Inorganica Chimica Acta, *147* (1988) 45–49

Electronic Absorption Spectra of *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ Complexes (M = Mo or W; α-diimine = 2,2′-bipyridine or 1,10-phenanthroline)

YUNG J. HAN and ALISTAIR J. LEES*

Department of Chemistry, University Center at Binghamton, State University of New York, Binghamton, N.Y. 13901, U.S.A.

(Received October 8, 1987)

Abstract

Syntheses, infrared spectra, and electronic absorption spectra of *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ (M = Mo, W; α-diimine = 2,2′-bipyridine, 1,10-phenanthroline) complexes are reported. Infrared spectra indicate carbonyl stretching frequencies in the 1700–1800 cm^{-1} region, consistent with strong $M(d\pi) \rightarrow (\pi^*)CO$ back-bonding in these dicarbonyl complexes. Electronic absorption spectra illustrate several intense $M(d\pi) \rightarrow (\pi^*)\alpha$-diimine transitions throughout the visible region. A comparison of the solvent effects on the absorption spectra of the *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ species is made with the well known $M(CO)_4(\alpha\text{-diimine})$ complexes.

Introduction

There has been intense interest in the spectroscopic and photochemical properties of substituted metal carbonyl complexes that exhibit low energy metal-to-ligand charge-transfer (MLCT) excited states [1]. Although *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ complexes, where M = Cr, Mo or W, and α-diimine = 2,2′-bipyridine (bpy) or 1,10-phenanthroline (phen), have been known for some time [2], very little information on their electronic absorption spectra is presently available [3].

In this paper we report syntheses, infrared spectra, and electronic absorption spectra of several *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ complexes. These complexes were found to be extremely unstable and, consequently, we have employed a rapid scanning diode-array UV–Vis spectrometer to obtain the electronic absorption data. Solvent effects on the electronic absorption spectra of these complexes have been determined, and these provide a valuable comparison to the well-studied $M(CO)_4(\alpha\text{-diimine})$ complexes [4].

Experimental

Materials

All starting materials used in this work were commercially available and used without further purification. The parent hexacarbonyls and α-diimine ligands were obtained at >99% purity. Reagent grade hexanes and tetralin were used and spectroscopic grades were obtained for acetonitrile, chloroform, dimethyl sulfoxide, and methylene chloride. Nitrogen gas used in the syntheses and solution purging experiments was dried and deoxygenated according to a described literature procedure [5].

Synthesis of $M(CO)_4(\alpha\text{-diimine})$ (M = Mo, W; α-diimine = bpy, phen)

The $M(CO)_4$(diimine) complexes were prepared by photolysis with a 200 W Hg lamp of $M(CO)_6$ in N_2-purged hexanes containing excess α-diimine ligand according to published procedures [6]. Typical yields obtained were 80%. The $M(CO)_4(\alpha\text{-diimine})$ complexes are sparingly soluble in nonpolar solvents and they precipitated during light irradiation. These compounds were purified by repeated washings with hexanes to remove reactants, followed by column chromatography on alumina. These complexes were further purified by recrystallization from methylene chloride/hexanes solutions. Electronic absorption and infrared spectra obtained from the products were in good agreement with those reported previously [7].

Synthesis of cis-$M(CO)_2(\alpha\text{-diimine})_2$ (M = Mo, W; α-diimine = bpy, phen)

The *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ complexes were prepared via both thermal and photochemical routes. In the thermal procedure the product compounds were obtained by reacting the appropriate $M(CO)_4(\alpha\text{-diimine})$ complex with excess α-diimine in boiling tetralin under N_2 according to a literature procedure [3c]. In our synthesis we scaled down the previously reported quantities of all materials by a factor of 5 and the purification of the products by washing with hot benzene typically took 3–4 h. The photo-

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*Author to whom correspondence should be addressed.

chemical procedure involved irradiation at either 313 or 488 nm of 10^{-4} M $M(CO)_4(\alpha\text{-diimine})$ in deoxygenated methylene chloride containing 0.1 M α-diimine ligand. The conversion to *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ was monitored by UV–Vis spectroscopy over a 2 h period.

Physical Measurements

Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer and are considered accurate to ±2 cm^{-1}. UV–Vis spectra were obtained on a Hewlett-Packard 8450A microprocessor-controlled diode-array spectrometer that was used in conjunction with a Hewlett-Packard 82901M disk drive unit. Spectra were typically recorded in the 300–800 nm region with an acquisition time of 1 s. Absorption band maxima are considered accurate to ±1 nm in the ultraviolet region and ±2 nm in the visible region. Emission spectra were obtained on a SLM Instruments 8000/8000S spectrometer with excitation and detector slits at 16 nm. Photolysis experiments were performed with either the 313 nm line of an Ealing Corp. 200 W mercury arc lamp or the 488 nm line of a Lexel Corp. 95-4 4W argon-ion laser.

Results and Discussion

Synthesis

In addition to the established thermal procedure [3c] we have found that the *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ complexes can be formed photochemically according to eqn. (1). However, at $\lambda_{ex} = 488$ nm the long photolysis time required to generate even small

$$M(CO)_4(\alpha\text{-diimine}) \xrightarrow[\text{excess } \alpha\text{-diimine in } CH_2Cl_2]{h\nu} M(CO)_2(\alpha\text{-diimine})_2 + 2CO \qquad (1)$$

quantities of the product complexes and the general instabilities of these products indicate that this is not a useful preparative procedure. In contrast, photolysis at $\lambda_{ex} = 313$ nm was observed to be effective in producing the *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ derivatives.

General Properties

The *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ complexes are darkly colored crystalline materials and were observed to be highly light- and air-sensitive. Consequently, these compounds were handled under N_2 in sealed vessels at all times and exposed to minimum quantities of light. The compounds were typically only soluble in polar organic solvents such as dimethyl sulfoxide, acetonitrile, methylene chloride and chloroform, and in these solutions the complexes underwent fairly rapid thermal decomposition.

TABLE I. Infrared Spectral Data for *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ Complexes in the Carbonyl Stretching Region

Complex	Bands (cm^{-1})
cis-$Mo(CO)_2(bpy)_2$[a]	1794, 1720
cis-$Mo(CO)_2(phen)_2$[b]	1794, 1730
cis-$W(CO)_2(bpy)_2$[c]	1780, 1714
cis-$W(CO)_2(phen)_2$[a]	1780, 1716

[a] Recorded in acetonitrile. [b] Recorded in methylene chloride. [c] Recorded in dimethyl sulfoxide.

Infrared Spectra

Infrared spectra of *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ (M = Mo and W) complexes have been recorded in solution and the band maxima in the carbonyl stretching region are shown in Table I. These results are in agreement with those previously obtained from solid-state spectra [2, 3a, 3b] and recently reported solution data of the molybdenum derivatives [3c], and they confirm the *cis*-configuration of these complexes in the solution phase. The exceptionally low values of $\nu(CO)$ indicate unusually strong $M(d\pi) \rightarrow (\pi^*)CO$ back-bonding in these complexes. Moreover, these $\nu(CO)$ values are at lower energies than other Mo(0) dicarbonyl complexes that contain phosphine ligands [8], consistent with the $P > N$ order of ligand π-acidity.

Electronic Absorption Spectra

Electronic absorption spectra have been recorded from *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ (M = Mo and W) complexes on a diode-array spectrophotometer. Due to the thermal instabilities of these complexes each spectrum was recorded within 5 s of dissolution. Spectra recorded for *cis*-$M(CO)_2(phen)_2$ (M = Mo, W) in methylene chloride and *cis*-$M(CO)_2(bpy)_2$ (M = Mo, W) in dimethyl sulfoxide are shown in Figs. 1 and 2 and absorption data obtained from all the complexes studied are summarized in Table II. The visible region of these *cis*-$M(CO)_2)(\alpha\text{-diimine})_2$ complexes are dominated by intense bands ($\epsilon = 1500\text{–}8000$ M^{-1} cm^{-1}) which are assigned to $M(d\pi) \rightarrow (\pi^*)$diimine transitions, as previously reported for the molybdenum derivatives [3]. It may be noted that these metal-to-ligand charge-transfer (MLCT) transitions are generally at lower energies for the dicarbonyl complexes than the corresponding tetracarbonyl compounds [4]. This result is concordant with the increased ease of metal oxidation expected for the dicarbonyl species in which two strong π-acid carbonyl ligands have been replaced by a weaker π-acceptor α-diimine ligand.

Weaker ligand field (LF) transitions are also expected to lie in the visible region and α-diimine $\pi \rightarrow \pi^*$ transitions have been observed at wavelengths shorter than 300 nm. The d-orbital degeneracy can

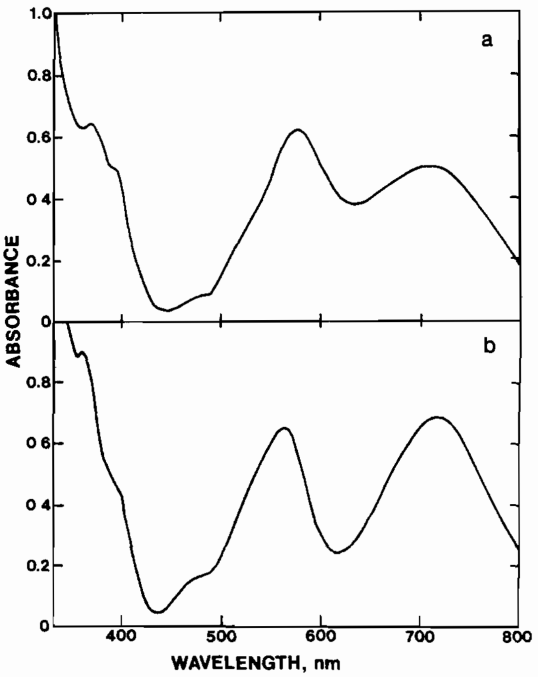

Fig. 1. Electronic absorption spectra of (a) *cis*-$Mo(CO)_2(phen)_2$ and (b) *cis*-$W(CO)_2(phen)_2$ in methylene chloride at 298 K.

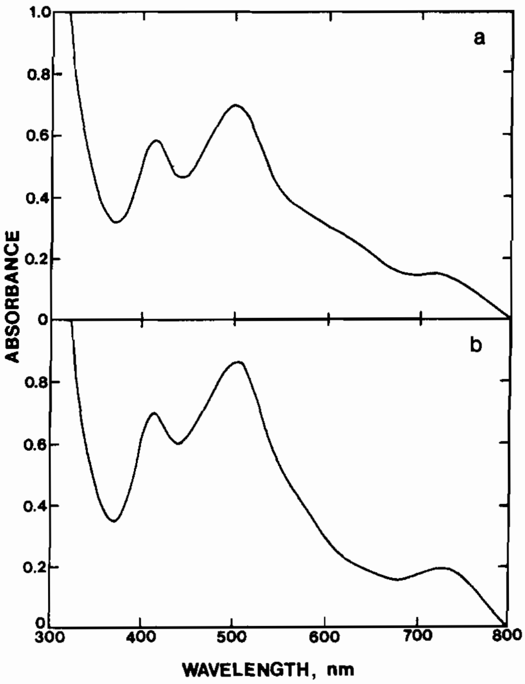

Fig. 2. Electronic absorption spectra of (a) *cis*-$Mo(CO)_2(bpy)_2$ and (b) *cis*-$W(CO)_2(bpy)_2$ in dimethyl sulfoxide at 298 K.

be assumed to be effectively removed in these low symmetry dicarbonyl complexes and hence several MLCT and LF spin-allowed transitions are predicted (see Fig. 3). In an effort to determine the positions of the LF bands of these *cis*-$M(CO)_2$(α-diimine) complexes we attempted to prepare *cis*-$W(CO)_2(en)_2$ (en = ethylenediamine) according to the procedures described in 'Experimental' for the bpy and phen derivatives. Electronic absorption data of *cis*-$M(CO)_2(en)_2$ (M = Mo and W) complexes would be informative as no low-lying MLCT transitions are possible and LF transitions should be readily observable [4]. However, to date we have been unable to isolate the en derivatives.

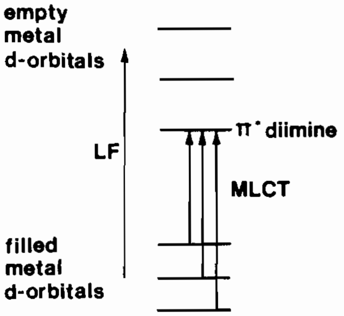

Fig. 3. Orbital scheme for *cis*-$M(CO)_2$(α-diimine)$_2$ (M = Mo and W) complexes illustrating possible MLCT transitions.

Solvent effects on the absorption spectra have been measured for the *cis*-$W(CO)_2$(α-diimine)$_2$ complexes and these are shown in Table II. Although the dicarbonyl compounds are soluble in relatively few media, the recorded spectral data illustrate that the $M(d\pi) \rightarrow (\pi^*)$α-diimine MLCT transitions are

TABLE II. Electronic Absorption Spectral Data for *cis*-$M(CO)_2$(α-diimine)$_2$ Complexes at 298 K

Complex	Solvent	Absorption maxima (nm)
cis-$Mo(CO)_2(bpy)_2$	dimethyl sulfoxide	416, 500, 600[a], 722
cis-$Mo(CO)_2(phen)_2$	methylene chloride	368, 392[a], 480[a], 576, 712
cis-$W(CO)_2(bpy)_2$	dimethyl sulfoxide	418, 504, 580[a], 730
	methylene chloride	418, 510, 588[a], 740
cis-$W(CO)_2(phen)_2$	dimethyl sulfoxide	364, 396[a], 480[a], 556, 712
	methylene chloride	360, 396[a], 480[a], 562, 718
	chloroform	360, 396[a], 478[a], 546, 724

[a] Observed as a shoulder.

TABLE III. Electronic Absorption Spectral Data for MLCT Bands of *cis*-$M(CO)_4(\alpha\text{-diimine})$ Complexes at 298 K

Complex	Solvent	Absorption maxima (nm)
$W(CO)_4(bpy)$	dimethyl sulfoxide	450
	methylene chloride	480
	chloroform	505
$W(CO)_4(phen)$	dimethyl sulfoxide	450
	methylene chloride	478
	chloroform	501

remarkably unaffected on varying the solvent. This contrasts sharply with the strong solvent dependence that has been observed for the low-lying MLCT bands of $W(CO)_4(bpy)$ and $W(CO)_4(phen)$ complexes. As a comparison, absorption data have been obtained from the tetracarbonyl complexes in the same media as used for the dicarbonyl complexes, and these results are shown in Table III.

The solvent sensitivity of the metal tetracarbonyl complexes (a 'negative solvatochromism' effect) has been explained previously in terms of a reduced excited-state electric dipole moment and differences in solvent polarizability interactions in the ground and excited MLCT states of these molecules [4b, 9]. The relative lack of solvent influence on the absorption spectra of the dicarbonyl complexes reveals that the specific solvent interactions are similar for both the ground and MLCT excited states. In contrast to the metal tetracarbonyl complexes the change in the electric dipole moment between the ground and $M(d\pi) \rightarrow (\pi^*)\alpha$-diimine excited states may be quite small for the lower symmetry dicarbonyl derivatives. Additionally, it is recognized that the exceptionally strong π back-bonding in these *cis*-$M(CO)_2(\alpha\text{-diimine})_2$ complexes will result in substantial mixing of the metal d and ligand π^* orbitals and, in essence, this will completely change the character of the MLCT transition to one more accurately depicted as $M(d\pi) \rightarrow (d\pi{-}\pi^*)\alpha$-diimine. This type of MLCT state will produce charge localization primarily along the metal–nitrogen bond and, therefore, specific solvent and induced dipolar interactions with the ligand π^*-system will be less influential. In this connection the MLCT transitions of $W(CO)_4(R\text{-dab})$ and $W(CO)_4(R\text{-pyca})$ complexes (R-dab = 1,4-diaza-1,3-butadiene and R-pyca = pyridine-2-carbaldehyde imine ligands) are known to have substantially different characters than those of $W(CO)_4(bpy)$ and $W(CO)_4(phen)$ and they exhibit considerably less solvatochromism [1k, 10].

Emission Spectra

A weak emission band (λ_{max} = 612 nm; half-width = 2450 cm^{-1}) was recorded from *cis*-$W(CO)_2(phen)_2$ in deoxygenated methylene chloride at 298 K following excitation at 400 nm. This band may arise from one of the low-lying MLCT excited states in this complex, but due to the high photosensitivity and tendency of this complex to thermally decompose we were unable to investigate the emission behavior in further detail.

Acknowledgements

We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemical Society for financial support of this research. We also thank Dr David E. Marx for assistance with the experimental work.

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