Early Excited State Dynamics of W(CO)$_5$(4-cyanopyridine) and W(CO)$_5$(4-formylpyridine): Observation of an Ultrafast Intersystem Crossing

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Picosecond time-resolved absorption spectra of W(CO)$_5$(4-cyanopyridine) and W(CO)$_5$(4-formylpyridine) complexes were measured following excitation into the ligand-field, LF (355 nm), and, for the latter complex, also into the metal to ligand charge-transfer, MLCT (532 nm), absorption bands. In each case, formation of the transient absorption spectrum of the long-lived ^{3}MLCT excited state was observed. Its population follows biphasic kinetics. The faster component is a sub-picosecond process (probably hundreds of femtoseconds) whereas the lifetimes of the slower component in toluene solution under 355-nm excitation were estimated as 45 and 36 ps for W(CO)$_5$(4-cyanopyridine) and W(CO)$_5$(4-formylpyridine), respectively. These results were interpreted as two intersystem crossings: one is ultrafast and takes place from a (near) Franck–Condon excited state; the other is slower, occurring from a vibrationally relaxed ^{1}MLCT state.

Introduction

Although metal to ligand charge-transfer, MLCT, excited states are best known for their electron-transfer reactivity, they are also implicated in other chemical processes which involve bond activation. For example, a CO ligand was found[1] to dissociate promptly from the spin-singlet MLCT state of Cr(CO)$_4$bpy, leading to a dissociative CO substitution.[2–4] The analogous tungsten complex W(CO)$_4$phen undergoes associative CO substitution[4,5] from its MLCT state(s) which is (are) apparently populated on a sub-picosecond time scale.[6]

As in these tetracarbonyls, MLCT states are the lowest lying excited states also in W(CO)$_5$(4-X-pyridine) complexes where X is an electron-withdrawing substituent, *e.g.* CN, formyl, benzoyl, or acetyl group.[7] Two MLCT states, derived from $d_\pi(e) \rightarrow \pi^*$(py) and $d_\pi(b_2) \rightarrow \pi^*$(py) excitations are present.[8] Corresponding long-lived (292 ns at room temperature) emissive ^{3}MLCT states are separated by 990 cm,$^{-1}$ and they are in thermal equilibrium in fluid solution, as was found[8] for W(CO)$_5$(4-NC-py). Other W(CO)$_5$(4-X-pyridine) complexes exhibit qualitatively similar behavior.[7,9] Nanosecond time-resolved spectra reported previously[9,10] show that the lower ^{3}MLCT state is populated within 10 ns following the laser excitation (355 or 510 nm) for all of the investigated W(CO)$_5$(4-X-pyridine) complexes.

W(CO)$_5$(4-X-pyridine) complexes undergo[7] photosubstitution of the pyridine ligand:

$$\mathrm{W(CO)_5(4\text{-}X\text{-}pyridine) + S \xrightarrow{h\nu} W(CO)_5S + 4\text{-}X\text{-}pyridine} \quad (1)$$

The quantum yield of this reaction is approximately 0.1 when the complexes are irradiated into the higher energy ligand-field, LF, absorption band[11] and drops to about 0.02 when the irradiation is into the MLCT absorption band[7,9,13,14] in the visible. Spin-triplet, ^{3}MLCT, states are clearly involved in the photosubstitution reaction (1) under direct MLCT excitation, as both the phosphorescence and the reaction quantum yield are quenched by anthracene with identical quenching constants.[9,14] Moreover, the absorption spectrum of W(CO)$_5$S, the reaction product, appears between 150 ns and 5 μs after MLCT excitation along with the decay of the ^{3}MLCT excited-state spectrum.[9,10] The activation energy of reaction 1, 12 660 cm^{-1} for W(CO)$_5$(4-NC-py) under MLCT excitation,[9,14] is rather high for a direct substitution from the ^{3}MLCT state. It was thus suggested that a highly reactive, presumably ^{3}LF, state is thermally populated from the long-lived ^{3}MLCT states. Pressure dependence of photochemical quantum yields strongly supports this mechanism.[13] Positive volumes of activation suggest an identical dissociative mechanism for both LF and MLCT excitations. Furthermore, apparent volumes of activation found for the substitution under MLCT excitation are larger than those measured for direct photosubstitution from LF states. Observed differences (4.3 and 1.8 cm^3 mol^{-1} for 4-acetylpyridine and 4-cyanopyridine, respectively)[13] correspond to the usual expansion of the molecule when going from the MLCT to the LF state.[15]

It is thus obvious that the MLCT excited states in W(CO)$_5$(4-X-pyridine) complexes do not possess a chemical reactivity of

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(1) Vichová, J.; Hartl, F.; Vlček, A., Jr. *J. Am. Chem. Soc.* **1992**, *114*, 10903.

(2) Balk, R. W.; Snoeck, T.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015.

(3) Manuta, D. M.; Lees, A. *Inorg. Chem.* **1986**, *25*, 1354.

(4) Wieland, S.; Reddy, K. B.; van Eldik, R. *Organometallics* **1990**, *9*, 1802.

(5) van Dijk, H. K.; Servaas, P. C.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1985**, *104*, 179.

(6) Lindsay, E.; Vlček, A., Jr.; Langford, C. H. *Inorg. Chem.*, in press.

(7) Wrighton, M. S.; Abrahamson, H. B.; Morse, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 4105.

(8) Rawlins, K. A.; Lees, A. J.; Adamson, A. W. *Inorg. Chem.* **1990**, *29*, 3866.

(9) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3804.

(10) Glyn, P.; Johnson, F. P. A.; George, M. W.; Lees, A. J.; Turner, J. J. *Inorg. Chem.* **1991**, *30*, 3543.

(11) Pyridine ligand photodissociation is much more efficient (0.5–0.8) in analogous complexes with lowest excited states of LF character,[7,12,13] *e.g.* W(CO)$_5$(pyridine).

(12) Moralejo, C.; Langford, C. H.; Sharma, D. K. *Inorg. Chem.* **1989**, *28*, 2205.

(13) Wieland, S.; van Eldik, R.; Crane, D. R.; Ford, P. C. *Inorg. Chem.* **1989**, *28*, 3663.

(14) Lees, A. J.; Adamson, A. W. *J. Am. Chem. Soc.* **1980**, *102*, 6876.

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their own. In this way, the photobehavior of pentacarbonyl complexes strongly contrasts that of analogous tetracarbonyl–diimine complexes of group 6 metals.[1-6] However, the ^{3}MLCT state(s) is (are) of crucial importance for the photosubstitutional reactivity of $W(CO)_5$(4-X-pyridine) complexes under visible irradiation. They act as a long-lived "excitation energy sink" from which another reactive excited state can be subsequently populated. Although the processes following the population of the ^{3}MLCT states are well understood, nothing is known about the early-excited-state dynamics of these complexes, *i.e.* about the processes that populate the ^{3}MLCT states and that are thus responsible for selection of the photoreactive pathway. To this goal, we have investigated the picosecond time-resolved absorption spectra of $W(CO)_5$(4-cyanopyridine) and $W(CO)_5$(4-formylpyridine) following excitations into their LF and MLCT absorption bands at 355 and 532 nm.

Experimental Section

Methylcyclohexane and toluene were used as supplied by Aldrich in spectrograde quality. $W(CO)_5$(4-NC-py) and $W(CO)_5$(4-FM-py) (FM = formyl) complexes were synthesized and purified according to a published procedure[9] using substitution of the photoproduced $W(CO)_5$(THF) complex. $W(CO)_5$(4-NC-py) synthesized by this method was provided by Prof. A. J. Lees.

Electronic absorption spectra were recorded on a Hewlett Packard Model 8452A diode array spectrophotometer. Picosecond experiments were carried out using a system[12] based on a Nd:YAG laser which provides 355- or 532-nm pulses, fwhm = 30 ps. A white picosecond continuum, used as a probe beam, was generated by focusing part of the excitation beam onto a cell with D_2O. Transient spectra were detected with an optical multichannel analyzer. Nine measurements were averaged to obtain the spectra which are presented as absorbance changes with respect to the spectra recorded prior to the excitation. The samples were degassed with N_2 and placed in 2-mm quartz cells (Hellma). An area of 1.5-mm diameter was excited by the laser pulse. Sample concentrations were approximately 1.3×10^{-4} M and 2.4×10^{-4} M for $W(CO)_5$(4-NC-py) and $W(CO)_5$(4-FM-py), respectively.

Results

Electronic Absorption Spectra. Both $W(CO)_5$(4-NC-py) and $W(CO)_5$(4-FM-py) exhibit a LF absorption band in the near-UV region which is solvent-independent. A strongly solvatochromic MLCT band appears in the visible region. It is composed of at least two components. In methylcyclohexane solutions, the MLCT band is found at low energy and is well separated from the LF band. $W(CO)_5$(4-NC-py) exhibits[9] LF and MLCT absorptions at 404 nm ($\epsilon = 7280$ M^{-1} cm^{-1}) and 454 nm ($\epsilon = 8680$ M^{-1} cm^{-1}), respectively. For $W(CO)_5$(4-FM-py), the LF and MLCT bands occur[9] at 402 nm ($\epsilon = 5990$ M^{-1} cm^{-1}) and 470 nm ($\epsilon = 7640$ M^{-1} cm^{-1}), respectively. LF and MLCT bands overlap in the spectra of toluene solutions of both complexes. $W(CO)_5$(4-NC-py) shows a band with a maximum at 404 nm and a shoulder at 432 nm. For $W(CO)_5$(4-FM-py), an almost identical spectrum (402 nm, 430 nm, sh) is observed. Absorption spectra of both complexes in solvents used for photochemical experiments are depicted in Figure 1.

Picosecond transient absorption spectra were measured in the 425–675-nm spectral range from 0 ps (coincident with the 30-ps excitation pulse) until 500 ps (5 ns for $W(CO)_5$(4-FM-py) in toluene) after the maximum of the excitation pulse. Spectra observed following the LF (355 nm) and MLCT (532 nm) excitations of $W(CO)_5$(4-FM-py) are depicted in Figure 2. In both cases, the ground-state absorption is bleached and strong excited-state absorption in the visible spectral region is formed very rapidly, within the 30-ps excitation pulse. The growth of absorption between 0 and 20 ps is expected for the formation of a long-lived transient as the sample is still being excited in this time interval.[16] More importantly, a further small growth in absorbance was observed between 20 and 80 ps after the MLCT excitation at 532 nm. After 80 ps, the absorbance was constant. The spectrum obtained with LF (355 nm) excitation revealed that the transient formed within the laser pulse, as observed at time delays 0 and 20 ps. After 20 ps, the spectrum does not change. Transient spectra of $W(CO)_5$(4-FM-py) obtained in a toluene solution (Figure 3) show that approximately 70% of the transient is formed within the excitation pulse. However, a significant growth in intensity was observed between 20 and 100 ps with an apparent 36-ps lifetime, followed by a small gradual decrease in absorbance (by about 22%) between 100 ps and 5 ns.

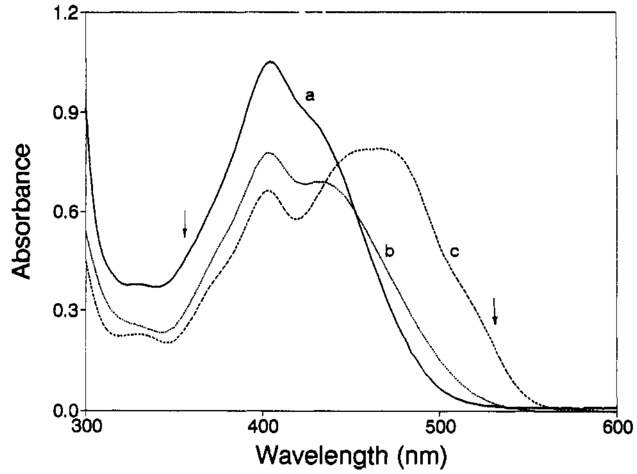

Figure 1. Electronic absorption spectra of $W(CO)_5$(4-NC-py) in toluene (a) and of $W(CO)_5$(4-FM-py) in toluene (b) and methylcyclohexane (c). Spectra of solutions used for picosecond experiments are shown. Arrows indicate 355- and 532-nm excitation wavelengths.

Because of low solubility and negligible absorbance at 532 nm, the transient spectra of $W(CO)_5$(4-NC-py) were recorded only in toluene solution using 355-nm excitation into the LF absorption band (Figure 4). The formation of an intense broad transient absorption with a maximum at approximately 575 nm is 75% complete within the excitation pulse. Its formation is then completed between 20 and 100 ps with an apparent rate constant 2.5×10^{10} s^{-1}, *i.e* with a 45-ps lifetime.

The intensity loss in the bleached ground-state absorption is always much smaller than the initial absorbance before the excitation (1.8 for $W(CO)_5$(4-FM-py) and 1.1 for $W(CO)_5$(4-NC-py)) despite the fact that the number of photons in the laser pulse is more than enough to excite all molecules in the irradiated zone of the sample. This observation indicates that the strong transient absorption extends into the blue and near-UV spectral regions. Because of large ground-state absorption of both samples, the transient spectra are very inaccurate in the spectral region of the ground-state absorption. No conclusions can thus be drawn from the temporal changes in the bleach region. (Due to low extinction coefficients at excitation wavelengths, the measurements could not have been performed in more dilute solutions.)

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(15) van Eldik, R.; Asano, T.; le Noble, W. J. *Chem. Rev.* **1989**, *89*, 549.

(16) The effect of the excitation by the "tail" of the laser pulse and/or of the instrument response on the early increase of transient absorption was checked by an independent experiment using $[Ru(bpy)_3]Cl_2$. Its excited-state absorption spectrum is known to be formed within a time interval shorter than the time resolution of our instrument (Serpone, N.; Jamieson, M. A. *Coord. Chem. Rev.* **1989**, *93*, 87). An aqueous solution containing $[Ru(bpy)_3]^{2+}$ was excited with a 355-nm pulse. Both the transient absorbance in the visible and the bleached absorbance increased in intensity by less than 4% on going from the 20- to 40-ps time delay after the laser pulse; *i.e.*, the change observed was within the experimental error. It may thus be safely concluded that all changes observed for $W(CO)_5$(4-FM-py) and $W(CO)_5$(4-NC-py) at time delays longer than 20 ps are due to the excited-state dynamics of the samples investigated. On the other hand, the absorbance changes observed between 0 and 20 ps have no quantitative meaning. However, the comparison of the shape of the transient absorption bands observed at these two time delays is possible, as the band shape is not affected by instrumental factors.

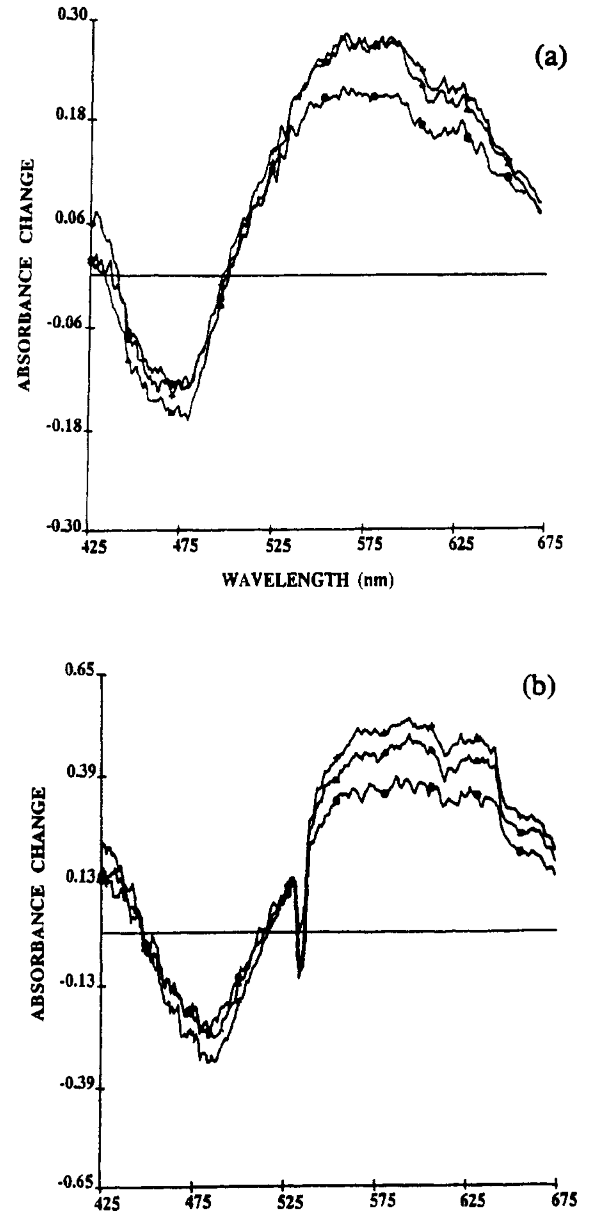

Figure 2. Picosecond absorption spectra of W(CO)$_5$(4-FM-py) in methylcyclohexane solution: (a) 355-nm, 1.2-mJ excitation, time delays in the order of increasing absorbance 0, 40, and 500 ps; (b) 532-nm, 2.5-mJ excitation, time delays in the order of increasing absorbance 0, 40, and 80 ps.

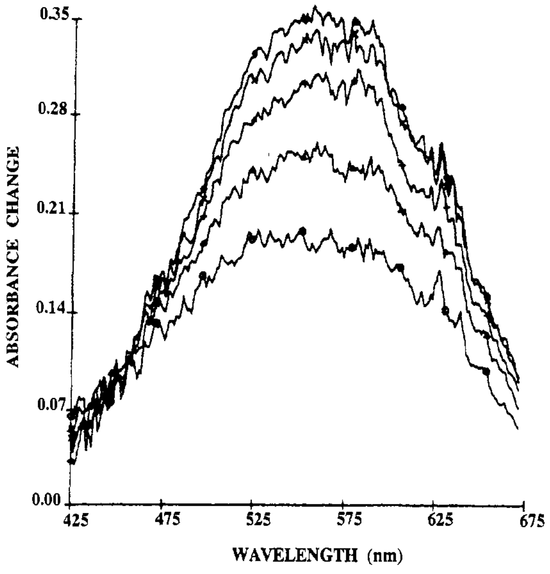

Figure 3. Picosecond absorption spectra of W(CO)$_5$(4-FM-py) in toluene solution following 355-nm, 1.2-mJ excitation. Time delays in the order of increasing absorbance are 0, 20, 40, 80, and 100 ps.

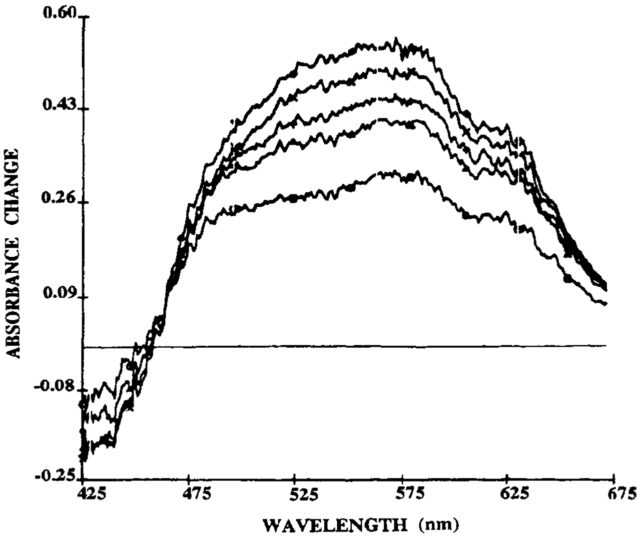

Figure 4. Picosecond absorption spectra of W(CO)$_5$(4-NC-py) in toluene solution following 355-nm, 2.5-mJ excitation. Time delays in the order of increasing absorbance are 0, 17, 40, 70, and 100 ps.

Discussion

Picosecond absorption spectra of both complexes studied may be assigned to their lowest MLCT excited states. The shape of the absorption band observed for W(CO)$_5$(4-NC-py) resembles that previously found in the nanosecond transient spectrum and attributed[9] to the ^{3}MLCT state.[17] Its intensity does not decrease with time, in accord with its known 292 ns lifetime. Alternative assignments of the transient can easily be excluded. It is too long-lived for either LF or ^{1}MLCT states. The photochemically induced substitution reaction to form W(CO)$_5$S occurs on a microsecond time scale,[9,10] and the product spectrum[9] is very different from the picosecond spectra. The picosecond spectrum of W(CO)$_5$(4-FM-py) can also be assigned to the lowest MLCT excited state. The observation that it slowly decays in toluene but not in methylcyclohexane is in accord with the much shorter excited-state lifetime previously[9] found in benzene compared with methylcyclohexane. However, our experiment suggests either a faster or more complicated decay mechanism than that reported earlier.[9]

The time-dependent shape of the picosecond absorption spectrum observed over the whole time range investigated (starting at 0 ps[16]) does not indicate the presence of vibrational relaxation or thermal equilibration of the ^{3}MLCT manifold on this time scale. (These processes should be manifested by a blue shift of the absorption band with increasing delays. However, it cannot be excluded that such subtle changes are obscured by the broadness of the transient absorption and by very strong bleaching of the ground-state absorption band.) Thus, it may be concluded that the temporal changes observed are due to the kinetics of the formation of the vibrationally cold ^{3}MLCT state by a ^{1}MLCT → ^{3}MLCT or ^{1}LF → ^{3}MLCT intersystem crossing, ISC, under 532- or 355-nm excitation, respectively. The spectra show that the population of the lowest ^{3}MLCT excited state follows a

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[17] Although the use of spin labels for electronic states of heavy-atom organometallic compounds might be disputed, it is an experimental fact that they possess excited states which behave much as spin singlets and triplets of organic compounds and the use of spin labels is thus commonly accepted.[18]

[18] Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

biphasic kinetics. The dominant component occurs within the excitation pulse whereas the slower minor component has lifetimes of approximately 36 and 45 ps for $W(CO)_5$(4-FM-py) and $W(CO)_5$(4-NC-py), respectively. The slower component manifests itself by an increase in the transient absorbance at time delays longer than 20 ps.[16] Only the fast component was observed under LF excitation of $W(CO)_5$(4-FM-py) in methylcyclohexane, but the slow component is more prominent in toluene (Figure 3). The slow component significantly contributes to the excited-state dynamics of $W(CO)_5$(4-NC-py) in toluene as well (Figure 4). It is important to note that the ^{3}MLCT state is efficiently formed even under the excitation into the LF transition. This observation agrees with earlier measurements[7] of quantum yields of the reaction (1) induced by near-UV excitation into the most reactive[12] $_1$LF state. Their values significantly drop[7] upon going from $W(CO)_5$(4-X-pyridine) complexes with lowest LF excited states to those which possess MLCT lowest lying excited states where the LF → MLCT relaxation pathway is available.

Picosecond absorption spectra together with known[7,10,19] quantum yields of the ^{3}MLCT formation allow us to estimate the upper limit of the rate of the fast kinetic component of the ^{3}MLCT formation. The extinction coefficient of the visible absorption band of the ^{3}MLCT excited state of $W(CO)_5$(4-NC-py) was previously estimated[9] as 2.5×10^3 M^{-1} cm^{-1}. From this value and observed picosecond absorbance values, it can be concluded that the conversion of the ground-state $W(CO)_5$(4-NC-py) complex into its ^{3}MLCT state is at least 70% complete within the 30-ps excitation pulse. Transient nanosecond IR spectra[10] together with the known photosubstitution quantum yield (0.02)[7] make it possible to estimate[19] the quantum yield of the ^{3}MLCT formation as 0.04. Given this low yield, we conclude that to convert 70% of the molecules present in the irradiated zone to the ^{3}MLCT state requires approximately 18 successive excitations[10] which have to occur within the 30-ps pulse. This consideration allows us to estimate the upper limit of the time constant for the ^{3}MLCT formation as 6×10^{11} s^{-1}, *i.e.* a 1.7-ps lifetime. (The number of photons absorbed during the excitation by 355- and 532-nm pulses of 2.5-mJ energy in the irradiated sample area is sufficient for approximately 26 and 38 excitations, respectively.) However, most of the photons are delivered within the short intense central part of the laser pulse. Hence, the actual lifetime for the fast component of the ^{3}MLCT population must be much shorter, on the order of hundreds of femtoseconds. Although no extinction coefficients were reported for the excited-state absorption of $W(CO)_5$(4-FM-py), qualitatively similar behavior is obvious from Figures 2 and 3. The fraction of ^{3}MLCT states populated already within the excitation pulse appears to be even larger and, hence, the lifetime of their formation shorter than that estimated for $W(CO)_5$(4-NC-py).

One possible interpretation of the biphasic kinetics would be to assign the faster and slower components to ISC from the higher and lower ^{1}MLCT levels, respectively. However, absorption spectra obtained 40 and 80 ps after the 532-nm excitation of $W(CO)_5$(4-FM-py) shows that the ^{3}MLCT state is populated to about 80% within the excitation pulse; *i.e.*, the faster component dominates.[20] From Figure 1, it is apparent that the 532-nm excitation is directed into the low-energy shoulder of the MLCT band and is energetically insufficient to populate the higher ^{1}MLCT level. Consequently, the faster component cannot be assigned to ISC from this state.

To interpret the biphasic kinetics of the formation of the lowest ^{3}MLCT state, it must be taken into account that the rate of the faster component of the ISC is comparable to or even higher than the rate of vibrational relaxation which, in transition metal carbonyls, occurs[21,22] on the time scale of tens or even hundreds of picoseconds. The dominant sub-picosecond component thus apparently involves directly excited Franck–Condon vibronic levels or levels in their close energetic proximity. The slower, minor, component might correspond to ISC from the vibrationally relaxed ^{1}MLCT state. This interpretation is also corroborated by the observed solvent effect on the rate of the ^{3}MLCT-state formation. The slow component is much more prominent in toluene, where the ^{1}LF–^{1}MLCT energy gap is much smallear than in methylcyclohexane, making the ^{1}LF → ^{1}MLCT conversion more probable. On the other hand, only the ultrafast ^{1}LF → ^{3}MLCT process was observed in methylcyclohexane, where this energy gap is large. Present data do not provide any information on the mechanism of this ISC from optically excited (near) Franck–Condon states. However, this process might be conceptually similar to the ^{1}MLCT → ^{5}LF ISC in Fe(II) polypyridyl complexes that was recently found[23,24] to be an ultrafast (<700 fs) direct process occurring without any intermediates. ^{3}MLCT states are apparently populated on the sub-picosecond time scale also in $W(CO)_4$(phen), for which a complete formation of ^{3}MLCT states was observed[6] to take place within the 30-ps excitation pulse. Even in a complex containing a much lighter transition metal, $Cr(CO)_4$bpy, the ^{3}MLCT states are, in part, produced within 30 ps, along with a slower, approximately 50 ps, process.

Despite the limits on wavelengths available for excitation and the pulse width, it is strongly indicated that for $W(CO)_5$(4-X-py) complexes the intersystem crossing, which populates ^{3}MLCT excited state(s) involved in photoreactivity, follows biphasic kinetics. The dominant ultrafast component occurs on the same, or even shorter, time scale as vibrational relaxation. These results might bear more general implications for excited-state dynamics and photochemistry of organometallic and coordination compounds. It is implied that the excited-state-relaxation pathways are, in these compounds, selected very shortly after the electronic excitation, on time scales where the Born–Oppenheimer approximation is no longer applicable. Involvement of optically excited vibronic levels might provide specific vibrational coupling needed for activation of particular photophysical (e.g. ISC) as well as prompt photochemical processes. It might be manifested by unusual excitation-wavelength effects.[1,6,25] It appears that the usual and convenient interpretation of molecular photochemistry in terms of temporarily well-separated subsequent processes, such as vibrational relaxation, internal conversion, and intersystem crossing, is only of limited use for transition metal compounds where these steps are often strongly coupled with each other and not generally separable.

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(19) Vlček, A., Jr. *Chemtracts: Inorg. Chem.* **1991**, *3*, 363–367.

(20) It cannot be excluded that a portion of the ^{3}MLCT states are populated by a direct ground state → ^{3}MLCT excitation at 532 nm, as the very red shoulder of the absorption band might correspond to this spin-forbidden transition.

(21) Joly, A. G.; Nelson, K. A. *Chem. Phys.* **1991**, *152*, 69.

(22) Yu, S.-C.; Xu, X.; Lingle, R., Jr.; Hopkins, J. B. *J. Am. Chem. Soc.* **1990**, *112*, 3668.

(23) McCusker, J. K.; Walda, K. N.; Dunn, R. C.; Simon, J. D.; Magde, D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1992**, *114*, 6919.

(24) McCusker, J. K.; Walda, K. N.; Dunn, R. C.; Simon, J. D.; Magde, D.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 298.

(25) Langford, C. H. *Acc. Chem. Res.* **1984**, *17*, 96.