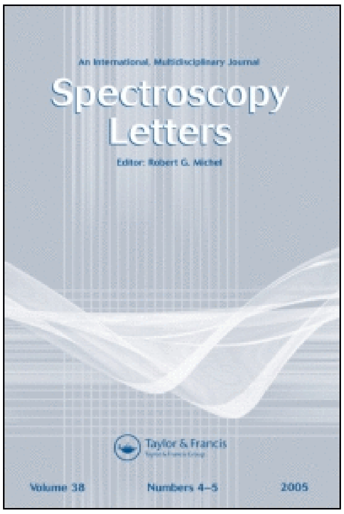

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Cis-Trans Isomerism in the Complex $BrMn(CO)_2dppm(P(OPh)_3)$ An Electronic Spectroscopy Study

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CIS-TRANS ISOMERISM IN THE COMPLEX $BrMn(CO)_2dppm[P(OPh)_3]$ AN ELECTRONIC SPECTROSCOPY STUDY

Key Words: Electronic Absorption Spectroscopy, Manganese-carbonyl complexes, cis-trans isomerism

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ABSTRACT

The UV-Visible absorption Spectra for the complexes cis and trans $BrMn(CO)_2dppm[P(OPh)_3]$ dppm = $Ph_2PCH_2PPh_2$ in several solvents are reported and an assignment of their bands is proposed. The cis isomer present one characteristics band in the visible region while that the trans isomer exhibits two well defined absorption bands. This spectral behavior is in agreement with early thermodynamic considerations.

INTRODUCTION

Dicarbonyl-metal complexes currently exhibit a cis-trans isomeric behavior. Chemical and electrochemical studies on complexes $M(CO)_2(diphos)_2$ M=Cr, Mo or W, diphos=tertiary disphophines and $XMn(CO)_2(diphos)L_2$ L=neutral ligands show the existence of cis and trans isomers. In general the redox-induced isomerisation of the cis-form is detected by cyclic voltammetry[1,2]. In addition the cis and trans geometries are easily distinguished by IR-carbonyl spectroscopy the former giving rise to two bands and the latter resulting in one.

The cis and trans isomers could be also distinguished by their different color although absorption spectroscopy studies have been not performed on such types of compounds.

Here we report the electronic spectra of the cis and trans isomer of the complex $BrMn(CO)_2dppm\{P(OPh)_3\}$[3] and an assignment of their bands is proposed in basis of the solvent effects as well as with aid of molecular orbital calculation for similar compounds.

RESULTS AND DISCUSSION

The compound cis-$BrMn(CO)_2dppm\{P(OPh)_3)\}$ exhibits an intense band around 390 nm which is not sensitive to

TABLE 1

Solvent[a] Dependence On Electronic Absorption Bands Of Cis And Trans BrMn(CO)$_2$ dppm [P(OPh)$_3$]

Solvent	ϵ[b]	Cis	Trans	
Chloroform	4.8	390	412	593
Dichloromethane	8.9	395	412	527
Acetone	20.7	395	415	525
Nitromethane	35.9	390	410	525
Dimethylformamide	36.1	395	411	528
Acetonitrile	37.5	390	409	528
Propane-1,2-diol carbonate	69.0	390	415	525

a. at room temperature

b. dielectric constant values from ref. 9

the solvent and responsible of their yellow colour. The spectrum is shown in figure 1 and the max(ϵ) values in chloroform are: 255 (13.000), 275 (9207); 390 (1383). Solvent effect data are display in table 1. On the other hand their trans isomer shows two well defined bands in the visible region as shows figure 1. These absorption bands are not sensitive to the solvent as can be viewed from table 1. The absorption at c.a. 529 nm explains the

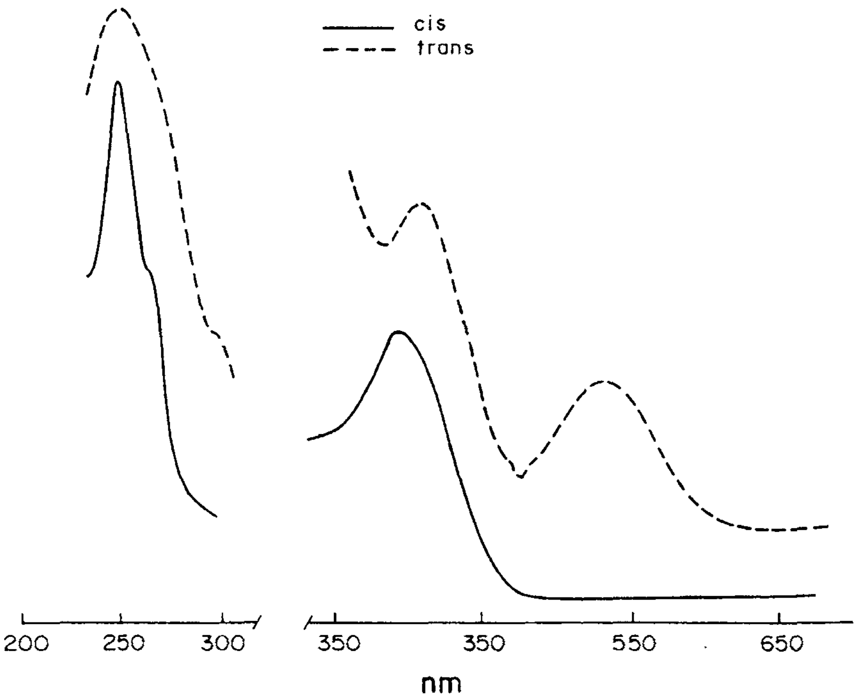

FIGURE 1.- Ultraviolet-visible absorption spectra of the complexes BrMn(CO)$_2$dppm(P(OPh)$_3$).CIS(-) AND TRANS(....) IN CHCl$_3$ AT ROOM TEMPERATURE.

red colour of the trans-isomer. The max(ϵ) values in chloroform are: 265 (6017), 300 (3809), 412 (916) and 593 (81).

The non-solvent effect[4] and the low extintion coefficient values for the absorption bands of cis and trans isomers of BrMn(CO)$_2$dppm [(P(OPh)$_3$] suggest the d-d character of these transitions. Assignments can be

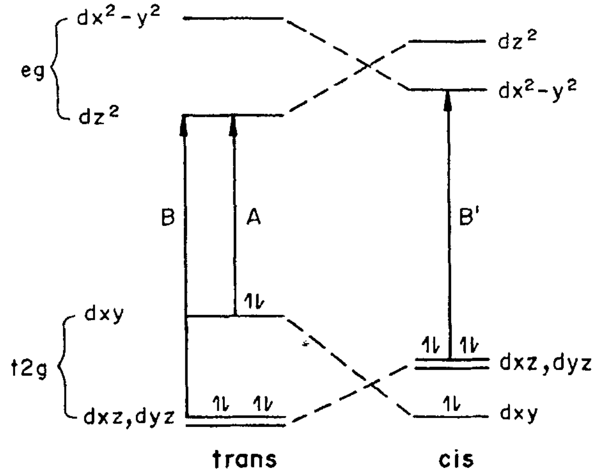

FIGURE 2.- MOLECULAR ORBITAL DIAGRAM FOR CIS AND TRANS $BrMn(CO)_2dppm(P(OPh)_3)$

made with aid of the molecular orbital diagram shown, figure 2, which was adapted from molecular orbital calculations performed on cis and trans $M(CO)_2L_4$ complexes[5]. Although the actual symmetry of the $BrMn(CO)_2$ dppm $\{P(OPh)_3\}$ complexes could be lower than those of $M(CO)_2L_4$ complexes[5], the primary change that could be expected is some splitting of the t_{2g} orbitals by lowering of the symmetry of the complex[6]. In this diagram the molecular orbital have been labelled according to the predominant metal d character and derived from the t_{2g} and eg set of the parent octahedron. The arrows represents the observed transitions.

For the trans-$BrMn(CO)_2dppm[P(OPh)_3]$ complex the lowest absorption band can be assigned to a metal centered dxy ——> dz^2 transition (transition A in figure 2) . The next lowest energy absorption band observed at c.a. 410 nm can be attributed to a dxz, dyz ——> dz^2 transition (B in figure 2). In the cis isomer the lowest absorption band occurs at higher energy than the trans isomer which can be explained by the decreasing of the HOMO energy in going from the trans to the cis isomer (transition B' in figure 2). This argument has been also used for explain the thermodynamically preferred cis isomer[5]. The next another possible d-d band of the cis isomer (dxy ——> dx^2-y^2 in the scheme) can overlap with the first observed band which in fact is some broad (see figure 1).

The absorption behavior for the two isomer in the 300-200 mm region is very similar as can be viewed from figure 1. For both the spectra is dominated by a strong absorption band around 260 nm and a shoulder in the low-energy flank of this band.

The very high energy, high intensity band can be attributed to a predominantly Metal ——> π* CO charge transfer transition in basis of their position and intensity values. Thus, intense Mn ——> π* CO charge transfer bands at about 230 mm have been observed for manganese-carbonyl complexes[7]. Absorptions due to transition of the phenyl groups of the diphenylphosphine methane and triphenyl-phosphite ligands can also be involved in this band although they are less intense[8].

The 275 nm and 300 nm shoulders observed for the cis and trans isomer respectively are probably due to a transition both Metal ——> π* CO and d-d in character.

EXPERIMENTAL

Cis and trans $BrMn(CO)_2dppm\{P(OPh)_3\}$ were prepared as previously described[3]. The solvents used were spectrophotometric or gold label grade (Aldrich) or Flucka and were purified according standard procedure.

UV-Visile absorption spectra were recorded with a Cary 17 and Variant DMS-90 spectrophotometers in 1 cm lenght cuvettes.

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