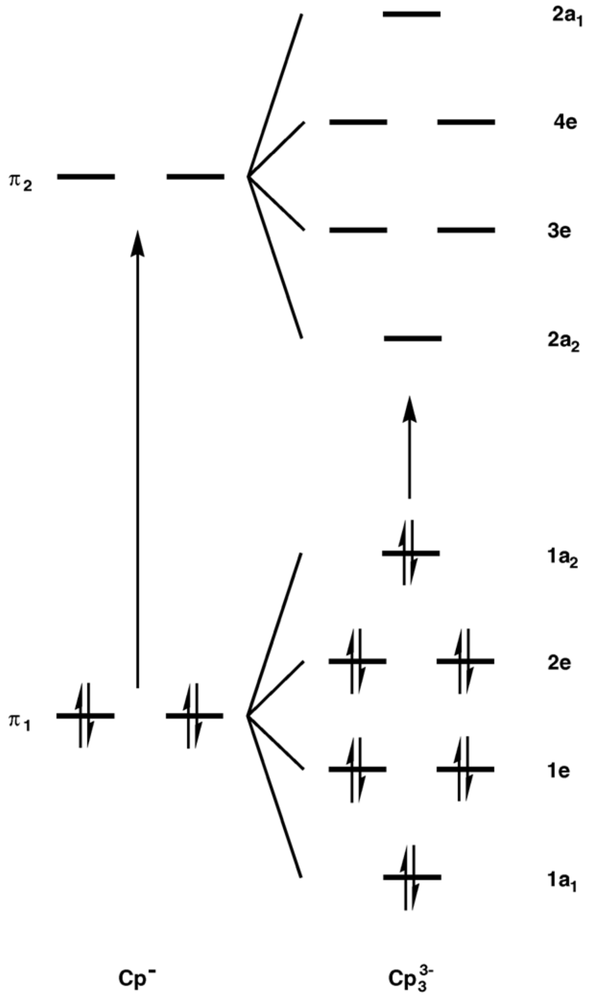


Fig. 3. Qualitative MO scheme for the frontier orbitals of $Cp_3{}^{3-}$ in C_{3v} symmetry. The arrows indicate the lowest-energy π–π^* transitions.

For simplicity, the C_{3v} symmetry is applied to the bonding interaction in $LnCp_3L$ complexes as well as in $LnCp_3$ ligand fragments [20–22]. Since the bonding in $LnCp_3$ is largely ionic the $Cp_3{}^{3-}$ ligand frame can be treated separately [21,23]. The interligand interaction in $LnCp_3$ (Fig. 3) leads then to consequences, which also apply to $MgCp_2$ (see above). However, the specific role of gadolinium must be taken into account [24]. Gd^{3+} does also not participate in low-energy CT or metal-centered (ff) transitions owing to the very high stability of its half-filled f-shell (f^7). But in contrast to Mg^{2+}, Gd^{3+} is a very heavy ion and strongly paramagnetic with an octet ground state. Accordingly, it induces a considerable heavy-atom effect in the ligands. The increased spin–orbit coupling enhances the intersystem crossing. The spectroscopic consequences are obvious. $GdCp_3$ also shows an emission from the lowest-energy interligand excited state (Fig. 4) [24], which is bonding with respect to the interaction within the $Cp_3{}^{3-}$ moiety. However, the fluorescence is completely absent while a strong green phosphorescence ($\lambda_{max} \sim 500$ nm) appears even in solution at RT ($\phi = 0.2$ in ether). The interligand triplet of solid $GdCp_3$ decays with $\tau = 2.3$ μs. Of course, other $LnCp_3$ complexes with lanthanides which have available low-energy ff states (e.g., $TbCp_3$ and $YbCp_3$) do not show interligand emissions. In

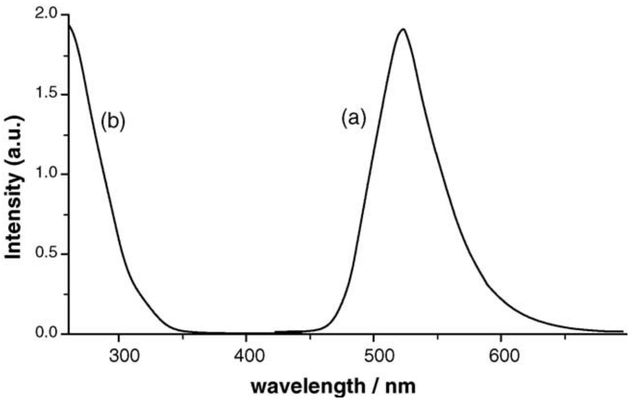
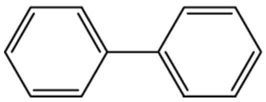


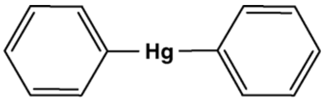
Fig. 4. Electronic emission (a) and excitation (b) spectrum of $GdCp_3$ in dry diethylether at 298 K, $\lambda_{exc} = 250$ nm and $\lambda_{em} = 500$ nm.

this case, the luminescence originates from metal-centered ff states [25–27].

4. Diphenylmercury

As has been discussed above, an intramolecular coupling of two aromatic molecules takes place in the paracyclophanes. In this case, the π-electron systems of both arenes undergo a transannular interaction. As an alternative an electronic coupling occurs also when two aromatic fragments are connected by a regular bond. Biphenyl is a suitable example. The question arises if this type of phenyl–phenyl interaction is also observed for $HgPh_2$.





When biphenyl is viewed as a composition of two benzene molecules a splitting of the MOs occurs [28] (Fig. 5). With regard to the phenyl–phenyl interaction, the HOMO ($2b_{2g}$) is antibonding while the LUMO ($3b_{3u}$) is bonding. In the ground state, there is no π-conjugation between the rings. However, the lowest-energy excitation ($2b_{2g} \rightarrow 3b_{3u}$) is associated with the removal of an electron from an antibonding and the addition of an electron to a bonding MO. Accordingly, in the excited state both phenyl rings are connected by an additional bond, which must lead to a decrease of the distance between both rings. This structural change is reflected by a relatively large Stokes shift of the luminescence of biphenyl [10]. We suggest that the interligand interaction in $HgPh_2$ can be described by analogous considerations.

Solid $HgPh_2$ shows a RT luminescence (Fig. 6) at $\lambda_{max} = 482$ nm [29]. This emission is certainly a molecular property because there are no short intermolecular contacts in the solid material [30]. Moreover, it appears also in low-temperature glasses. The emission of $HgPh_2$ is unlikely to be a fluorescence since luminescence and absorption spectra (Fig. 6) do not overlap. Accordingly, the emission of $HgPh_2$ is assumed to be a phosphorescence, which is facilitated by the heavy-atom effect of mercury. In analogy to some other Hg(II) complexes [31–33], the emission of $HgPh_2$ is certainly of the intraligand type. However, the phosphorescence of $HgPh_2$ does not seem to originate from single phenyl ligands because the emission appears at much longer wavelength than the phosphorescence of benzene or simple phenyl compounds [34]. Since the emission spectrum of $HgPh_2$ resembles that of biphenyl in a glassy matrix at 77 K ($\lambda_{max} = 470$ nm) we suggest that the luminescence of $HgPh_2$ comes from

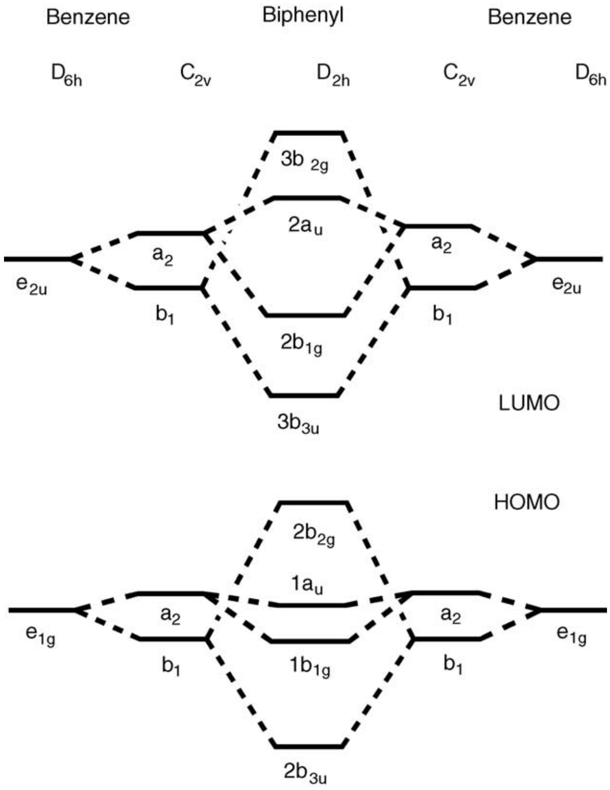


Fig. 5. Qualitative MO diagram of biphenyl derived from the interaction of two benzene molecules adapted from Ref. [28].

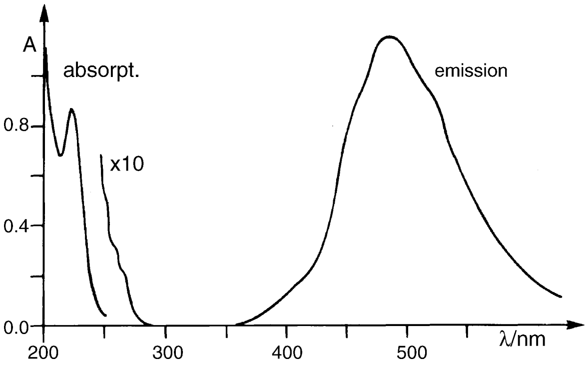


Fig. 6. Electronic absorption and emission spectra of diphenylmercury under argon at RT absorption: 6.27×10^{-5} M in CH_3CN, 1-cm cell; emission: solid, $\lambda_{exc} = 300$ nm, intensity in arbitrary units.

the interligand triplet of both interacting phenyl ligands [29].

In solution at RT, $HgPh_2$ is not luminescent but photoreactive [29]. The photolysis proceeds according to the following scheme:

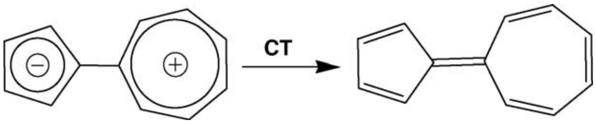
$$Hg^{II}Ph_2 \xrightarrow{h\nu} Hg^{I}Ph + \text{Ph-radical} \tag{3}$$

$$Hg^{I}Ph \rightarrow Hg^{0} + \text{Ph-radical} \tag{4}$$

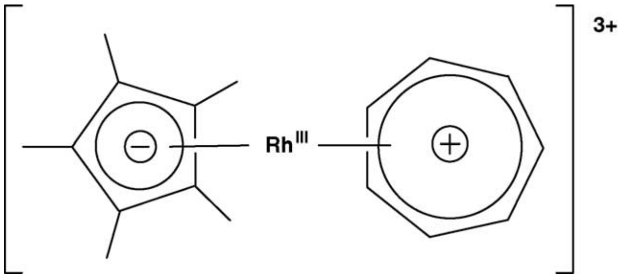
Elemental mercury is finally formed while the phenyl radicals participate in secondary processes, in particular hydrogen abstractions. In agreement with the general behavior of Hg(II) complexes [35], this photoredox reaction is initiated by ($\text{phenyl}^{-} \rightarrow Hg^{II}$) ligand-to-metal charge transfer (LMCT) excitation. It is assumed that this LMCT state can be populated from the emitting interligand triplet, which is located at lower energies [29]. In the solid state, the rigid lattice apparently prevents the photolysis and thus facilitates the interligand triplet emission.

5. (Pentamethylcyclopentadienyl) (cycloheptatrienyl) rhodium(III) cation

As discussed above, with regard to the π-electron system biphenyl can be viewed as a composition of two coupled benzene rings. When both benzene rings are replaced by the isoelectronic Cp^{-} and Ch^{+} rings, a redox asymmetry is introduced since Cp^{-} is a CT donor while Ch^{+} is a CT acceptor. The resulting sesquifulvalene, which is an isomer of biphenyl, is characterized by a low-energy CT transition [36] ($\lambda_{max} = 395$ nm) [37]. Electronic excitation reduces the polarity, which prevails in the ground state.



Such a CT should also occur when two benzene rings of $M(C_6H_6)_2$ are replaced by the isomeric combination Cp^{-} and Ch^{+}. Indeed, various sandwich-type complexes with the general composition $M(Cp^{-})(Ch^{+})$ have been described [38]. Moreover, MO calculations have shown that these complexes should have available $Cp^{-} \rightarrow Ch^{+}$ CT transitions at relatively low energies [38–40] (Fig. 7). These transitions are now of the LLCT type. Unfortunately, in most cases such LLCT transitions are obscured by other low-energy transitions of different origin (e.g., LF, LMCT and MLCT). However, these complications may be avoided by an appropriate choice of the central metal and a suitable modification of the ligands. The cation $[Cp^{*}Rh^{III}Ch]^{3+}$ seems to meet these requirements [41].



Cp^{*-} is a much stronger CT donor than Cp^{-} [42,43]. In addition, since Rh(III) is rather redox inert it does not participate in low-energy CT transitions. Moreover, LF excitation of Rh(III) occurs only at high energies.

The electronic spectrum of $[Cp^{*}Rh^{III}Ch]^{3+}$ (Fig. 8) shows a longest-wavelength absorption at $\lambda_{max} = 340$ nm which is assigned to the spin-allowed $Cp^{*-} \rightarrow Ch^{+}$ LLCT transition [41]. The lowest-energy excited state of the complex is apparently a LLCT triplet which emits at $\lambda_{max} = 596$ nm.

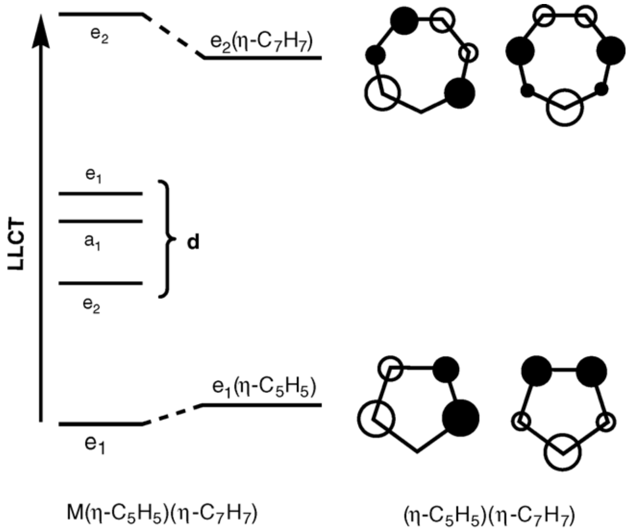


Fig. 7. Qualitative MO diagram for the frontier orbitals of $(\eta\text{-}C_5H_5)M(\eta\text{-}C_7H_7)$ in $C_{\infty v}$ symmetry adapted from Refs. [38–40].

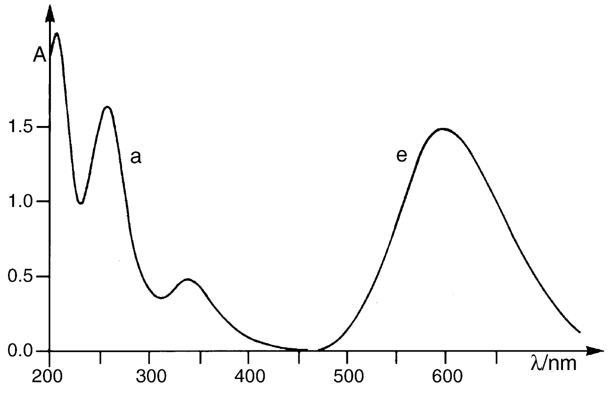


Fig. 8. Electronic absorption, a and emission, e spectra of 1.51×10^{-4} M $[Cp^{*}Rh(C_7H_7)](PF_6)_3$ under argon. Absorption: in CH_3CN at RT, 1-cm cell; emission: in EtOH at 77 K, $\lambda_{exc} = 340$ nm, intensity in arbitrary units.

6. Conclusion

Ligand–ligand interactions between aromatic ligands of organometallic compounds are associated with the generation of low-energy interligand excited states. While complexes such as $Mg^{II}(C_5H_5)_2$, $Gd^{III}(C_5H_5)_3$ and $Hg^{II}(C_6H_5)_2$ are characterized by delocalized interligand states, a LLCT state determines the excited behavior of $[(C_5H_5)Rh^{III}(C_7H_7)]^{3+}$.

References

[1] A. Vogler, H. Kunkely, Comments Inorg. Chem. 9 (1990) 201.
[2] A. Vogler, H. Kunkely, Comments Inorg. Chem. 19 (1997) 283.
[3] F. Vögtle, Cyclophane Chemistry, Wiley, Chichester, 1993.
[4] F. Diedrich, Ccylophanes, in: J.F. Stoddart (Ed.), Monographs in Supramolecular Chemistry, The Royal Society of Chemistry, Cambridge, 1991.
[5] T. Förster, Angew. Chem. Int. Ed. Engl. 8 (1969) 333.
[6] J.B. Birks, The Photophysics of Aromatic Molecules, Wiley, New York, 1970.
[7] G.L. Geoffroy, M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979, p. 230.
[8] W. Bündner, E. Weiss, J. Organomet. Chem. 92 (1975) 1.
[9] S. Evans, M.L.H. Green, B. Jewitt, A.F. Orchard, C.F. Pygall, J. Chem. Soc. Faraday Trans. 2 68 (1972) 1847.
[10] I.B. Berlman, Handbook of Fluorescence Spectra of Aromatic Molecules, Academic Press, New York, 1971, p. 108.
[11] H. Kunkely, A. Vogler, J. Organomet. Chem. 689 (2004) 2940.
[12] M.S. Wrighton, L. Pdungsap, D.L. Morse, J. Phys. Chem. 79 (1975) 66.
[13] G.A. Crosby, G.D. Hager, K.W. Hipps, M.L. Stone, Chem. Phys. Lett. 28 (1974) 497.
[14] K.W. Hipps, A.H. Francis, J. Chem. Phys. 83 (1979) 1879.
[15] G.J. Hollingsworth, K.-S.K. Shin, J.I. Zink, Inorg. Chem. 29 (1990) 2501.
[16] H. Riesen, E. Krausz, W. Luginbühl, M. Biner, H.-U. Güdel, A. Ludi, J. Chem. Phys. 96 (1992) 4131.
[17] C. Daul, H.-U. Güdel, J. Weber, J. Chem. Phys. 98 (1993) 4023.
[18] H. Kunkely, A. Vogler, Trans. Met. Chem. 25 (2000) 234.
[19] S.H. Eggers, W. Hinrichs, J. Kopf, W. Jahn, R.D. Fischer, J. Organomet. Chem. 311 (1986) 313, and reference cited therein.
[20] J.W. Lauher, R. Hoffmann, J. Am. Chem. Soc. 98 (1976) 1729.
[21] K. Tatsumi, A. Nakamura, J. Organomet. Chem. 272 (1984) 141.
[22] R.J. Strittmatter, B.E. Bursten, J. Am. Chem. Soc. 113 (1991) 552.
[23] B.E. Bursten, L.F. Rhodes, R.J. Strittmatter, J. Am. Chem. Soc. 111 (1989) 2758.
[24] A. Strasser, A. Vogler, Chem. Phys. Lett. 379 (2003) 287.
[25] C.J. Schlesener, A.B. Ellis, Organometallics 2 (1983) 529.
[26] H.G. Brittain, J.H. Meadows, W.J. Evans, Organometallics 2 (1983) 1661.
[27] G.K. Liu, J.V. Beitz, J. Alloys Compd. 180 (1992) 157.
[28] M. Rubio, M. Merchan, E. Orti, B.O. Roos, Chem. Phys. Lett. 234 (1995) 373.
[29] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 7 (2004) 741.
[30] D. Grdenic, B. Kamenar, A. Nagl, Acta Cryst. B 33 (1977) 587, and reference cited therein.
[31] C.-W. Chan, S.-M. Peng, C.-M. Che, Inorg. Chem. 33 (1994) 3656.
[32] H. Kunkely, A. Vogler, J. Photochem. Photobiol. A: Chem. 144 (2001) 69.
[33] M.R. Haneline, M. Tsunoda, F.P. Gabbai, J. Am. Chem. Soc. 124 (2002) 3737.
[34] J.B. Birks, The Photophysics of Aromatic Molecules, Wiley, New York, 1970.
[35] H. Kunkely, O. Horváth, A. Vogler, Coord. Chem. Rev. 159 (1997) 85.
[36] M. Yang, D. Jacquemin, B. Champagne, Phys. Chem. Chem. Phys. 4 (2002) 5566, and reference cited therein.
[37] H. Prinzbach, L. Knothe, A. Dieffenbacher, Tetrahedron Lett. (1969) 2093.
[38] M.L.H. Green, D.K.P. Ng, Chem. Rev. 95 (1995) 439.
[39] J.C. Green, S.Y. Kaltsoyannis, K.H. Sze, M. McDonald, J. Am. Chem. Soc. 116 (1994) 1994.
[40] J.C. Green, S.Y. Ketkov, Organometallics 15 (1996) 4747.
[41] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 7 (2004) 650.
[42] A. Vogler, H. Kunkely, Coord. Chem. Rev. 211 (2001) 223.
[43] S. Lu, V.V. Strelets, M.F. Ryan, W.J. Pietro, A.B.P. Lever, Inorg. Chem. 35 (1996) 1013.