ELSEVIER

Coordination Chemistry Reviews 230 (2002) 243–251

COORDINATION
CHEMISTRY REVIEWS

www.elsevier.com/locate/ccr

Excited state properties of transition metal phosphine complexes

Arnd Vogler *, Horst Kunkely

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

Received 6 June 2001; accepted 21 September 2001

Dedicated to Professor Dick Stufkens on the occasion of his retirement

Contents

Abstract

Phosphine ligands determine the excited state properties of a variety of coordination compounds. Phosphines not only influence metal-centered excited states, but participate directly in charge transfer transitions owing to their electron donating and accepting ability. Moreover, intraligand excited states are accessible if the phosphine carries suitable substituents. This diversity is illustrated by selected examples. The excited state behavior is discussed on the basis of spectral (absorption and emission) and photochemical properties of appropriate phosphine complexes. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Absorption spectra; Emission spectra; Charge transfer; Photochemistry; Phosphine complexes

1. Introduction

Organic phosphines (or phosphanes) PR_3 play an important role as ligands in coordination chemistry in general and organometallic chemistry in particular [1,2]. Phosphines are well known to stabilize transition metals in low oxidation states but their versatility as ligands is also documented by their ability to coordinate to transition metals in higher oxidation states including metals with a d^0 electronic configuration [1–3]. In view of their general importance it is quite surprising that relatively little is known about the excited state behavior of phosphine complexes. This notion applies to the direct participation of phosphine ligands while the spectral and photochemical properties of numerous mixed-lig-

---

* Corresponding author. Tel.: +49-941-943-4485; fax: +49-941-943-4488

E-mail address: arnd.vogler@chemie.uni-regensburg.de (A. Vogler).

0010-8545/02/$ - see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0010-8545(01)00438-6

and complexes with phosphines as spectator ligands are well known [4,5]. Of course, a strict distinction between phosphine ligands with an active and passive role is certainly not possible. In this account the excited state properties of mixed-ligand complexes with phosphines as spectator ligands are largely neglected. Frequently, our discussion is restricted to homoleptic phosphine complexes in order to avoid any interference by other ligands.

The majority of phosphine ligands PR_3 carry alkyl and aryl substituents at the phosphorus atom. In a more general sense, R may be also a halogen atom (phosphorus halides, PX_3) or, for example, an OR group (phosphites, $P(OR)_3$). While in this article alkyl and aryl phosphines as ligands are emphasized, complexes with other phosphines are occasionally included in order to provide a more complete picture. In some cases relevant data are only available for complexes which contain isoelectronic arsine (AsR_3) ligands.

In the following sections the electronic spectra (absorption and emission) as well as the photoreactivity are discussed. The complexes are classified according to the nature of the excited states:

metal-centered (MC): dd (or ligand field, LF), ds, dp,
ligand-to-metal charge transfer (LMCT) with phosphines as donors,
metal-to-ligand charge transfer (MLCT) with phosphines as acceptors,
ligand-to-ligand charge transfer (LLCT) with an arsine as acceptor,
metal-to-metal charge transfer (MMCT); e.g. with phosphines as bridging ligands, and
intraligand (IL) or intraligand charge transfer (ILCT) at phosphines.

Generally, this classification applies to the lowest-energy excited states, although the excited state behavior is occasionally also determined by higher-energy excited states.

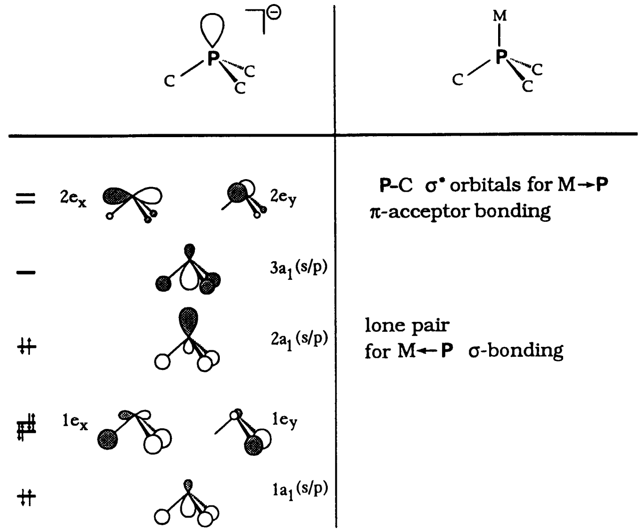


Fig. 1. Qualitative MO diagram of PR_3 (C_{3v} symmetry) and schematic representation of the interaction of PR_3 with a transition metal. Adopted from Ref. [70].

Our short review does not cover this topic comprehensively. The different types of excited states are illustrated by selected examples. Frequently, our own observations are emphasized, but some relevant observations by other groups are also included in order to demonstrate the diversity of this subject.

2. Metal–phosphine bonding

Phosphine ligands provide a lone pair at the phosphorus atom which is used for the formation of a $M{-}PR_3$ σ-bond. In the case of d^0 complexes, only this σ-bond exists. However, for electron-rich d^n metals in low oxidation states, π back bonding becomes important. In classical concepts empty phosphorus 3d orbitals are used for this purpose. However, it is now generally recognized that these d orbitals which are very high in energy play only a minor role. For π back bonding the P–R antibonding σ orbitals are utilized [6–10] (Fig. 1).

The strongest π-acceptor is apparently the PF_3 ligand. This notion is supported by the chemistry of PF_3 complexes which resembles that of carbonyl complexes [11,12]. In particular, homoleptic PF_3 and CO complexes share many chemical and physical features.

3. Metal-centered states

3.1. Absorption spectra

In this section the discussion is restricted to homoleptic phosphine complexes in order to exclude any ambiguity which is based on the presence of other ligands.

Frequently, important spectral parameters such as the ligand field strength are derived from the absorption spectra of octahedral d^6 complexes. Unfortunately, the spectra of such homoleptic phosphine complexes have not apparently been studied [13]. Accordingly, little information is available on the ligand field strength of phosphines [14,15]. On the contrary, the absorption spectra of a few homoleptic arsine complexes have been investigated [16–18]. For example, $[Fe^{II}(edas)_3]^{2+}$ with edas = *cis*-1,2-bis(dimethylarsino)ethylene displays long-wavelength LF bands at $\lambda_{max} = 680$ nm ($^1A_1 \rightarrow {}^3T_1$), 465 nm ($^1A_1 \rightarrow {}^1T_1$) and 365 nm ($^1A_1 \rightarrow {}^1T_2$) [17].

Much more information is available on the absorption spectra of square-planar phosphine complexes of d^8 metals [19–21]. In these complexes the metal $(n+1)$p orbitals of π symmetry are stabilized by the interaction with π acceptor orbitals of the phosphine ligands. As a consequence MC $d \rightarrow (n+1)p$ transitions occur at relatively low energies. However, since these transitions terminate at MOs which are of mixed metal and phosphine parentage they can be also viewed as MLCT transitions. This ambiguity has been emphasized by Crosby et al. [21]. MC/MLCT bands of this type have been identified in the absorption spectra of various homoleptic phosphine complexes [19–21], e.g.:

$[Ir^{I}(diphos)_2]^+$	$\lambda_{max} = 526$ nm	[19,21]
diphos = 1,2-bis(diphenylphosphino)ethane		
$[Pt^{II}(diphos)_2]^{2+}$	$\lambda_{max} = 307$ nm	[19]

These longest-wavelength bands are assigned to spin-forbidden singlet–triplet transitions which gain intensity by spin-orbit coupling.

In analogy to d^8 complexes, low-energy MC dp/MLCT transitions occur also in phosphine complexes of d^{10} metals such as Pd^0, Pt^0 [22–24] or Au^I [24–26] which have been studied in great detail. In these cases, LF transitions cannot exist.

$Pt[P(t\text{-}Bu)_3]_2$	$\lambda_{max} = 384$ nm	[24]
$[Au^{I}(PEt_3)_2]^+$	$\lambda_{max} = 251$ nm	[25]

Again, the longest-wavelength absorptions belong to spin-forbidden $d \rightarrow p(\pi)$ transitions.

In polynuclear phosphine complexes of d^{10} metals a direct metal–metal interaction may exist. In such cases the HOMO is frequently an antibonding σ(M–M) orbital which is generated by an overlap of d-orbitals while the LUMO is a bonding σ(M–M) orbital derived from $(n+1)$p orbitals. In particular, the p orbitals are affected by the phosphine ligands. The lowest-energy transitions are then of the $\sigma_d^* \rightarrow \sigma_p^b$ type. Corresponding absorption bands have been detected in the electronic spectra of various bi- and polynuclear d^{10} complexes [22,23,26–30], e.g.:

$Pt_2^0(dppm)_3$	$\lambda_{max} = 488$ nm	[23]
dppm = bis(diphenyl-phosphino)methane	= 592 nm (spin-forbidden)	
$[Au_2^I(dppm)_2]^{2+}$	$\lambda_{max} = 293$ nm	[27,29]
$[Au_2^I(dmpm)_2]^{2+}$	$\lambda_{max} = 269$ nm	[30]
dmpm = bis(dimethylphosphino)methane		
$[Au_2^I(dmpm)_3]^{2+}$	$\lambda_{max} = 256$ nm	[28]
$[Au_3^I(dmmp)_2]^{3+}$	$\lambda_{max} = 315$ nm	[30]
dmmp = bis(dimethylphosphinomethyl)methylphosphine		

3.2. Emission spectra

Various homoleptic phosphine complexes of d^8 and d^{10} metals have been reported to emit from MC dp excited states. As outlined above these excited states are of mixed MC and MLCT parentage. The emitting states are the lowest-energy triplets. The phosphorescence (ϕ = quantum yield, τ = lifetime) of the d^8 complexes appears at low temperature [19,21,31], e.g.:

$[Rh^{I}(diphos)_2]^+$	$\lambda_{max} = 614$ nm	$\phi = 0.05$	$\tau = 21$ μs	[19]
$[Ir^{I}(diphos)_2]^+$	$\lambda_{max} = 585$ nm	$\phi = 0.25$	$\tau = 10$ μs	[19]

Many phosphine complexes of d^{10} metals show this phosphorescence, which originates also from MC dp (+MLCT) triplets even at r.t. [22,23,26,32,33]:

$Pd^0(PEt_3)_3$ in THF	$\lambda_{max} = 646$ nm	$\phi \sim 0.01$	$\tau \sim 5$ μs	[22]
$Pd^0(PPh_3)_4$ in THF	$\lambda_{max} = 660$ nm	$\phi \sim 0.02$	$\tau \sim 4$ μs	[22]
$Pt^0(PPh_3)_4$ in THF	$\lambda_{max} = 740$ nm	$\phi \sim 4 \times 10^{-4}$	$\tau \sim 1$ μs	[22]
$[Au^{I}(PPh_3)_3]^+$ in CH_3CN	$\lambda_{max} = 512$ nm		$\tau = 10$ μs	[32]
$[Au^{I}(TPA)_3]^+$ in H_2O	$\lambda_{max} = 547$ nm		$\tau \sim 1$ μs	[33]
TPA = 1,3,5-triaza-7-phosphaadamantane				

The complexes with coordination numbers three and four have trigonal-planar and tetrahedral structures, respectively.

As described above, the lowest-energy excited states of various polynuclear phosphine complexes of d^{10} metals are MC ($\sigma_d^* \sigma_p^b$ or $\delta_d^* \sigma_p^b$) triplets. The phosphorescence from these states is frequently observed at r.t., e.g.:

$Pd_2^0(dppm)_3$ in THF	$\lambda_{max} = 740$ nm	$\phi \sim 0.02$	$\tau \sim 5$ μs	[22]
$Pt_2^0(dppm)_3$ in 2-Me-THF (at 77 K)	$\lambda_{max} = 787$ nm		$\tau < 0.02$ μs	[23]
$[Au_2^I(dppm)_2]^{2+}$ in CH_3CN	$\lambda_{max} = 593$ nm	$\phi \sim 0.3$	$\tau \sim 20$ μs	[27]
$[Au_3^I(dmmp)_2]^{3+}$ in CH_3CN	$\lambda_{max} = 580$ nm		$\tau \sim 7$ μs	[30]

It is quite interesting that in the emitting state a metal–metal bond exists which is absent in the ground state.

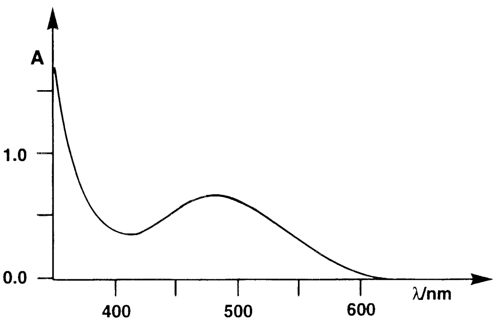


Fig. 2. Electronic absorption spectrum of PPh_3 dissolved in $TiCl_4$ under argon at r.t., 1 cm cell.

3.3. Photochemistry

LF (or dd) excited states of complexes with d^n metals are well known to initiate photosubstitutions of ligands. This photoreactivity is largely based on the population of M–L σ-antibonding d-orbitals. In analogy to a variety of metal carbonyl complexes which release CO upon LF excitation [4,5,34], phosphine complexes are expected to show the same photochemical behavior. Surprisingly, mixed carbonyl–phosphine complexes apparently undergo a photosubstitution of CO but not PR_3 ligands [4,5,34]. The most promising candidates for the observation of a phosphine photosubstitution are homoleptic complexes. Indeed, such a photolysis has been observed [11]:

$$Fe(PF_3)_5 + 2PPh_3 \xrightarrow{h\nu} Fe(PF_3)_3(PPh_3)_2 + 2PF_3 \qquad (1)$$

Although the reactive excited state has not been identified, there is little doubt that this photosubstitution is initiated by a LF state in analogy to $Fe(CO)_5$ [4].

A few homoleptic d^{10} phosphine complexes also possess photoreactive MC excited states. In the case of $Pd(PPh_3)_4$ a dp state seems to induce an oxidative addition [22]:

$$Pd^0(PPh_3)_4 + C_6H_5Cl \xrightarrow{h\nu} trans\text{-}Pd^{II}(PPh_3)_2(Ph)(Cl) + 2PPh_3 \qquad (2)$$

Details have not been reported. It is conceivable that this reaction is initiated by an excited state electron transfer from Pd(0) to chlorobenzene. Unfortunately, it is not known if a concomitant luminescence quenching takes place.

Binuclear d^{10} complexes with lowest-energy $\sigma_d^*\ \sigma_p^b$ states are also photoreactive, e.g. [22]:

$$Pd_2^0(dppm)_3 + CH_2Cl_2 \xrightarrow{h\nu} Pd_2^I(\mu\text{-}CH_2)(dppm)Cl_2 + 2dppm \qquad (3)$$

Both metal centers are affected by this oxidative addition. In the case of $[Au_2^I(dppm)_2]^{2+}$, an excited state electron transfer mechanism has been confirmed. The emission from the $\sigma_d^*\ \sigma_p^b$ triplet is quenched by electron donors (e.g. tetramethyl–*p*-phenylenediamine) as well as acceptors such as paraquat^{2+} and organic halides [29,35]. In the primary photochemical step, mixed valence compounds with the formal oxidation states Au^IAu^0 and Au^IAu^{II} should be generated. However, persistent photoproducts are not formed because the initial electron transfer is completely reversed by thermal recombination.

In the presence of oxygen the trinuclear complex $[Au_3^I(dmmp)_2]^{3+}$ induces the photochemical cleavage of DNA [36]. It is assumed that the excited triplet undergoes an electron or energy transfer to oxygen. Superoxide or singlet oxygen which are thus generated could then attack and oxidatively cleave DNA.

4. Ligand-to-metal charge transfer states

It is quite surprising that despite their well known reducing ability, very little is known about phosphines as donor ligands for CT interactions. Jensen and Jørgensen estimated the optical electronegativity of PEt_3 (~ 2.6) on the basis of ligand-to-metal charge transfer assignments of absorption bands in the electronic spectra of $Co(PEt_3)_2X_2$ with X = Cl and Br [37]. However, these complexes may not be well suited for an unambiguous detection of LMCT absorptions, as Co(II) is hardly oxidizing. It follows that complexes of oxidizing metals should be much better candidates to identify LMCT transitions. In order to avoid any interference by LF transitions, oxidizing d^0 complexes would be most suitable to investigate CT spectra of complexes with phosphines as donor ligands. Unfortunately, such complexes are not very common [1,2]. Nevertheless, several compounds of the type $TiCl_4(PR_3)$ and $TiCl_4(PR_3)_2$ have been described [38–41]. They are brightly colored. Since $TiCl_4$ is colorless, the colors of the phosphine complexes should be attributed to the presence of long-wavelength phosphine → Ti^{IV} LMCT absorptions. Since these compounds are extremely sensitive to solvolysis, in particular to water even in traces, it was not possible to record reproducible spectra. When PPh_3 is dissolved in neat $TiCl_4$, a red color appears owing to an absorption at $\lambda_{max} \sim 480$ nm (Fig. 2). It seems quite reasonable to assign this band to a LMCT absorption of a complex with the composition $TiCl_4(PPh_3)_n$ ($n = 1$ or 2).

More reliable results were obtained with the complex $MeRe^{VII}O_3(PPh_3)$ [42]. $MeRe^{VII}O_3$ is a pseudo-tetrahedral d^0 complex that easily expands its coordination sphere by accepting a further ligand [43,44]. The excited state properties of such adducts of the type $MeRe^{VII}O_3 \times L$ have been studied in some detail [45]. The yellow color which instantly develops when solutions of $MeReO_3$ and PPh_3 are mixed is attributed to the complex $MeReO_3(PPh_3)$ [42]. The new absorption maximum (Fig. 3) at 380 nm ($\varepsilon = 85$) is logically assigned to a LMCT transition from the reducing phosphine to the oxidizing d^0 metal center. This assignment is supported by additional evidence. When PPh_3 is replaced by $P(p\text{-Cl–phenyl})_3$, the LMCT band is shifted to a shorter wavelength ($\lambda_{max} \sim 315$ nm) in agreement with the decreased donor strength of this phosphine.

At r.t., $MeReO_3(PPh_3)$ is not stable but reacts thermally according to Eq. (4) [46]:

$$MeRe^{VII}O_3(PPh_3) \rightarrow MeRe^{V}O_2 + O{=}PPh_3 \quad (4)$$

This oxidation of the phosphine ligand apparently takes place as an oxygen transfer process. The primary reduction product $MeReO_2$ is coordinatively unsaturated, but can be stabilized in the presence of $MeReO_3$ and PPh_3:

$$MeRe^{V}O_2 + 2PPh_3 + MeRe^{VII}O_3 \rightarrow MeRe^{V}(PPh_3)_2O_2 \times MeRe^{VII}O_3 \quad (5)$$

The binuclear mixed-valence compound is formed as a final product.

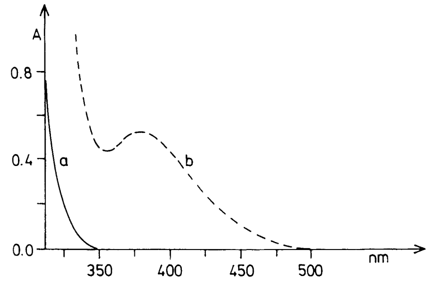


Fig. 3. Electronic absorption spectra of 1.25×10^{-2} M $MeReO_3$ and 1.25×10^{-2} M PPh_3 in CH_2Cl_2 as separate solutions (a, —) and as a mixture (b, ---) under argon at 5 °C, 1 cm tandem cell.

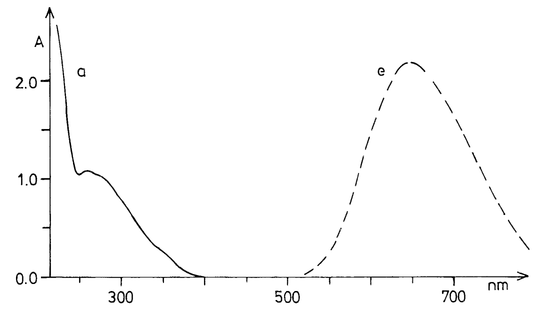


Fig. 4. Electronic absorption (a, —) and emission (e, ---) spectra of $Ni^0(PPh_3)_2(CO)_2$ under argon at r.t. Absorption: 5.04×10^{-5} M in CH_3CN, 1 cm cell. Emission: solid state, $\lambda_{exc} = 380$ nm, intensity in arbitrary units.

At 0 °C this thermal reaction proceeds slowly enough to allow the examination of the photoreactivity of $MeReO_3(PPh_3)$ [42]. Upon LMCT ($PPh_3 \rightarrow Re^{VII}$) excitation the complex undergoes the same transformation as thermally at r.t. The quantum yield of product formation was $\phi = 0.09$ at $\lambda_{irr} = 405$ nm. Although the optical LMCT transition is a one-electron transfer, the LMCT excited state should easily find a deactivation channel which leads to an oxygen atom transfer from $MeReO_3$ to the phosphine ligand. In agreement with the general reactivity of LMCT states, the metal finally undergoes a reduction while the ligand is oxidized.

5. Metal-to-ligand charge transfer states

Owing to the presence of empty acceptor orbitals at phosphine ligands (see Section 4), MLCT transitions may occur. Phosphine complexes should show such MLCT absorptions at long wavelength if the metal is reducing. Generally, this reducing character is provided when the metal exists in low oxidation states. Nevertheless, little is known about such MLCT transitions terminating at phosphine ligands.

As discussed in Section 3, in phosphine complexes of various d^8 (Rh^I, Ir^I and Pt^{II}) and d^{10} metals (Au^I), the interaction of metal p_π and phosphine π-acceptor orbitals generates low-energy empty π orbitals which are available as acceptor orbitals for MLCT transitions. However, the lowest-energy transitions are then of mixed MLCT/MC character since the acceptor orbital is of mixed metal and phosphine parentage. These transitions are discussed in the section on MC transitions (see Section 3).

Under favorable conditions a distinction between MLCT and MC transitions can be made. For example, the complex $Ni^0(PPh_3)_2(CO)_2$ shows its longest-wavelength absorption (Fig. 4) at $\lambda_{max} = 356$ nm [47]. This band is assigned to a $Ni^0 \rightarrow PPh_3$ MLCT transition. The assignment is based on a comparison with the spectrum of $Ni(CO)_4$, which displays its longest-wavelength MLCT absorptions at 270 and 230 nm. The MC ds and dp transitions of $Ni(CO)_4$ occur at much higher energies. While $Ni(CO)_4$ is light sensitive, $Ni(PPh_3)_2(CO)_2$ is luminescent (Fig. 4) at r.t. in the solid state ($\lambda_{max} = 650$ nm at $\lambda_{exc} = 380$ nm) and weakly in solution. It has been concluded that this emission originates from the lowest-energy $Ni^0 \rightarrow PPh_3$ MLCT triplet.

The d^6 complex $W^0(CO)_2(diphos)_2$ shows a phosphorescence in methyl–tetrahydrofuran at 77 K [48]. This emission which appears at $\lambda_{max} = 568$ nm ($\phi = 0.14$, $\tau = 0.14$ μs) was also assumed to come from a $W^0 \rightarrow$ phosphine MLCT triplet. However, in view of its high

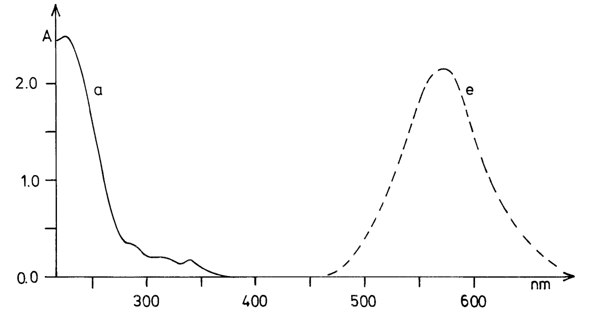
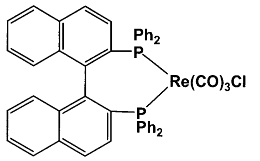


Fig. 5. Electronic absorption (a, —) and emission (e, ---) spectra of 3.23×10^{-5} M Re(binap)(CO)$_3$Cl in ethanol at r.t., 1 cm cell. Emission: $\lambda_{exc} = 340$ nm, intensity in arbitrary units.

energy the phosphorescent state may also be of the phosphine IL type (see Section 6).

A very promising acceptor ligand for low-energy MLCT transitions is the well-known binap (2,2′-bis-(diphenylphosphino)-1,1′-binaphthyl) ligand. It contains the binaphthyl substituent with an extended π-electron system. Accordingly, the phosphine should have available low-energy π* acceptor orbitals for MLCT transitions. A first example has been reported by Tsubomura et al. in 1995. The complex Pt^0(binap)$_2$ shows a longest-wavelength absorption at 530 nm which was assigned to a MLCT transition [49]. The MLCT triplet emits at $\lambda_{max} = 730$ nm ($\tau = 1.5$ μs) in benzene at r.t. Unfortunately, this emission is very close to that of Pt^0(PPh$_3$)$_4$ ($\lambda_{max} = 740$ nm) and Pt^0(PPh$_3$)$_3$ ($\lambda_{max} = 705$ nm) [22,23]. In these cases, the π* orbitals of the phenyl substituents are certainly located at much higher energies compared to binap. The phosphorescence of Pt(PPh$_3$)$_n$ ($n = 3$ and 4) has been assumed to come from MC dp (+MLCT) triplets (see Section 3).

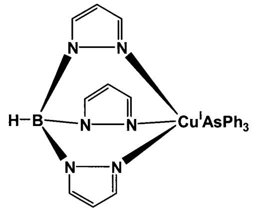
The d^6 complex Re^I(binap)(CO)$_3$Cl (structure **1**) is an example which is less ambiguous [50].



This complex shows its longest-wavelength absorption (Fig. 5) at $\lambda_{max} = 338$ nm. It is attributed to a MLCT transition terminating at the binap ligand. The MLCT triplet is emissive ($\lambda_{max} = 570$ nm, Fig. 5) under ambient conditions. The MLCT assignment is based on a comparison with the spectra of the free binap ligand and the complex Re(diphos)(CO)$_3$Cl.

6. Ligand-to-ligand charge transfer states

Complexes which simultaneously contain donor and acceptor ligands are characterized by LLCT transitions at relatively low energies [51,52]. Since phosphines are donor as well as acceptor ligands they could participate in LLCT transitions, but corresponding examples are not yet known. However, AsPh$_3$ has recently been shown to function as an LLCT acceptor. The complex Cu^I(Tp)(AsPh$_3$) (structure **2**) with Tp$^-$ = hydridotrispyrazolylborate displays a Tp$^-$ → AsPh$_3$ LLCT absorption at $\lambda_{max} = 400$ nm [53].



The complex shows an emission ($\lambda_{max} = 606$ nm) which originates from the LLCT triplet. This assignment is consistent with MO calculations and supported by comparison with the spectra of Cu(Tp)(NEt$_3$) and Cu(Tp)(PPh$_3$).

7. Metal-to-metal charge transfer states

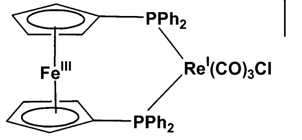
Two types of MMCT transitions may occur in bi- or polynuclear metal complexes, which simultaneously contain reducing and oxidizing metal centers [52]. If both metals are connected by a direct but polar metal–metal bond, a σσ* transition occurs which can be also viewed as MMCT transition because the σ^b_{M-M} orbital is predominantly localized at the reducing metal while the corresponding σ* orbital has a large contribution from the oxidizing metal. The Au^{I}PPh$_3$ moiety forms polar M–M bonds with various reducing metal centers. This type of polar M–M bond exists in PPh$_3$Au^I–Co^{-I}(CO)$_4$ and PPh$_3$Au^I–Sn^{II}Cl$_3$, which are characterized by Co^{-I} and Sn^{II} to Au^I MMCT absorptions at $\lambda_{max} = 305$ and 290 nm, respectively [54,55]. Both complexes are light sensitive. MMCT excitation of the cobalt complex leads to the reduction of Au(I) and oxidation of Co^{-I} [54]:

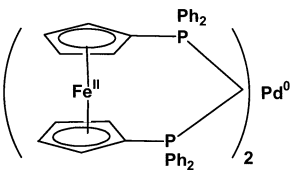
$$\mathrm{PPh_3Au^I\text{–}Co^{-I}(CO)_4} \xrightarrow{h\nu} \mathrm{PPh_3 + Au^0 + 1/2Co^0_2(CO)_8} \quad (6)$$

The binuclear complex disappears with $\phi = 0.1$ at $\lambda_{irr} = 333$ nm. The photolysis of the tin complex also yields metallic gold with $\phi = 0.41$ at $\lambda_{irr} = 282$ nm [55].

The second type of MMCT transition exists in complexes with bridging ligands which mediate the interaction between reducing and oxidizing metals [13,52]. Recently, it has been shown that this electronic interaction is also provided by phosphine bridges. The binuclear complex ion [Fe^{III}(C$_5$H$_4$PPh$_2$)$_2$Re^I(CO)$_3$Cl]$^+$ (structure **3**) shows a broad absorption at $\lambda_{max} = 700$

nm (Fig. 6) which is assigned to a $Re^{I}\rightarrow Fe^{III}$ MMCT transition [56].





The trinuclear complex $Pd^0[(PPh_3C_5H_4)_2Fe^{II}]_2$ (structure **4**) does not show a MMCT absorption since both metal centers, Fe^{II} and Pd^0, are only reducing [57]. However, Fe^{II} can be photooxidized to Fe^{III} by charge-transfer-to-solvent (CTTS) excitation [57] in analogy to ferrocene itself [4,5]. The resulting Fe^{III}/Pd^0 complex would be expected to display a Pd^0 to Fe^{III} MMCT absorption in its electronic spectrum. This MMCT transition requires so little energy that it takes place as a thermal electron transfer [57]. As a consequence, Pd^0 is finally oxidized to Pd^{II} while Fe^{III} is reduced to Fe^{II}.

8. Intraligand and intraligand charge transfer states

8.1. Electronic spectra

Aromatic amines and phosphines are characterized by low-energy transitions which involve a shift of electron density from the lone pair at N or P to the π* orbitals of the aromatic substituents [58,59]. This nπ* transition can be also viewed as a CT process. The longest wavelength absorptions of aromatic amines and phosphines are frequently assigned to such nπ* or $l-a_\pi$ (lone pair to antibonding π orbital) transitions. The emission from these $l-a_\pi$ states consists of a r.t. fluorescence and a low-temperature phosphorescence.

Upon coordination of aromatic amines or phosphines, the lone pair at N or P is used for σ-bonding to the metal. The $l-a_\pi$ transition is now converted to a $\sigma-a_\pi$ transition. This $\sigma-a_\pi$ transition which may be also labeled as ILCT should be shifted to higher energies in comparison to the $l-a_\pi$ transition of the free ligands owing to the stabilization of the lone pair by the metal. Such a shift is indeed observed for Pt^{II}(2,2′-diamino-1,1′-binaphthyl)Cl_2 [60]. The longest-wavelength absorptions of various Cu^I arylphosphine complexes are also assumed to be of this $\sigma-a_\pi$ type [59], e.g.

$[Cu^I(PPh_3)_3]Cl$ in CH_2Cl_2/cyclohexane	λ_{max} = 290–300 nm	[59,61]
$[Cu^I(prophos)(BH_4)]$ in cyclohexane	λ_{max} = 300–320 nm	[59,62]

prophos = 1,3-bis(diphenylphosphino)propane

$Cu^I(PPh_3)_2(NO_3)$ in CH_3CN	λ_{max} = 275 nm	[63]

However, the spectral shifts of the $\sigma-a_\pi$ absorptions of Cu^I arylphosphine complexes do not follow a simple pattern. Several explanations including copper–phosphine π-back bonding and steric effects have been given to account for these observations [59].

Various phosphine complexes of d^{10} metals show an emission which originates from $\sigma-a_\pi$ triplets, e.g.

$Cu^I(prophos)(BH_4)$ in benzene, r.t.	λ_{max} = 593 nm $\tau\sim$4 μs	[62]
$Cu^I(PPh_3)(NO_3)$ in ethanol, 77 K	λ_{max} = 450 nm	[63]
$[Au^I_2(dmpm)_2]^{2+}$ in CH_3CN, r.t.	λ_{max} = 455 nm $\tau\sim$1 μs	[30]

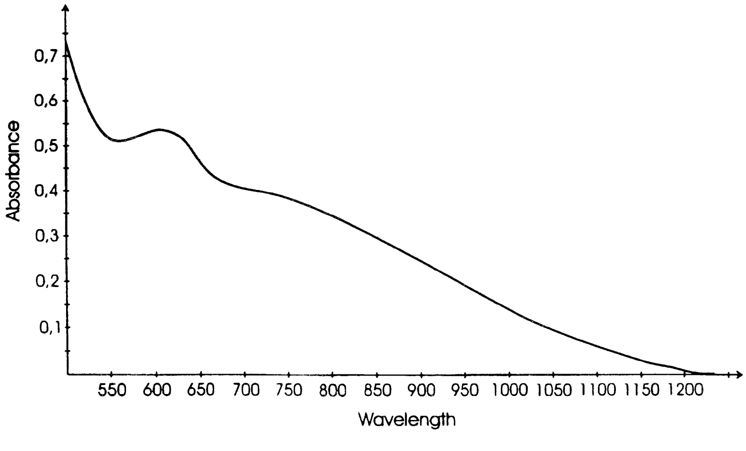


Fig. 6. Electronic absorption spectrum of 1.8×10^{-4} M $[Fe^{III}(C_5H_4PPh_2)_2Re^I(CO)_3Cl]BF_4$ in argon-saturated CH_2Cl_2, 1 cm cell.

$[Hg(PPh_3)_2]^{2+}$ $\lambda_{max} = 490$ nm [64]

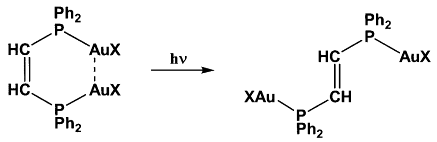
Some arylphosphine complexes show a luminescence which seems to come from ππ* triplets of the aryl substituents [59]. Occasionally, a phosphorescence from ππ* and σ–a_π triplets is observed. This dual emission appears when the ππ* state is located at higher energies than the σ–a_π state. In other cases only the ππ* state emits, provided it occurs at lowest energy. A few d^{10} phosphine complexes emit either exclusively or in addition from such ππ* states, e.g.:

$Cu^I(PPh_3)_2(BH_4)$ in toluene, 77 K $\lambda_{max} = 395$ nm $\tau \sim 2$ µs [65]
$Au^I_2(PPhMe_2)_2Br_2$ solid, 1.4 K $\lambda_{max} = 360$ nm $\tau \sim 200$ µs [66]

8.2. Photochemistry

The σ–a_π states of coordinated arylphosphines do not seem to be intrinsically reactive [59]. Of course, these ILCT states can undergo deactivation to lower excited states of different origin, which may initiate a photoreaction. For example, the photolysis of $Cu(PPh_3)_2NO_3$ is induced by a $Cu^I \rightarrow NO_3^-$ MLCT state which can only be populated via initial ILCT excitation of the coordinated PPh_3 [63]. Moreover, σ–a_π states are also able to transfer their excitation energy to substrates. This leads to a sensitized photolysis. The energy transfer is accompanied by quenching of emissive ILCT triplets [59,62].

Finally, substituents at phosphines may be photoreactive too. Olefin complexes participate in a variety of photochemical reactions including *trans*/*cis* isomerization of the olefin ligand [67]. Frequently, these isomerizations are induced by ππ* IL excitation. Binuclear gold(I) complexes of the type Au_2X_2(dppe) with X = halogen and dppe = bis(diphenylphosphino)-ethylene undergo a *cis* to *trans* photoisomerization at the olefinic double bond [68]:



In the ground state the *cis* isomer is apparently stabilized by an aurophilic interaction between both Au^+ ions. The photoactivity seems to originate from a ππ* IL (ethylene) excited state which is strongly modified by the complex fragments [69]. Interestingly, there is no ethylene IL contribution to the lowest-energy excited states of the *trans* isomer. This explains the absence of any *trans* → *cis* photoisomerization of the complex.

Acknowledgements

Support for this research by the Fonds der Chemischen Industrie is gratefully acknowledged.

References

[1] C.A. McAuliffe (Ed.), Transition Metal Complexes of Phosphorous, Arsenic, and Antimony Ligands, MacMillan Press, London, 1973.
[2] C.A. McAuliffe, W. Levason, Phosphine, Arsine and Stibine Complexes of the Transition Elements, Elsevier, Amsterdam, 1979.
[3] F. Montilla, A. Monge, E. Gutierrez-Puebla, A. Pastor, D. del Rio, N.C. Hernandez, J.F. Sanz, A. Galindo, Inorg. Chem. 38 (1999) 4462.
[4] G.L. Geoffroy, M.S. Wrighton, Organometallic Photochemistry, Academic Press, New York, 1979.
[5] D.M. Roundhill, Photochemistry and Photophysics of Metal Complexes, Plenum Press, New York, 1994.
[6] A.G. Orpen, N.B. Connelly, J. Chem. Soc. Chem. Commun. (1985) 1310.
[7] D.S. Marinick, J. Am. Chem. Soc. 106 (1984) 4064.
[8] G. Pacchioni, P.S. Bagus, Inorg. Chem. 31 (1992) 4391.
[9] S.-X. Xiao, W.C. Trogler, D.E. Ellis, Z. Berkovitch-Yellin, J. Am. Chem. Soc. 105 (1983) 7033.
[10] R.J. Morris, G.S. Girolami, Inorg. Chem. 29 (1990) 4167.
[11] T. Kruck, Angew. Chem. Int. Ed. Engl. 6 (1967) 53.
[12] R.J. Clark, M.A. Busch, Acc. Chem. Res. 6 (1973) 246.
[13] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[14] M.A. Bennett, R.J.H. Clark, A.D.J. Goodwin, Inorg. Chem. 6 (1967) 1625.
[15] D.M. Klassen, G.A. Crosby, J. Mol. Spectr. 25 (1968) 398.
[16] R.D. Feltham, W. Silverthorn, Inorg. Chem. 7 (1968) 1155.
[17] R.D. Feltham, H.G. Metzger, W. Silverthorn, Inorg. Chem. 7 (1968) 2003.
[18] R.D. Feltham, W. Silverthorn, Inorg. Chem. 9 (1970) 1207.
[19] G.L. Geoffroy, M.S. Wrighton, G.S. Hammond, H.B. Gray, J. Am. Chem. Soc. 96 (1974) 3105.
[20] G.L. Geoffroy, H. Isci, J. Litrenti, W.R. Mason, Inorg. Chem. 16 (1977) 1950.
[21] W.A. Fordyce, G.A. Crosby, Inorg. Chem. 21 (1982) 1455.
[22] J.V. Caspar, J. Am. Chem. Soc. 107 (1985) 6718.
[23] P.D. Harvey, H.B. Gray, J. Am. Chem. Soc. 110 (1988) 2145.
[24] H.-R.C. Jaw, W.R. Mason, Inorg. Chem. 28 (1989) 4370.
[25] M.M. Savas, R.W. Mason, Inorg. Chem. 26 (1987) 301.
[26] T.M. McCleskey, H.B. Gray, Inorg. Chem. 31 (1992) 1734.
[27] C. King, J.-C. Wang, M.N.I. Khan, J.P. Fackler Jr., Inorg. Chem. 28 (1989) 2145.
[28] H.-R.C. Jaw, M.M. Savas, W.R. Mason, Inorg. Chem. 28 (1989) 4366.
[29] C.-M. Che, H.-L. Kwong, C.-K. Poon, J. Chem. Soc. Dalton Trans. (1990) 3215.
[30] V.W.-W. Yam, T.-F. Lai, C.-M. Che, J. Chem. Soc. Dalton Trans. (1990) 3747.
[31] W.A. Fordyce, H. Rau, M.L. Stone, G.A. Crosby, Chem. Phys. Lett. 77 (1981) 405.
[32] C. King, M.N.I. Khan, J.P. Fackler Jr., Inorg. Chem. 31 (1992) 3263.
[33] J.M. Forward, Z. Assefa, J.P. Fackler Jr., J. Am. Chem. Soc. 117 (1995) 9103.
[34] A. Vogler, in: A.W. Adamson, P.D. Fleischauer (Eds.), Concepts of Inorganic Photochemistry, Wiley, New York, 1975, p. 269 chapter 6.

[35] C.-M. Che, H.-L. Kwong, V.W.-W. Yam, K.-C. Cho, J. Chem. Soc. Chem. Commun. (1989) 885.
[36] V.W.-W. Yam, S.W.-K. Choi, K.K.-W. Lo, W.-F. Dung, R.Y.-C. Kong, J. Chem. Soc. Chem. Commun. (1994) 2379.
[37] K.A. Jensen, C.K. Jørgensen, Acta Chem. Scand. 19 (1965) 451.
[38] J. Chatt, R.G. Hayter, J. Chem. Soc. (1963) 1343.
[39] G.W.A. Fowles, R.A. Walton, J. Chem. Soc. (1964) 4330.
[40] A.D. Westland, L. Westland, Can. J. Chem. 43 (1965) 426.
[41] F. Calderazzo, S.A. Losi, B.P. Susz, Helv. Chim. Acta 54 (1971) 1156.
[42] H. Kunkely, A. Vogler, J. Organomet. Chem. 606 (2000) 207.
[43] W.A. Herrmann, J. Organomet. Chem. 500 (1995) 149.
[44] W.A. Herrmann, F.E. Kuehn, Acc. Chem. Res. 30 (1997) 169.
[45] A. Vogler, H. Kunkely, Coord. Chem. Rev. 200-202 (2000) 991.
[46] W.A. Herrmann, P.W. Roesky, M. Wang, W. Scherer, Organometallics 13 (1994) 4531.
[47] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 3 (2000) 143.
[48] A. Caruana, H. Kisch, Angew. Chem. Int. Ed. Engl. 18 (1979) 328.
[49] H. Tominaga, K. Sakai, T. Tsubomura, J. Chem. Soc. Chem. Commun. (1995) 2273.
[50] H. Kunkely, A. Vogler, Inorg. Chem. Commun. 2 (1999) 533.
[51] A. Vogler, H. Kunkely, Comments Inorg. Chem. 9 (1990) 201.
[52] A. Vogler, H. Kunkely, Comments Inorg. Chem. 19 (1997) 283.
[53] A. Acosta, J.I. Zink, J. Cheon, Inorg. Chem. 39 (2000) 427.
[54] A. Vogler, H. Kunkely, Z. Naturforsch. 44b (1989) 132.
[55] V. Pawlowski, H. Kunkely, A. Vogler, J. Inf. Rec. Mats. 21 (1994) 673.
[56] K. Oldenburg, A. Vogler, J. Organomet. Chem. 559 (1997) 101.
[57] H. Kunkely, A. Vogler, J. Organomet. Chem. 559 (1998) 215.
[58] N. Mataga, Bull. Chem. Soc. Jpn. 36 (1963) 654.
[59] C. Kutal, Coord. Chem. Rev. 99 (1990) 213.
[60] H. Kunkely, A. Vogler, J. Photochem. Photobiol. A Chem. 114 (1998) 193.
[61] D.J. Fife, K.W. Morse, Inorg. Chem. 23 (1984) 1545.
[62] B. Liaw, S.W. Orchard, C. Kutal, Inorg. Chem. 27 (1988) 1311.
[63] H. Kunkely, A. Vogler, J. Am. Chem. Soc. 117 (1995) 540.
[64] H. Kunkely, A. Vogler, Chem. Phys. Lett. 164 (1989) 621.
[65] D.P. Seegers, M.K. DeArmond, P.A. Grutsch, C. Kutal, Inorg. Chem. 23 (1984) 2874.
[66] B. Weissbart, D.V. Toronto, A.L. Balch, D.S. Tinti, Inorg. Chem. 35 (1996) 2490.
[67] A. Vogler, H. Kunkely, Comments Inorg. Chem. 21 (1999) 149.
[68] J.B. Foley, A.E. Bruce, M.R.M. Bruce, J. Am. Chem. Soc. 117 (1995) 9596.
[69] P. Schwerdtfeger, A.E. Bruce, M.R.M. Bruce, J. Am. Chem. Soc. 120 (1998) 6587.
[70] V. Pawlowski, H. Kunkely, A. Vogler, Inorg. Chim. Acta 234 (1995) 55.