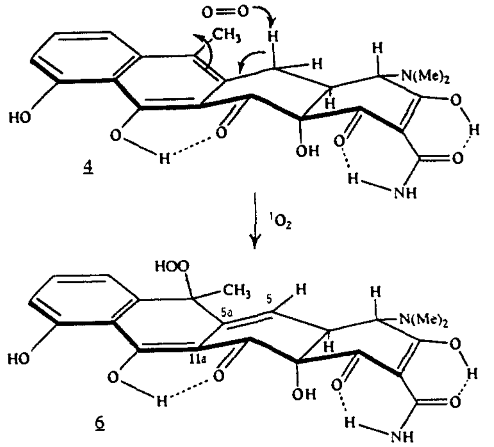
factory route to the parent antibiotic, requiring only the optical resolution of (±)-3 to complete the total synthesis of tetracycline. In addition, the successful outcome of the dye-sensitized oxidation allows the preparation of 5a,11a-dehydrotetracycline (5; OOH = OH), a promulgated (but hitherto untested) intermediate in the biosynthesis of tetracycline.[1e]

The remarkable stereospecificity in the introduction of the hydroperoxide from the β-face at C-6 may be attributed to the operation of an ene reaction involving the 5β-proton yielding the kinetic intermediate 6, a 5a,5-double bond isomer of 5, followed by equilibration of the double bond in 6 to the 5a,11a-position in 5.



**Acknowledgment.** H.H.W. and T.-J.L. acknowledge support from NIH grant GM13854. We express our appreciation to Dr. M. Kunstmann of Lederle Laboratories for his invaluable help in providing samples of tetracycline derivatives. We also thank Professor G. Stork and Dr. A. Hagedorn for advice on the polyamide chromatography. A.I.S. thanks the Robert A. Welch Foundation for financial support.

**Supplementary Material Available:** ¹H NMR, infrared, and UV data, physical constants, rotations, and purification procedures for **4**, **5**, and **1a** (4 pages). Ordering information is given on any current masthead page.

## On Visible Transients in Gas Phase UV Photolysis of Transition Metal Compounds: Experimental and Theoretical Results for $Ni(CO)_4$

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*Received February 25, 1986*

In this paper we present and discuss the luminescence spectrum resulting from photolysis of $Ni(CO)_4$ with a XeCl laser (308 nm). To our knowledge this is the first observation of an emission from a metal carbonyl compound. Based on LCGTO-Xα calculations we propose the following three-step mechanism (excitation, dissociation, fragment luminescence) involving a transition-metal carbonyl fragment:

$$\mathrm{Ni(CO)_4} + h\nu \rightarrow \mathrm{Ni(CO)_4}^* \rightarrow \mathrm{Ni(CO)_3}^* + \mathrm{CO} \rightarrow \mathrm{Ni(CO)_3} + h\tilde{\nu} \quad (1)$$

Our calculations indicate that the excited states of both $Ni(CO)_4$ and of $Ni(CO)_3$ show pronounced metal-to-CO charge-transfer character.[1]

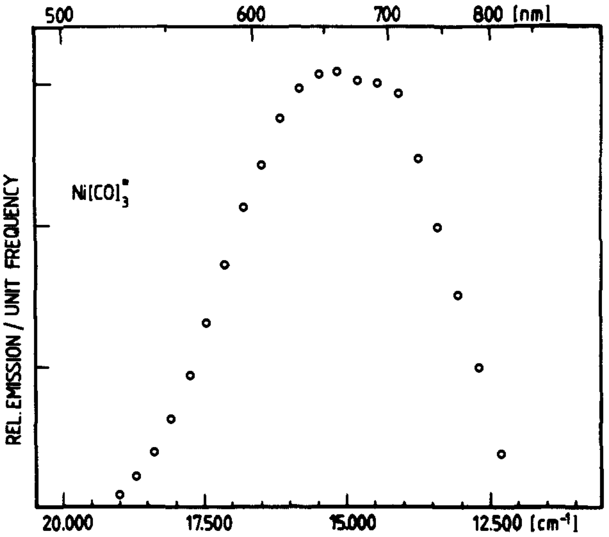

**Figure 1.** Luminiscence spectrum resulting from one-photon excitation of $Ni(CO)_4$ with a XeCl laser ($\lambda$ = 308 nm, $\sigma = 2.4 \times 10^{-18}$ cm²). According to our analysis this emission can be assigned to a CT transition of an electronically excited $Ni(CO)_3$* photofragment.

Our study is prompted by the rapidly increasing interest in photolytic reactions of homoleptic complexes resulting from their central role in photocatalysis[2] and laser-induced metal vapor deposition.[3] It is well-known that these compounds readily decompose upon pulsed UV laser excitation. However, until now, only the bare metal atom[4] or the CO ligands[5] could be detected in the vapor phase. Consequently, detailed information on the linking reaction channels are quite scarce; a notable exception is the recent work on $Cr(CO)_6$.[6] Furthermore, electronically excited fragments may act as energy reservoirs in the course of a multistep laser-induced decomposition process.[7]

To our knowledge, in the case of transition-metal carbonyls no direct evidence for such excited transients has been reported previously. This is somewhat surprising because we find that the fragment emission is strong enough to make the structure of a pulsed $Ni(CO)_4$ molecular beam visible with the naked eye after excitation with a KrF or XeCl laser. The emission spectrum obtained after excitation with a XeCl laser (4.0 eV) is shown in Figure 1. It has been corrected for the spectral sensitivity of the spectrometer. Experimental details have been discussed elsewhere.[8]

The spectrum is surprisingly broad and seems to be continuous. From our experience with related compounds,[8] no further structure is to be expected when the resolution is enhanced. The emission intensity maximum occurs at 650 nm (1.90 eV), giving the beam a reddish appearance. The luminiscence lifetime is >10 μs, therefore the spectrum was recorded during the first 5 μs using a gated optical spectrum analyzer at a pressure of 6 μbar to exclude perturbing collision processes. The one-photon nature of the absorption process leading to luminiscence was established by continuously reducing the laser intensity. We preliminarily

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estimate the quantum yield to be less than 10%. A (nonstatistical) branching into several dissociation channels in the first step of the photolysis has already been suggested for other metal carbonyls.[7]

To support proposed mechanism 1, we have carried out LCGTO-X$\alpha$ calculations[9] for the ground state and for several excited state potential energy curves of $Ni(CO)_4$ and of $Ni(CO)_3$. A detailed discussion of the theoretical investigations will be given elsewhere.[1] The basis sets were identical with those used in a previous study on $Ni(CO)_4$[10] except for the addition of one *f*- and *g*-function (exponents 0.56) to both of the auxiliary basis sets (charge and exchange fitting). The energies of the excited singlet (open shell) states were obtained by correcting the energy of the configuration with opposite spins for its triplet admixture.[11]

First, one metal-carbon bond of $Ni(CO)_4$ was elongated, keeping the $Ni(CO)_3$ moiety frozen in the experimental geometry of the parent complex.[12] Besides the $Ni(CO)_4$ ground state ($^1A_1$ symmetry in $C_{3v}$), the first excited singlet state, $^1E$, is pertinent to mechanism 1. The latter may be characterized as the Ni $d_{xz},d_{yz}(e) \rightarrow$ CO $2\pi(a_1)$ transition, belonging to the HOMO-LUMO excitation manifold in $Ni(CO)_4$ ($8t_2 \rightarrow 9t_2$, $T_d$). This lowest lying excited state $^1E$ is repulsive. At equilibrium geometry, it is calculated to lie 4.83 eV above the ground state. Thus one may assume a one-photon excitation into this state to be the first step of the photolysis, if one takes into account the well-known tendency of local density methods to favor high d occupations.[1,13] The next singlet state (derived from a Ni $d_{xz},d_{yz}(e) \rightarrow$ CO $2\pi(e)$ excitation) is not expected to be involved in the photolysis since it is bound with respect to removal of one CO moiety. All other singlet states lie at least 1 eV higher in energy[1] and therefore should not be relevant in the present case.

Furthermore, the bending (umbrella mode) of a $Ni(CO)_3$ fragment has been investigated. For the pyramidal configuration of the fragment these curves are connected to those discussed above in the asymptotic limit of Ni-C separation. Therefore all bond lengths were kept unchanged in our model.[1] At tetrahedral fragment angle the lowest excited singlet state $^1E$ lies 2.46 eV above the corresponding ground state $^1A_1$. However, the shape of the potential curves for the bending motion is quite different for these two states. The ground state curve shows a pronounced minimum at planar geometry (in agreement with matrix isolation experiments[13]) whereas the potential curve of the first excited state is predicted to exhibit a rather shallow double well, with the minima at a C-Ni-C angle of about 115°. Consequently, the excitation energy $^1A_1 \rightarrow {}^1E$ varies strongly with this bending angle (from 3.14 eV at planar geometry to 2.16 eV at an angle of 102°). This variation is considered responsible for the rather wide spectrum observed. Except for a uniform overestimation of all excitation energies by about 0.8 eV due to the local density approximation[1] this energy range is in almost quantitative agreement with that of the experimental luminiscence spectrum. These limitations of the LCGTO-X$\alpha$ method certainly do not invalidate proposed mechanism 1.[9,10]

The correlation between both ground and lowest excited states of $Ni(CO)_4$ and $Ni(CO)_3$ is in remarkable contrast to the situation found in calculations on the dissociation of $Fe(CO)_5$.[14] The $Fe(CO)_4$ fragment has been found to have an open-shell ground state, the spatial symmetry of which is correlated with the excited state of the parent molecule. Therefore no luminiscence is to be expected during photolysis of $Fe(CO)_5$.

The shape of the LUMO of $Ni(CO)_3$ which becomes occupied in the $^1E$ state has been discussed previously.[15] At nonplanar geometries it was found to be a bonding linear combination of the CO $2\pi^*$ orbitals with a $s-p_z-d_{z^2}$ hybrid on Ni, the latter pointing away from the remaining carbonyl ligands. This low-lying Ni orbital serves as an acceptor for the $5\sigma$ lone pair of a carbonyl ligand approaching the fragment, resulting in a strong bonding interaction.[15] The antibonding partner of this interaction forms the LUMO of the dissociating $(CO)_3Ni-CO$ system. Its occupation will weaken the corresponding metal-ligand bond. As the calculations indicate, this effect is strong enough to make the potential energy curve strongly repulsive in the corresponding excited state.

The luminiscence of the excited $Ni(CO)_3$ fragment occurs in the visible since its HOMO-LUMO gap is smaller than that of $Ni(CO)_4$ for two reasons. Taking one-electron energies as an indicator, one can attribute about two-thirds of the reduction to the lowering of the LUMO as a consequence of the lesser $\sigma$ repulsion and one-third to the rising metal 3d levels due to reduced back-donation.

Luminiscence from charge-transfer excited fragments seems to be a rather general phenomenon following the photolysis of transition-metal complexes in the gas phase.[8] Several other systems are currently being investigated.

After completion of this work, transient *absorption* spectra observed after photolysis of $Cr(CO)_6$ have been published and an interpretation has been given attributing them to the fragment $Cr(CO)_5$.[16]

**Acknowledgment.** This work was partially supported by the Deutsche Forschungsgemeinschaft and by a grant from the Humboldt Foundation to S.M.

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## $^{29}Si$ NMR Observation of an Unprecedented Rearrangement in Tetraaryldisilenes

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*Received February 25, 1986*

We report here the first observation of a facile intramolecular rearrangement of tetraaryldisilenes involving the exchange of two aryl substitutents between the silicon atoms of the silicon-silicon double bond.[1]

The disilenes were generated photochemically by irradiation of their trisilane precursors[2,3] in pentane solution at -60 °C and the crude photolysates were examined by $^{29}Si$ NMR in benzene. Pure disilenes **11** and **22** were produced by photolysis of trisilanes **1** or **2** and gave in each case only a single $^{29}Si$ signal in the disilene

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