NaFe(CO)$_2$Cp **3a**, and 0.171 g (0.471 mmol) of Fe$_2$(CO)$_9$ was dissolved in a minimum amount of toluene at room temperature; then the solution was cooled at –20 °C, affording red crystals of **6a** (0.198 g, 0.297 mmol, 62% yield based upon **1**), mp 238–240 °C. Anal. Calcd for C$_{21}$H$_{29}$Fe$_2$N$_2$O$_8$SbSi: C, 37.81; H, 4.39; N, 4.20. Found: C, 38.21; H, 4.53; N, 4.25.

Some crystals (~10^{-5} mol) were dissolved in refluxing hexane (25 mL); the solution was filtered, cooled to 0 °C, and left overnight at this temperature, affording red single crystals.

Synthesis of Tetracarbonyl{1,3-di-*tert*-butyl-2,2-dimethyl-4-[(tricarbonyl-η^5-cyclopentadienyl)molybdenio]-1,3,2,4-diazasilastibetidine}iron, [Fe(CO)$_4$]Cp(CO)$_3$MoSb(N-*t*-Bu)$_2$SiMe$_2$, 6b. Hexane (5 mL) was added to the powder of **6b** obtained from 0.208 g (0.582 mmol) of Me$_2$Si(N-*t*-Bu)$_2$SbCl, **1**, 0.292 g (1.09 mmol) of NaMo(CO)$_3$Cp, **3b**, and 0.209 g (0.575 mmol) of Fe$_2$(CO)$_9$. The resulting brown suspension was vigorously magnetically stirred and then allowed to settle. Solvent was removed by aid of a pipet, and hot toluene (3 mL) was added to the unsoluble material. The resulting mixture was filtered to give a red solution, which was cooled overnight at –20 °C. **6b** was obtained as red crystals (0.269 g, 0.366 mmol, 63% yield based upon **1**), mp 230–232 °C. Anal. Calcd for C$_{22}$H$_{29}$FeMoN$_2$O$_7$SbSi: C, 35.94; H, 3.98; N, 3.81. Found: C, 36.47; H, 4.06; N, 3.74.

Crystals of **6b** were dissolved in a minimum amount of hot toluene, and the resulting solution was slowly cooled overnight from 100 °C to room temperature, affording single crystals of **6b**.

Synthesis of Tetracarbonyl{1,3-di-*tert*-butyl-2,2-dimethyl-4-[(tricarbonyl-η^5-cyclopentadienyl)tungstenio]-1,3,2,4-diazasilastibetidine}iron, [Fe(CO)$_4$]Cp(CO)$_3$WSb(N-*t*-Bu)$_2$SiMe$_2$, 6c. The brown powder of **6c** obtained from 0.201 g (0.563 mmol) of Me$_2$Si(N-*t*-Bu)$_2$SbCl, **1**, 0.391 g (1.10 mmol) of NaW(CO)$_3$Cp, **3c**, and 0.201 g (0.552 mmol) of Fe$_2$(CO)$_9$ was dissolved in toluene (~15 mL) and cooled at –20 °C. **6c** was obtained as a red powder (0.273 g, 0.332 mmol, 59% yield based upon **1**). **6c** is not soluble enough in benzene to allow molecular weight measurement; mp 227–229 °C. Anal. Calcd for C$_{22}$H$_{29}$FeN$_2$O$_7$SbSiW: C, 32.10; H, 3.56; N, 3.40. Found: C, 32.62; H, 3.65; N, 3.42.

X-ray Studies. Crystal Structure Determinations. Suitable crystals of each compound **4c, 5b, 6a**, and **6b** were examined by using similar procedures.

The crystallographic data are summarized in Tables II and III. Unit cell parameters were determined from 18–26 carefully centered reflections in the range 20 < 2θ < 25°. Data were collected by using the ω–θ scan technique up to a 45° 2θ angle. An empirical absorption correction based on a series of ψ scans was made.

The structures were solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares analysis with anisotropic thermal parameters for all metal, oxygen, nitrogen, and some carbon atoms (see Tables II and III).

All hydrogen atoms were fixed at their carbon atoms and refined together as rigid groups. In **6b** the Cp ring (C(8)–C(12)) was refined as a fixed regular pentagon. One of the *tert*-butyl groups (C18–C20) is disordered, so each carbon atom occupies two positions with a half weight.

All calculations were carried out on a DEC Micro VAX II computer using the SHELXS-86 and SHELX-76 programs.[11]

Registry No. 1, 118083-14-0; **2**, 118083-15-1; **3a**, 12152-20-4; **3b**, 12107-35-6; **3c**, 12107-36-7; **4a**, 126457-14-5; **4b**, 126457-15-6; **4c**, 126457-16-7; **5a**, 126422-15-9; **5b**, 126422-16-0; **5c**, 126422-17-1; **6a**, 126457-17-8; **6b**, 126457-18-9; **6c**, 126457-19-0.

Supplementary Material Available: Tables of atomic coordinates, bond distances and angles, and the anisotropic temperature values of the atoms of structures **4c, 5c, 6a**, and **6b** (12 pages); listings of structure factor amplitudes of **4c, 5c, 6a**, and **6b** (28 pages). Ordering information is given on any current masthead page.

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Ligand-Field and Charge-Transfer Photochemistry of M(CO)$_4$(1,10-phenanthroline) (M = Cr, Mo, W). Mechanistic Information from High-Pressure Effects

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The pressure dependence of the quantum yield for photosubstitution of CO in M(CO)$_4$(1,10-phenanthroline) (M = Cr, Mo, W) was studied at different excitation wavelengths in order to resolve the nature of the substitution mechanism operating from the ligand-field and charge-transfer excited states. Irradiation at 366 nm results in positive volumes of activation (between +6 and +10 cm^3 mol^{-1}) for ligand-field photosubstitution, in agreement with a dissociative substitution mode. Irradiation at 546 nm results in significantly negative volumes of activation (between –12 and –14 cm^3 mol^{-1}) for charge-transfer photosubstitution in the case of M = Mo and W, which is interpreted as strong evidence for an associative substitution reaction originating from the MLCT excited state. The corresponding value is small positive for the Cr complex and ascribed to a dissociative process operating from the charge-transfer excited state.

Introduction

The application of high-pressure kinetic techniques in mechanistic studies on the reactions of inorganic and organometallic complexes in solution has received much attention from various groups in recent years.[3–6] Especially the application of this method in the elucidation of the mechanisms of thermal reactions has been rather successful. We and others[7] have in recent years investi-

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gated the possibility of applying this technique to the study of photochemical and photoinduced processes. In such reactions the traditional activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) usually reveal little mechanistic information, and the application of alternative methods is required. In this respect we are convinced that the physical variable pressure can reveal additional, and in some cases unique, mechanistic information. This expectation is on one hand based on our experience with the study of thermal reactions and on the other hand on the fact that pressure-dependence studies of rate constants reveal information on partial molar volume changes during the reaction, whereas temperature-dependence studies reveal information on the energetics of the process. In this way the pressure work results in a reaction volume profile compared to a reaction energy profile in the temperature work.

We have recently undertaken a systematic investigation of the effect of pressure on photosubstitution reactions on complexes of the type $M(CO)_6$, $M(CO)_5L$, and $M(CO)_4L'L$, where M = Cr, Mo, W, and L is a N- or P-donor ligand.[8] The low oxidation states of these complexes and the use of neutral ligands simplify the interpretation of the observed pressure effects, since these can in the absence of major solvational changes be associated with intrinsic volume changes arising from changes in bond lengths and bond angles during the substitution process.[9]

In this paper we report our findings for the ligand-field and charge-transfer photochemistry of complexes of the type $M(CO)_4$phen, where M = Cr, Mo, and W and phen = 1,10-phenanthroline. The photochemistry and photophysics of these complexes have received significant attention from various groups mainly because of the important role of both ligand-field (LF) and charge-transfer (CT) excited states in such processes.[10-16] In general, photosubstitution reactions of the type in (1) exhibit a

$$M(CO)_4\text{phen} + L \xrightarrow{h\nu} fac\text{-}M(CO)_3(L)\text{phen} + CO \quad (1)$$
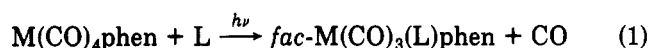
strong dependence of the quantum yield on the excitation wavelength,[10] which is interpreted in terms of the higher reactivity of the electronic excited LF states at higher energies compared to the energetically lower lying MLCT states. The observed photosubstitution is often considered to be purely dissociative and analogous to the corresponding hexa- or pentacarbonyl complexes. It is assumed that a low-energy excited LF state is populated thermally from a slightly lower lying MLCT state,[12] such that the observed chemistry originates from the LF state under all conditions. Other authors[16] argue that the MLCT states can exhibit their own photochemistry, and evidence in favor of an associative substitution mode originating from this state has been reported. We have studied the pressure dependence of these photosubstitution reactions in an effort to resolve this controversy. A preliminary communication on our results for the W(CO)₄phen system has appeared.[17]

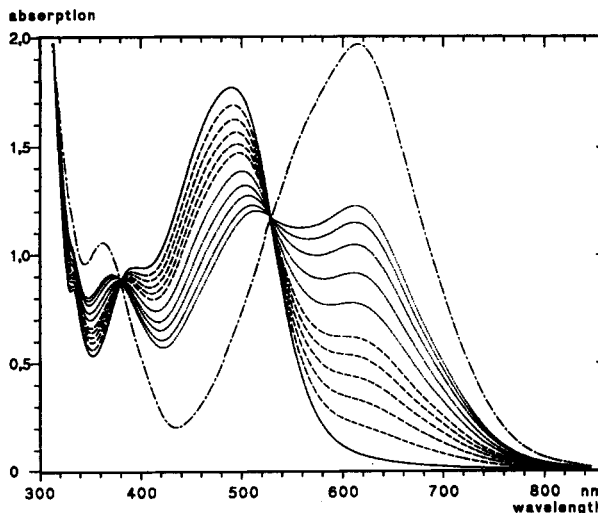**Figure 1.** Spectral changes accompanying the reaction Mo-(CO)₄phen + P(C₂H₅)₃ → *fac*-Mo(CO)₃[P(C₂H₅)₃]phen + CO. Irradiation wavelength is 546 nm; solvent used is toluene; (—) Mo(CO)₄phen; (-··-) Mo(CO)₃[P(C₂H₅)₃]phen.

Experimental Section

Materials. The complexes Cr(CO)₄phen, Mo(CO)₄phen, and W(CO)₄phen were prepared and purified according to published procedures.[18-22] The synthesized compounds were characterized by their UV–vis and IR spectra;[8] the spectral data were in good agreement with those reported before.[12,14,23,24] Elemental analyses were performed by Beller Analytical Laboratory (Göttingen, FRG) and gave results in good agreement with the theoretically expected.[8] The solvent toluene was of spectrophotometrical grade (Merck, Uvasol) and was degassed by freeze–pump–thaw cycles and then saturated with high-purity Ar. Triethylphosphine (Aldrich, 99%) was used without further purification.

Photoreaction Instrumentation and Procedures. Photolyses were carried out in a thermostated (25.0 ± 0.2 °C) high-pressure cell compartment[25] positioned on top of a magnetic stirrer. The solutions were irradiated in a pillbox[26] spectrophotometer cell (2.8-cm³ volume at ambient pressure) and stirred during irradiation with a Teflon-coated magnetic bar (2 × 6 mm). The test solutions were always handled under argon atmosphere and were transferred into the pillbox cell by using a combination of Schlenk and double-tip-needle techniques using a specially designed filling system.[27] A high-pressure mercury lamp (Osram HBO 100/2) was used for the photolysis, and light at 366 and 546 nm was selected by using Oriel interference filters. The light intensity was measured with the aid of a calibrated photodiode mounted on the rear window of the high-pressure cell.[28]

Calculation of Quantum Yields. Photolysis experiments were performed in the pressure range 0.1–200 MPa. The photochemical conversion was determined spectrophotometrically by following the UV–vis spectra as a function of irradiation time. Each quantum yield determination at one pressure is the mean value of between 3 and 10 independent measurements. Quantum yields were corrected for inner filter effects,[29,30] resulting from

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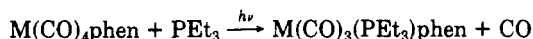(11) Lees, A. J. *Chem. Rev.* 1987, *87*, 711.
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Table I. Quantum Yield as a Function of Pressure for the Reaction[a]

$$M(CO)_4phen + PEt_3 \xrightarrow{h\nu} M(CO)_3(PEt_3)phen + CO$$

pressure, MPa	M = Cr		M = Mo		M = W	
	ϕ (366 nm)	ϕ (546 nm)	$\phi \times 10$ (366 nm)	$\phi \times 10$ (546 nm)	$\phi \times 10$ (366 nm)	$\phi \times 100$ (546 nm)
5	0.546 ± 0.002	0.112 ± 0.014	0.556 ± 0.012	0.102 ± 0.008	0.179 ± 0.002	0.60 ± 0.04
25				0.128 ± 0.007	0.154 ± 0.003	0.71 ± 0.02
50	0.515 ± 0.049	0.106 ± 0.003	0.509 ± 0.010	0.122 ± 0.008	0.158 ± 0.023	0.85 ± 0.01
75				0.155 ± 0.007	0.131 ± 0.010	0.95 ± 0.03
100	0.435 ± 0.035	0.101 ± 0.004	0.450 ± 0.020	0.168 ± 0.006	0.127 ± 0.013	1.06 ± 0.07
125				0.185 ± 0.009	0.117 ± 0.013	1.19 ± 0.06
150	0.417 ± 0.011	0.098 ± 0.003	0.400 ± 0.013	0.254 ± 0.025	0.110 ± 0.012	1.31 ± 0.09
175				0.230 ± 0.018	0.101 ± 0.007	1.54 ± 0.18
200		0.089 ± 0.007		0.318 ± 0.010	0.090 ± 0.006	1.53 ± 0.12
$[M] \times 10^4$, M	2.25	2.8	1.7	2.4	1.7	1.64
$[PEt_3] \times 10^2$, M	1.28	1.35	1.28	13.5	1.35	13.5
ΔV^*_ϕ, cm^3 mol^{-1}	(+5.0 ± 0.8)[b]	+2.7 ± 0.3	+5.7 ± 0.2	−13.3 ± 1.2	+8.1 ± 0.5	−12.0 ± 0.7
$\Delta V^*_{\phi/(1-\phi)}$, cm^3 mol^{-1}	+9.6 ± 1.6	(+3.0 ± 0.3)[b]	(+6.0 ± 0.2)[b]	(−13.6 ± 1.2)[b]	(+8.2 ± 0.5)[b]	(−12.0 ± 0.7)[b]

[a] Temperature, 25 °C; solvent, toluene. [b] Quoted for comparison reasons but not used in the discussion of the data.

absorbance by the product species at the irradiation wavelengths. Perkin-Elmer Lambda 5 and Hitachi U-3200 spectrophotometers were employed in this study.

Results and Discussion

The photosubstitution reactions of M(CO)$_4$phen (M = Cr, Mo, W) according to eq 1 were studied for L = PEt$_3$ in toluene. Other entering ligands such as amines, phosphites, or sterically hindered phosphines could not be studied since the quantum yield for the photosubstitution on W(CO)$_4$phen is too small to be measured accurately with the available instrumentation (i.e., irradiation intensity). Substitution of a CO ligand by PEt$_3$ results in a distinct color change from deep red for M(CO)$_4$phen to deep blue for M(CO)$_3$(PEt$_3$)phen, i.e., a substantial shift in the MLCT band to longer wavelength. A typical example of the observed spectral changes during photolysis is presented in Figure 1 for the irradiation of M-(CO)$_4$phen/PEt$_3$ at 546 nm. The intensive MLCT bands originate from transitions into π^*_{ligand} orbitals that occur at a lower energy than the unoccupied LF orbitals. Detailed studies on the solvatochromism of the emission spectra, the luminescence excitation spectrum, and the resonance Raman excitation profile led to the assignment of the observed absorption bands to specific electronic transitions.[11,14,15] In this way the lowest energy absorption and emission bands were assigned to MLCT transitions. For the purpose of this paper, the simplified energy-state diagram presented in Figure 2 is sufficient for the interpretation of the observed photochemistry.

On excitation in the UV region, photosubstitution occurs from an energetically higher lying LF excited state, which also accounts for the higher quantum yields at shorter wavelengths. Excitation at longer wavelengths is accompanied by a drastic decrease in quantum yield. This could be due to a substantially lower reactivity of lower lying states or to a lack of effective thermal back-population of the LF state from the lower lying MLCT state.[12] However, variation of the excitation wavelength within the MLCT absorption bands does not affect the quantum yield,[16] although lower lying MLCT states are populated at longer wavelengths so that the energy gap to the lowest electronically excited LF state increases and thermal back-population should become less important. The observed limiting quantum yield at longer wavelengths can therefore be interpreted in terms of direct photoactivity of the MLCT states. A correlation between the photosubstitution
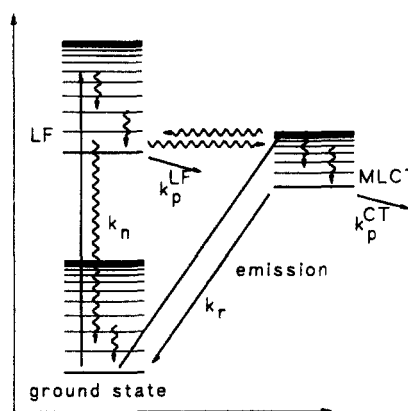
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Figure 2. Electronically excited states for W(CO)$_4$phen. LF = ligand field excited state, MLCT = metal-to-ligand change-transfer excited state. The rate constants for radiative, nonradiative, and chemical deactivation are denoted by k_r, k_n, and k_p, respectively. The superscript LF or CT denotes whether LF or MLCT states are responsible for the given reaction pathway.

quantum yield and the resonance Raman spectra suggested that in the MLCT states the electron density is delocalized over the cis-carbonyl ligands of M(CO)$_4$phen.[13,14] This reduces the π-back bonding ability to cis-CO and destabilizes the M–CO bond, such that both dissociative and associative substitution reactions are possible from the MLCT state.

The pressure dependence of the quantum yield for reaction 1 was studied for MLCT excitation at 546 nm and for LF excitation at 366 nm. The observed results are summarized in Table I. Plots of ln ϕ or ln $[\phi/(1 - \phi)]$ versus pressure are linear within the experimental error limits,[8,17] and the quoted ΔV^* values were calculated from the slope of these plots $(= -\Delta V^*/RT)$ in the usual way.[6] A higher ligand concentration was selected for the irradiation at 546 nm due to the low quantum yield in this region and its direct dependence on [L].[16] On the contrary, the quantum yield for the irradiation at 366 nm is independent of [L], as demonstrated by a series of such measurements during this investigation. The results in Table I clearly demonstrate that LF photolysis is accompanied by a positive volume of activation, whereas CT photolysis is accompanied by a significantly negative volume of activation for the Mo and W complexes and a small positive value for the Cr complex. These significantly different pressure dependencies of the quantum yields for photosubstitution reactions when irradiating into LF or CT bands could indicate the operation of different substitution mechanisms and therefore call for a more detailed analysis.

For the energy diagram given in Figure 2, the total observed quantum yield is given by eq 2, which reduces to

$$\phi_p^{TOT} = \phi_p^{LF} + \phi_p^{CT} \qquad (2)$$

$$\phi_p^{TOT} \approx \phi_p^{LF} = \frac{k_p^{LF}}{k_p^{LF} + k_n^{LF} + k_r^{LF}} \qquad (3)$$

$$\phi_p^{TOT} \approx \phi_p^{CT} = \frac{k_p^{CT}[L]}{k_p^{CT}[L] + k_n^{CT} + k_r^{CT}} \qquad (4)$$

(3) for LF excitation (at short wavelengths) when $\phi_p^{LF} \gg \phi_p^{CT}$. For the situation where the reaction mainly occurs from the MLCT state, i.e., for instance, the rest quantum yield at high wavelength, eq 2 reduces to (4). The investigated complexes all exhibit weak emissions such that $k_r \ll k_p + k_n$ under all conditions. Furthermore, eqs 3 and 4 can be modified to (5), using the indicated conditions.

$$\phi_p^{LF} = k_p^{LF}/k_n^{LF} \quad \text{at low } \phi_p$$
$$(k_n^{LF} \gg k_p^{LF}, \text{ M = Mo, W})$$

$$\phi_p^{LF} = k_p^{LF}/(k_p^{LF} + k_n^{LF}) \quad \text{at moderate to high } \phi_p \quad (5)$$

$$\phi_p^{LF}/(1 - \phi_p^{LF}) = k_p^{LF}/k_n^{LF} \quad (k_n^{LF} \approx k_p^{LF}, \text{ M = Cr})$$

$$\phi_p^{CT} = k_p^{CT}[L]/k_n^{CT} \quad \text{at low } \phi_p$$
$$(k_p^{CT}[L] \ll k_n^{CT}, \text{ M = Cr, Mo, W})$$

On the assumption that nonradiative deactivation is not very pressure sensitive, which is usually the case,[7,31] the corresponding volumes of activation for the photochemical reaction (k_p^{LF} and k_p^{CT}) can be calculated from the pressure dependence of ϕ_p^{LF} or $\phi_p^{LF}/(1 - \phi_p^{LF})$ and ϕ_p^{CT}, respectively. The estimated values are summarized in Table I, from which it follows that ϕ and $\phi/(1 - \phi)$ exhibit very similar ΔV^* values for low ϕ but considerably different ΔV^* values for high ϕ (M = Cr at 366 nm), in agreement with the applied relationships in (5).

The results in Table I clearly demonstrate that ΔV^* is significantly positive for photosubstitution following excitation in the UV region. The values of between +5.7 and +9.6 cm³ mol⁻¹ for $\Delta V^*(k_p^{LF})$ underline the operation of a dissociative (D) substitution mechanism as expected for LF photolysis in all cases. A number of thermal substitution reactions of metal carbonyl complexes have revealed typical ΔV^* values of between +20 and +24 cm³ mol⁻¹ for the dissociation of CO.[32,33] The significantly less positive value observed here for the photochemical reaction can be ascribed to an increase in volume of ca. 10 cm³ mol⁻¹ due to bond lengthening during LF excitation. This increase in volume is presumably directed along the M–CO bond on moving to the transition state and therefore can account for the smaller ΔV^* values observed for such ligand dissociation reactions in excited LF states. A similar trend was observed for the photodissociation of NH₃ in Rh(III) ammine complexes with typical ΔV^* values between +6 and +9 cm³ mol⁻¹ for the Rh(NH₃)₅Cl²⁺ and Rh(NH₃)₅Br²⁺ complexes in aqueous solution.[34] Our present results for the photodissociation of CO are of similar magnitude and therefore in close agreement with these data since the

partial molar volumes of CO and NH₃ (ca. 35 and 25 cm³ mol⁻¹, respectively) are not too different.

The significantly negative volume of activation reported for CT excitation in the case of the Mo and W complexes underlines the operation of an associative substitution process originating from the MLCT excited state. These values are very close to those found for the thermal substitution of CO in $(\eta^5\text{-}C_5H_5)Rh(CO)_2$ by PBu$^n_3$ and PPh₃, viz. −17.0 ± 0.7 and −14.3 ± 1.5 cm³ mol⁻¹, respectively,[35] which is generally accepted to follow an associative (A) mechanism.[36] For an associative process the absolute value of ΔV^* should depend on the partial molar volume of the entering ligand and the overlap of the van der Waals radii.[3,6] For MLCT excitation there is no complication as discussed above for LF excitation since the partial molar volume of the CT excited state is generally known to be significantly smaller than that of the LF excited state and presumably close to that of the ground state.[7,31,37] In addition, we do not expect that solvational changes on forming the MLCT state can account for this substantially more negative ΔV^* than observed for LF excitation. These results are in good agreement with other evidence reported in the literature in favor of an associative mechanism.[16] For a series of complexes of the type W(CO)₄N⌒N (N⌒N = substituted 1,4-diazabutadiene, phen, and substituted phen) it was shown that the observed quantum yield for CT photochemistry strongly depends on the concentration and basicity of the entering ligand, the Tolman cone angle of the phosphine as entering ligand, and the steric hindrance on N⌒N. We therefore conclude that the observed pressure dependence for the CT photosubstitution of Mo(CO)₄phen and W(CO)₄phen unequivocally supports the operation of an associative substitution mechanism. A shift in the electron density away from the metal center towards the phen ligand during MLCT excitation leads to the formation of a 17-electron metal center that will favor associative nucleophilic attack on the center in a similar way as described for the thermal substitution reactions of the quoted cyclopentadienyl complexes.[35,36]

The role of the ligand-concentration-dependent photosubstitution pathway (CT) is more significant for the heavier metal centers (Mo and W) than for the lighter Cr center. In the latter case the volume of activation found for CT photosubstitution is slightly positive (ca. +3 cm³ mol⁻¹), which indicates that the significantly smaller Cr center exhibits a tendency to undergo a dissociative substitution reaction. Thus the size of the metal center prevents associative attack as observed for the larger Mo and W complexes. Such steric effects have also been reported for thermal substitution reactions on complexes of the type M(CO)₄S⌒S, where S⌒S is a dithiaalkane or dithiaalkene.[38] Throughout these systems the Cr complexes exhibit positive ΔV^* values whereas the corresponding Mo complexes exhibit negative values, in agreement with dissociative and associative substitution modes, respectively. The significantly higher quantum yield observed for the CT photolysis of Cr(CO)₄phen (see Table I) compared to the Mo and W complexes may also indicate the operation of a dissociative mechanism similar to that usually suggested for LF photolysis. In addition, we found that an increase in the ligand concentration from 0.013 to 0.095 M had no significant influence on the photosubstitution quantum yield

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at 546 nm, also supporting the dissociative nature of the process. This observation is also in line with the resonance Raman data referred to before,[13,14] according to which the *cis*-metal–carbonyl bond is partially labilized during MLCT excitation, thus enabling the dissociative reaction mode. The labilization is obviously less than in the case of LF excitation as seen from the ΔV^* value of +2.7 cm³ mol⁻¹ as compared to +9.6 cm³ mol⁻¹ in the latter case. On the basis of this difference, we can also exclude the possibility of a reaction via back population of the LF excited state, since then the observed volume of activation should be larger than for the LF substitution process. LF excited states in general have a higher partial molar volume than MLCT states,[7,37] and this volume difference will then have to add on to the volume of activation for the LF substitution process. Such a situation was reported recently for the photosubstitution reactions of a series of W(CO)₅(4-X-pyridine) (X = H, acetyl, cyano) complexes, where the introduction of an electron-withdrawing group initiates MLCT excitation.[37] The unsubstituted pyridine (X = H) complex undergoes dissociative LF photosubstitution for which ΔV^* is +5.6 cm³ mol⁻¹, whereas the substituted pyridine complexes undergo partial MLCT excitation followed by back population of the LF excited state. The observed ΔV^* in the latter case is larger than reported for the unsubstituted complex, viz. +6.3 (X = cyano) and +9.9 (X = acetyl) cm³ mol⁻¹. It is therefore likely that Cr(CO)₄phen undergoes dissociative photosubstitution from both the LF and MLCT excited states. The absolute magnitude of ΔV^* suggests a D mechanism in the former

and I_d mechanism in the latter case, since less M–CO bond weakening is expected to occur during MLCT excitation as compared to LF excitation. Alternatively, the low ΔV^* found at 546 nm could be due to a combination of both (MLCT and LF) reaction paths. In this respect it is interesting to note that a limiting quantum yield was also found at high wavelengths for the photosubstitution of Cr(CO)₄(bipyridine), which presumably also points to a reaction occurring from the CT excited state.[39]

The significantly different ΔV^* values reported in this study for LF and CT photosubstitution of Mo(CO)₄phen and W(CO)₄phen clearly underline the different substitution mechanisms operating from these excited states and support earlier arguments in favor of the photoactivity of the MLCT states in such complexes.[13,14,16] The results furthermore underline the value of pressure as a key parameter to distinguish between associative and dissociative photosubstitution mechanisms. Mechanistic interpretation in terms of partial molar volume changes is more straightforward than in terms of energy changes, i.e., a volume profile treatment versus an energy profile treatment.

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Synthesis and X-ray Structure of an (Oxodimethylidenemethane)iron Dimer, [(CH₂COCH₂)(CO)₃Fe]₂

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An iron carbonyl π-complex of the oxyallyl species was synthesized in two steps by complexation of a silylenol ether of α-bromoacetone and subsequent dehydrohalogenation by pyridine/AgBF₄. The isolated intermediate, bromotricarbonyl(η³-2-hydroxy-2-propenyl)iron, shows an unexpectedly high acidity (pK_a = 5.2). The tricarbonyl(oxyallyl)iron complex exists as [(CH₂COCH₂)(CO)₃Fe]₂ only, a head-to-tail dimer, as revealed by ¹H and ¹³C NMR spectroscopy as well as by X-ray diffraction analysis. This complex shows a butterfly like bent skeleton of C_2 symmetry which inverts on the NMR time scale with an activation energy of 72 kJ/mol at room temperature. It crystallizes as orange hexagonal plates in the orthorhombic space group *Pbc2₁* with *a* = 11.658 (2) Å, *b* = 6.192 (1) Å, *c* = 20.311 (4) Å, and *Z* = 4. According to the analytical and chemical observations, this complex exhibits a structure halfway between a 2-substituted π-allylic complex and a metallacyclobutanone compound.

Introduction

Oxyallyl **1** has always intrigued chemists from both a theoretical[1] and a synthetic[2] point of view, as a still-elusive species, which may however be involved as a short-lived intermediate in well-known reactions like the Faworski rearrangement and the Noyori cycyloaddition. Cyclopropanone **2**, stable itself only in solution at low temper-

atures, and allene oxide **3**, unknown without stabilizing substituents, have been referred to as limiting structures of oxyallyl, based on one hand on calculated energies[1a,3] of the molecules and their interconversion barriers and on the other hand on reaction product analyses.[4]

The evident similarity of oxyallyl and trimethylidenemethane **4** (TMM) prompted us to attempt a stabilization of the species by complexation with a suitable transition

2   1   3
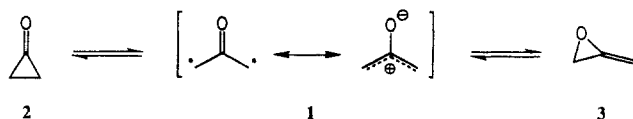
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