

Conclusion

This study clearly reveals structural differences accompanied by characteristic RR properties both for Ni(R-DAB)₂ complexes, for which structural differences have been reported, and for the previously unreported Ni(CO)₂(R-DAB) complexes. A new application of the RR technique is hereby introduced, demonstrating again the usefulness of this technique for the characterization of allowed electronic transitions of transition-metal complexes. These results will be used to interpret differences in photochemical reactions between Ni(CO)₂(R-DAB) complexes.¹

Acknowledgment. We wish to thank Dr. M. W. Kokkes for performing the first experiments leading to this study and Th. L.

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Registry No. Ni(CO)₂(tBu-DAB), 98756-63-9; Ni(CO)₂(cHex-DAB), 119679-76-4; Ni(CO)₂(iPr-DAB), 119679-77-5; Ni(CO)₂(4-MePh-DAB), 119679-78-6; Ni(CO)₂(2,6-Me₂Ph-DAB), 119679-79-7; Ni(CO)₂(2,6-iPr₂Ph-DAB), 116917-18-1; Ni(CO)₂(2,4,6-Me₃Ph-DAB), 119679-80-0; Ni(CO)₂(tBu-pyca), 119679-81-1; Ni(CO)₂(2,6-iPr₂Ph-pyca), 119679-82-2; Ni(tBu-DAB)₂, 63576-87-4; Ni(cHex-DAB), 63576-86-3; Ni(4-MePh-DAB)₂, 55926-98-2; Ni(2,6-Me₂Ph-DAB)₂, 78802-16-1.

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Spectroscopy and Photochemistry of Nickel(0)- α -Diimine Complexes. 2.¹ MLCT Photochemistry of Ni(CO)₂(R-DAB) (R = tBu, 2,6-iPr₂Ph): Evidence for Two Different Photoprocesses

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This article describes the low-temperature photochemistry of the complexes Ni(CO)₂(tBu-DAB) (I) and Ni(CO)₂(2,6-iPr₂Ph-DAB) (II) in different media, in both the absence and the presence of a substituting ligand. The complexes differ in their molecular structure and in the character of their lowest MLCT transitions. The results of this study show that these differences are also responsible for the different primary photoprocesses taking place upon low-energy excitation. Irradiation into the MLCT bands causes breaking of a metal-nitrogen bond in the case of complex I and loss of CO for complex II.

Introduction

Most mechanistic studies in the field of organometallic photochemistry have been concerned with reactions of transition-metal carbonyls such as the mononuclear complexes M(CO)₆ (M = Cr, Mo, W), Fe(CO)₅, and their derivatives as well as the binuclear metal-metal-bonded complexes M₂(CO)₁₀ (M = Mn, Re), Cp₂Fe₂(CO)₄, and Cp₂M₂(CO)₆ (M = Mo, W).²⁻⁴ All reactions appeared to occur from reactive ³LF states or from a repulsive ³ $\sigma\sigma^*$ state in the case of the binuclear complexes.

Introduction of an α -diimine ligand (e.g. 2,2'-bipyridine) in such a complex gives rise to the appearance of one or more metal to α -diimine (MLCT) transitions at low energy. Irradiation into this band leads to population of a ³MLCT state, which is normally much less reactive than the ³LF and ³ $\sigma\sigma^*$ states.⁵ For, although charge transfer to the ligand leads to a weakening of the metal to α -diimine covalent bond, the ionic interaction between metal and ligand will be strengthened in the excited state. As a result, many transition-metal complexes with a lowest ³MLCT state are not photoreactive, unless energy can be transferred from such a state to a reactive ³LF or ³ $\sigma\sigma^*$ state. Especially the energy transfer to a ³ $\sigma\sigma^*$ state can be very effective even at low energy, because of the repulsive character of this state.^{3,4} Thus, complexes of the type XMn(CO)₃(α -diimine) [X = Mn(CO)₅, Co(CO)₄, SnPh₃] reacted photochemically with quantum yields as high as 0.5-0.8 mol/einstein even upon irradiation with $\lambda = 600$ nm.⁶⁻⁸

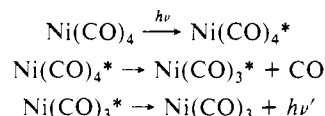
Only recently has a reaction been observed from a reactive ³MLCT state in the case of the α -diimine complexes Fe(CO)₃(R-DAB).⁹ Low-temperature irradiation with $\lambda > 500$ nm gave rise to a reaction from the lowest ³MLCT state. A completely different reaction was observed upon irradiation of these complexes with $\lambda \leq 500$ nm. The latter reaction occurred from a ³LF state close in energy to the ³MLCT state.

These results concerning the reactivity of ³MLCT states prompted us to study in more detail the photoreactivity of those

α -diimine complexes that have only low-energy ³MLCT states and no disturbing ³LF or ³ $\sigma\sigma^*$ states.

In this article we report the photochemistry of the two Ni(0) (d¹⁰) complexes Ni(CO)₂(R-DAB) [R-DAB = 1,4-diaza-1,3-butadiene, RN=CH-CH=NR; R = tertiary butyl (tBu), 2,6-diisopropylphenyl (2,6-iPr₂Ph)], which only have a low-energy ³MLCT state.

Up to now, attention has only been paid to the photochemistry of Ni(CO)₄, from which the Ni(CO)₂(R-DAB) complexes are derived.¹⁰⁻¹² Irradiation of this complex gave rise to loss of CO and the appearance of luminescence. These observations have recently been rationalized in terms of the following three-step mechanism:¹³



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Contrary to previous reports,¹⁰⁻¹² the CO-loss reaction was assumed to occur from a strongly Ni-CO antibonding 1E state, arising from a $Ni(d_{xz}, d_{yz}) \rightarrow CO(\pi^*)$ transition.

In order to interpret the photochemical data, to be described hereafter, the theoretical and spectroscopic (UV/visible, resonance Raman) properties of these $Ni(CO)_2(R-DAB)$ complexes have first been studied in detail. The main result of this study, described in the preceding article,¹ was the observation of drastic changes in the character of the HOMO and LUMO and of the electronic transition between these orbitals when the structure of the complex changed from tetrahedral to pseudoplanar. This change of character of the low-energy MLCT transition at about 500 nm was not visible from the electronic absorption spectra themselves but was nicely reflected in the resonance Raman spectra.

In this article the photochemistry of the complexes $Ni(CO)_2(tBu-DAB)$ (I) and $Ni(CO)_2(2,6-iPr_2Ph-DAB)$ (II) is discussed in terms of the above-mentioned changes in ground- and excited-state properties. Complex I has a tetrahedral conformation; complex II is pseudoplanar.

On several occasions the steric properties of the substituent R will appear to influence the course of the secondary thermal reactions following the primary photoprocess. Unfortunately, the corresponding complexes $Ni(CO)_2(R-DAB)$ [R = cyclohexyl (cHex), isopropyl (iPr), 4-methylphenyl (4-MePh)], possessing much less bulky R groups, could not be isolated as stable complexes although they could be identified in solution.

For the study of photosubstitution reactions use has been made of several PR_3 ligands, viz. R = phenyl (Ph), cyclohexyl (cHex), *n*-butyl (nBu), and phenoxy (OPh).

Experimental Section

Preparations and Sample Handling. The $Ni(CO)_2(R-DAB)$ complexes were synthesized from $Ni(COD)_2$ by a procedure described previously.¹ Both the solvents (all of spectroscopic grade) and the liquid phosphines were distilled several times and deoxygenated before use. PPh_3 and $P(cHex)_3$ were recrystallized. All spectroscopic samples were prepared by standard inert-gas techniques. Because of the high thermal reactivity of $Ni(CO)_2(R-DAB)$ complexes toward these phosphines, samples containing these ligands were made at low temperature by using baths of dry ice/acetone. Self-made needles, cooled externally by cold gas from liquid-nitrogen solutions, were used to fill the UV/visible and IR low-temperature cells.

Spectra. UV/visible absorption spectra were recorded on a Perkin-Elmer Lambda 5 Spectrophotometer. IR spectra were measured on a Nicolet 7199B FT-IR interferometer with a liquid-nitrogen-cooled Hg, Cd, Te detector (32 scans, resolution 0.5 cm^{-1}).

Photochemistry. The complexes were irradiated by an SP Model 2020 Ar^+ laser and a CR 490 tunable dye laser with Coumarin 6 as a dye pumped by an SP Model 171 Ar^+ laser. The matrix isolation technique, consisting of a modified Air Products Displex Model CSW-202B closed-cycle helium refrigerator, has been described elsewhere.¹⁴ During deposition the sample window of NaCl had a temperature of 10 K and the vacuum was better than 10^{-6} Torr. Methane with a purity of 99.9995% was used as matrix gas.

For the flash-photolysis experiments a Lambda Physik EMG-101 excimer laser filled with XeCl, yielding 308-nm pulses of 10-ns duration, was used as the excitation source (output 20 mJ/pulse). The monitoring beam consisted of an EG&G FX-42-C-R Xenon flashlamp (pulse duration 20 μs), and the excimer laser was fired when the output of the Xe lamp had reached its maximum. A Zeiss M4QIII single quartz prism monochromator in combination with an RCA C-31025 C GaAs photomultiplier was used for detection by a crossed-beam setup. The photomultiplier signal was fed to a Biomation 6500 transient digitizer, with a 6-bit A/D converter coupled via a homemade interface to a TRS-80 microcomputer. The systems time resolution was 10 ns.

Results and Discussion

Thermal Reactions. All complexes under study showed very fast thermal reactions with phosphines at 293 K, giving rise to the formation of $Ni(CO)_2(PR_3)_2$. The thermal lability of the Ni-R-DAB bonds was also evident from the reactions of $Ni(CO)_2(R-DAB)$ with other R'-DAB ligands. Mixtures of the parent compound and $Ni(CO)_2(R'-DAB)$ were then observed. In the presence of iPr-DAB 90% of the complex $Ni(CO)_2(tBu-DAB)$

Table I. IR $\nu(CO)$ Frequencies (cm^{-1}) and λ_{max} Values (nm) of the Lowest Energy Absorption Bands of Complexes I and II and Their Photoproducts

complex	$\nu(CO)$, cm^{-1}	λ_{max} , nm
$Ni(CO)_2(tBu-DAB)$ (I)	2003, 1940 ^a	522 ^a
	1987, 1918 ^b	505 ^b
	1989, 1920 ^c	508 ^c
$Ni(CO)_2(2,6-iPr_2Ph-DAB)$ (II)	2022, 1971 ^a	536 ^a
	2012, 1954 ^c	535 ^c
	2046 ^a	
$Ni(CO)_4$	2062, 1987 ^a	
$Ni(CO)_3(P(cHex)_3)$	2067, 1982, 1977 ^a	
$(CO)_3Ni(\mu-(\sigma-N, \sigma-N')tBu-DAB)-Ni(CO)(tBu-DAB)$	2063, 1980, 1976, 1927 ^a	490 ^a
$Ni(CO)_2(cHex-DAB)$		507 ^d
$Ni(CO)(P(cHex)_3)(tBu-DAB)$	1923 ^a	545 ^a
$Ni(CO)(PPh_3)(tBu-DAB)$	1914 ^b	565 ^b
$Ni(CO)(P(OPh)_3)(tBu-DAB)$	1935 ^b	
$Ni(CO)(P(nBu)_3)(tBu-DAB)$		540 ^c
$Ni(CO)(P(nBu)_3)(cHex-DAB)^e$		528 ^d
$Ni(CO)(P(nBu)_3)(2,6-iPr_2Ph-DAB)$		511 ^f
$Ni(CO)(PPh_3)(2,6-iPr_2Ph-DAB)$		540 ^f
$Ni(CO)(P(OPh)_3)(2,6-iPr_2Ph-DAB)$		546 ^f
$Ni(CO)(P(cHex)_3)(2,6-iPr_2Ph-DAB)$		521 ^f
$Ni(CO)(\sigma-N-tBu-DAB)(tBu-DAB)$	1918 ^a (1898 ^b)	499, 694 ^a
$Ni(CO)(\sigma-N-2,6-iPr_2Ph-DAB)-(2,6-iPr_2Ph-DAB)$	1957 ^c	
$Ni(tBu-DAB)_2$		470 ^a
$Ni(2,6-iPr_2Ph-DAB)_2$		491, 751 ^c
$Ni(cHex-DAB)(2,6-iPr_2Ph-DAB)$		468, 728 ^b

^a Measured in *n*-pentane at 170 K. ^b Measured in 2-MeTHF at 183 K. ^c Measured in toluene at 190 K. ^d Measured in toluene at 243 K. ^e Measured in situ (see text). ^f Measured in toluene at 213 K.

was already converted into $Ni(CO)_2(iPr-DAB)$ after standing in the dark at 293 K for 30 min. The thermal reactivity of the tBu-DAB complex with respect to R'-DAB ligands with R' = aryl groups appeared to be much lower. In this latter case, however, the initially formed dicarbonyl complexes reacted further to give $Ni(R'-DAB)_2$.

In order to avoid these thermal reactions, the photochemistry was studied at lower temperatures ($T \leq 200$ K) where no such reactions occurred.

Photochemical Reactions. Both complexes did not photodecompose at 293 K when solutions in benzene were irradiated into the MLCT band in the absence of a substituting ligand. Only a slow thermal decomposition occurred, producing $Ni(CO)_4$. However, this photostability does not necessarily imply that the metal-ligand bonds are not affected. In that case the complexes would also be photostable at low temperature with or without a substituting ligand present. For this purpose the photochemistry of the complexes in low-temperature solutions was studied both in the absence of a substituting ligand and in the presence of one of several PR_3 and R-DAB ligands. Unless stated otherwise the photochemical reactions were performed by irradiation into the lowest energy MLCT band (see Table I).

The reactions will be described separately for complexes I and II. Table I presents the IR (CO stretching region) and UV/visible spectral data of all photoproducts formed.

$Ni(CO)_2(tBu-DAB)$ (I). Reactions in the Absence of a Substituting Ligand. Irradiation of I in *n*-pentane at 170 K caused the formation of several photoproducts, depending on the starting concentration of the parent compound. Typical IR spectral changes observed upon irradiation of a low concentration of I with $\lambda = 514.5$ nm are presented in Figure 1. New bands show up at 2067, 1982, and 1977 cm^{-1} , respectively, belonging to a single photoproduct (b), while the bands of the parent compound (a) disappear. No free carbon monoxide ($\nu(CO) = 2138$ cm^{-1}) is observed.

The frequencies and relative intensities of the new bands closely correspond to those of $Ni(CO)_3$ (pyridine) (2073 and 1981 cm^{-1})¹⁷ and of other $Ni(CO)_3L$ complexes.^{11,12,15,16} They are therefore

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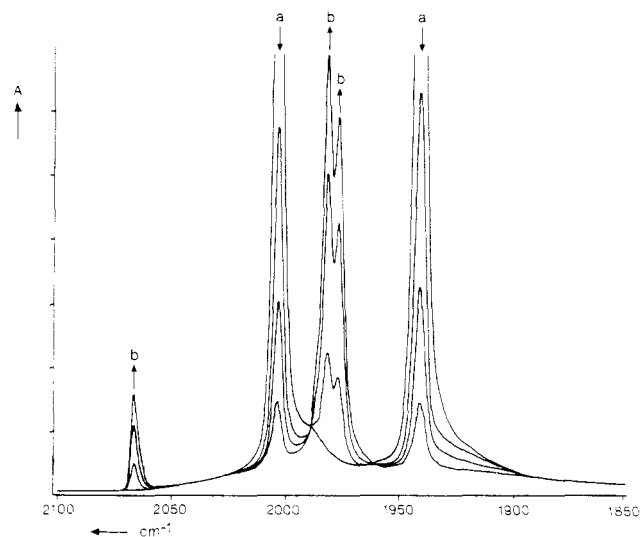
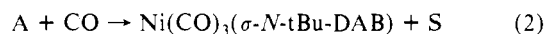
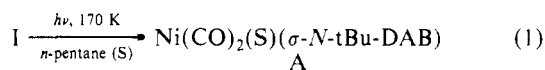


Figure 1. Infrared spectral changes upon photolysis of low starting concentrations of complex I with $\lambda = 514.5$ nm ($p = 150$ mW) in *n*-pentane at 170 K: (a) I; (b) $\text{Ni}(\text{CO})_3(\sigma\text{-}N\text{-tBu-DAB})$.

assigned to the photoproduct $\text{Ni}(\text{CO})_3(\sigma\text{-}N\text{-tBu-DAB})$, in which the tBu-DAB ligand is $\sigma\text{-N}$ (2 e) coordinated to Ni. Thus, the following reactions had occurred:



Since all photoproducts obtained by irradiation of I into its MLCT band will be shown to result from secondary thermal reactions of the primary photoproduct of reaction 1, this latter complex will be indicated hereafter as product A. At this low temperature, rechelation of the bulky tBu-DAB ligand is a slow process. The unstable solvent-coordinated photoproduct A will therefore partly decompose during its back-reaction to I. The CO ligands then released will react with the remaining complexes A according to reaction 2. The above decomposition reaction is a thermal process. A photodecomposition reaction is a priori excluded since photoproduct A does not absorb at the wavelength of irradiation (514.5 nm).

The product of reaction 2 was thermally unstable already at 170 K and slowly back-reacted to form the parent compound upon standing in the dark. Stable complexes¹⁸⁻²¹ as well as intermediates^{22,23} containing such a $\sigma\text{-N}$ (2 e) monodentate R-DAB ligand have been reported for several transition metals. Recently, the formation of $\text{M}(\text{CO})_5(\sigma\text{-}N\text{-tBu-DAB})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) was established with IR and UV/vis spectroscopy in liquid xenon at 223 K²⁴ and at 293 K with rapid-scan UV/vis spectroscopy.²⁵ The close correspondence between the spectral data of these latter complexes and those of $\text{M}(\text{CO})_5(\text{pyridine})$ ²⁶ also demonstrates

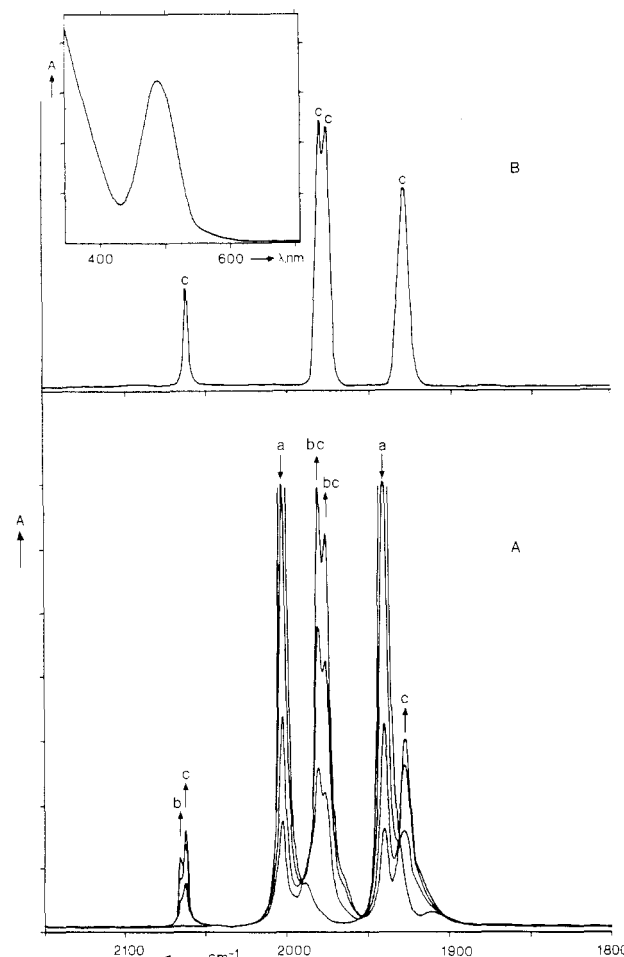


Figure 2. (A) Infrared spectral changes upon photolysis of high starting concentrations of complex I with $\lambda = 514.5$ nm ($p = 150$ mW) in *n*-pentane at 170 K: (a) I; (b) $\text{Ni}(\text{CO})_3(\sigma\text{-}N\text{-tBu-DAB})$; (c) $(\text{CO})_3\text{Ni}(\mu\text{-}(\sigma\text{-}N, \sigma\text{-}N')\text{tBu-DAB})\text{Ni}(\text{CO})(\text{tBu-DAB})$. (B) Infrared spectrum of photoproduct c, obtained by subtraction of the bands of a and b from spectrum A. Insert: Absorption spectrum of c.

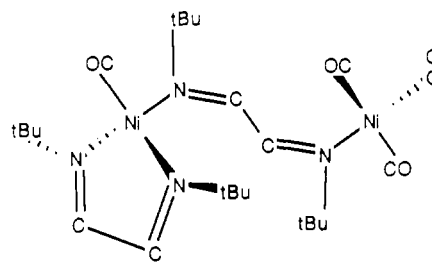


Figure 3. Proposed structure of $(\text{CO})_3\text{Ni}(\mu\text{-}(\sigma\text{-}N, \sigma\text{-}N')\text{tBu-DAB})\text{Ni}(\text{CO})(\text{tBu-DAB})$.

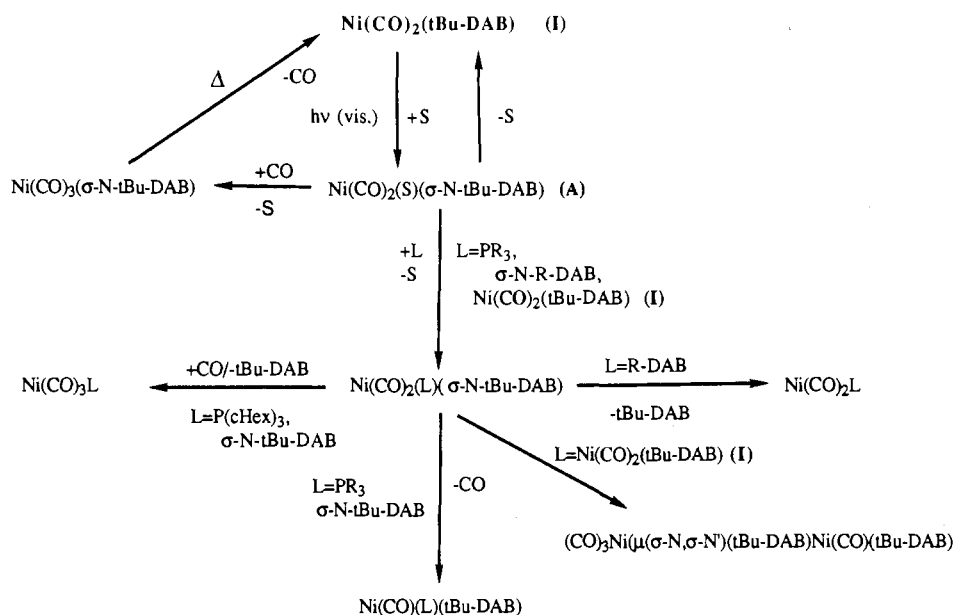
the similarity between the bonding properties of the $\sigma\text{-N}$ -bonded R-DAB and pyridine ligands.

A different reaction was observed when more concentrated solutions of I in *n*-pentane ($T = 170$ K) were irradiated. Figure 2A shows the IR spectral changes accompanying this reaction. Apart from $\text{Ni}(\text{CO})_3(\sigma\text{-}N\text{-tBu-DAB})$ (b), a second photoproduct (c) was formed having four bands in the CO-stretching region. These bands, shown in Figure 2B, were obtained by subtracting from the final spectrum of Figure 2A the bands of both the parent compound (a) and $\text{Ni}(\text{CO})_3(\sigma\text{-}N\text{-tBu-DAB})$ (b). These bands clearly belong to a single photoproduct since their relative intensities did not change in the course of the reaction.

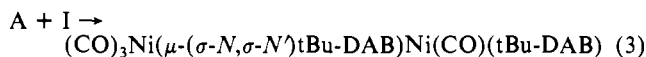
The bands at 2063, 1980, and 1976 cm^{-1} are assigned to a $\text{Ni}(\text{CO})_3(\text{N-donor})$ moiety since they are only slightly shifted to lower frequencies with respect to those of $\text{Ni}(\text{CO})_3(\sigma\text{-}N\text{-tBu-DAB})$ (Figure 1 and Table I). The fourth vibration at 1927 cm^{-1} most probably belongs to a monocarbonyl moiety since this frequency

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Scheme I. Proposed Mechanism for the Photochemistry of Complex I upon Irradiation into Its Lowest Energy MLCT Transition



is close to that of $\text{Ni(CO)}(\sigma\text{-N-tBu-DAB})(\text{tBu-DAB})$ and of other $\text{Ni(CO)(L)(tBu-DAB)}$ ($\text{L} = \text{Lewis base}$) complexes (vide infra). The photoproduct has an MLCT band at 490 nm (see insert of Figure 2), which is also very close to that of $\text{Ni(CO)}(\sigma\text{-N-tBu-DAB})(\text{tBu-DAB})$ (499 nm, Table I). From these observations it is concluded that photoproduct c is the dinuclear species $(\text{CO})_3\text{Ni}(\mu\text{-}(\sigma\text{-N},\sigma\text{-N}')\text{tBu-DAB})\text{Ni(CO)(tBu-DAB)}$, formed out of I according to reactions 1 and 3. The formation of such



binuclear complexes is a rather common process in photochemical reactions of concentrated metal carbonyl solutions.⁹ The structure proposed for the product of (3) is shown in Figure 3. The complex is thermally unstable and slowly back-reacts to the parent compound already at 170 K. Several such complexes with a $\sigma\text{-N},\sigma\text{-N}'$ (4e) bridging R-DAB ligand have been reported.^{16-18,27-29} They all have an *E-s-trans-E* conformation of the NCCN skeleton. From an X-ray study of $\text{P(nBu)}_3\text{Cl}_2\text{Pt}(\mu\text{-}(\sigma\text{-N},\sigma\text{-N}')\text{tBu-DAB})\text{PtCl}_2\text{P(nBu)}_3$, it was concluded that the σ - and π -electron density in the bridging DAB ligand is similar to that of a $\sigma,\sigma\text{-N},\text{N}'$ -chelated tBu-DAB molecule.¹⁹

In contrast to the above experiments no reaction was observed upon irradiation of I in 2-MeTHF at 170 K into its MLCT band. At this low temperature the 2-MeTHF molecules form rather stable solvent-coordinated complexes. As a result, the photoproduct A of reaction 1 does not (partially) decompose during its back-reaction to I, as in the case of the *n*-pentane solution. A similar apparent photostability of complex I was obtained when a solution of I in a CH_4 matrix ($T = 10\text{ K}$) was irradiated. Again no reaction was observed but under these conditions the formation of a $\sigma\text{-N}$ monodentate intermediate will be prohibited by the rather high activation barrier for rotation around the central C-C bond of the tBu-DAB ligand in order to obtain an *E-s-trans-E* conformation of the NCCN skeleton.

The above observations point to the breakage of a metal-nitrogen bond as the primary photoprocess taking place upon irradiation of I into its MLCT band. Unfortunately, this conclusion could not be verified by flash photolysis, since the output of the pulsed dye laser was too low ($<4\text{ mJ/pulse}$) for excitation into this band. These reactions of I observed upon irradiation into the

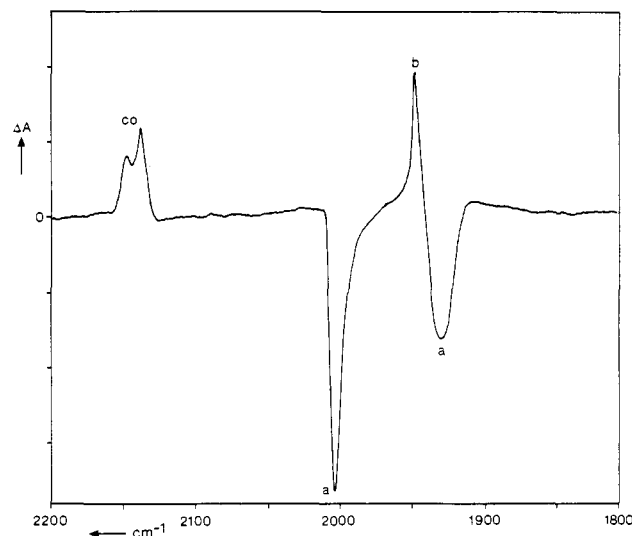
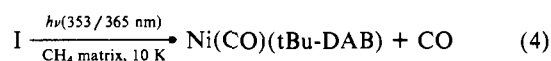


Figure 4. Infrared difference spectrum obtained after 45 min of irradiation with $\lambda = 353/365\text{ nm}$ ($p = 180\text{ mW}$) of complex I (a) in a CH_4 matrix at 10 K. Band b is Ni(CO)(tBu-DAB) .

MLCT band are presented in Scheme I together with those taking place in the presence of a PR_3 or R-DAB ligand (vide infra).

Complex I was also irradiated into its higher energy absorption band with the 353/365-nm lines of an Ar^+ laser. In contrast with the above experiments no photoproduct with a $\sigma\text{-N}$ monodentate tBu-DAB ligand was then formed. Instead, complex I photodecomposed slowly into Ni(CO)_4 ($\nu(\text{CO})$ at 2046 cm^{-1}) as the only carbonyl-containing product upon irradiation in *n*-pentane at 170 K. Excitation of I in a CH_4 matrix at 10 K caused release of CO, and the difference spectrum in the CO-stretching region after prolonged irradiation is shown in Figure 4.

Two bands are observed for free CO due to matrix-splitting effects. Band b at 1941 cm^{-1} is assigned to the only CO ligand of the coordinatively unsaturated photoproduct Ni(CO)(tBu-DAB) of reaction 4.



The formation of this photoproduct is accompanied by a shift of $\nu_s(\text{CN})$ of the tBu-DAB ligand from 1493 to 1473 cm^{-1} . A similar frequency lowering occurred upon formation of $\text{Fe(CO)}_2(\text{tBu-DAB})$ out of $\text{Fe(CO)}_3(\text{tBu-DAB})$ in an Ar matrix at 10 K.³⁰ Finally, the reaction of complex I upon UV excitation

(27) Van der Poel, H.; van Koten, G. *J. Organomet. Chem.* **1981**, *217*, 129.

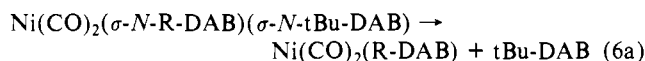
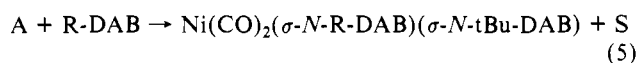
(28) Cavell, K. J.; Stufkens, D. J.; Vrieze, K. *Inorg. Chim. Acta* **1980**, *47*, 67.

(29) Van der Poel, H.; van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1981**, *51*, 241.

was studied at 293 K in toluene with flash photolysis by irradiation with the 308-nm line of an excimer laser. The MLCT band at 515 nm then disappeared, and a new band showed up at ca. 600 nm, 50 ns after the flash. This band is assigned to the solvent (S) coordinated photoproduct Ni(CO)(S)(tBu-DAB), formed after release of CO. In the case of breakage of a Ni-N bond, the MLCT band would have disappeared completely.

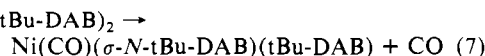
The above matrix and flash-photolysis data clearly show that release of CO is a major primary photoprocess upon irradiation of complex I with UV light. This result is not unexpected, since UV excitation takes place into the Ni → CO MLCT transitions. Apparently, the Ni(CO)(S)(tBu-DAB) photoproduct of reaction 4 is thermally or photochemically not stable in *n*-pentane at 170 K.

Reactions with R-DAB and PR₃. The photochemical reactions with R-DAB and PR₃ were studied by irradiating a low-temperature (170–200 K) toluene or *n*-pentane solution of I into the MLCT band in the presence of one of these ligands. Irradiation in the presence of excess R-DAB (R = cHex, iPr, 2,6-iPr₂Ph) caused the photosubstitution of the tBu-DAB according to reactions 1, 5, and 6.



Again the primary photoprocess is breakage of a Ni-N bond and the photoproducts were formed by secondary thermal reactions of the primary photoproduct A of reaction 1. Reaction 6b only gave rise to back-formation of the parent complex. The Ni(CO)₂(R-DAB) complexes produced by reaction 6a were identified by their UV/vis and IR spectral data¹ (Table I). No evidence was found for any CO-substitution product of the kind Ni(CO)(σ-N-R-DAB)(tBu-DAB) or Ni(R-DAB)(tBu-DAB). In the case of the 2,6-iPr₂Ph-DAB ligand the initially formed photoproduct Ni(CO)₂(2,6-iPr₂Ph-DAB) (II) reacted photochemically to give Ni(2,6-iPr₂Ph-DAB)₂, which was characterized by its absorption bands at 491 and 751 nm. For a short time during this latter reaction an extra IR ν(CO) band was observed at 1957 cm⁻¹, which was assigned to the intermediate Ni(CO)(σ-N-2,6-iPr₂Ph-DAB)(2,6-iPr₂Ph-DAB) (vide infra). In the case of the other two R-DAB ligands used (R = cHex, iPr) no such secondary photochemical reactions occurred.

In the case of irradiation of I in the presence of excess tBu-DAB, reactions 1, 5, and 6 will only give rise to back-formation of the parent compound. Yet, when this reaction was performed in *n*-pentane at 170 K, Ni(CO)(σ-N-tBu-DAB)(tBu-DAB) and Ni(CO)₃(σ-N-tBu-DAB) were formed. The latter photoproduct was also obtained when complex I was irradiated in the absence of a substituting ligand (vide supra, reaction 2). It will be formed when the products of reaction 1 or 5 partially decompose. The complex Ni(CO)(σ-N-tBu-DAB)(tBu-DAB) will be produced out of the intermediate Ni(CO)₂(σ-N-tBu-DAB)₂ according to reaction 7. Rechelation of the tBu-DAB ligand then gives rise to



release of CO instead of loss of the σ-N-tBu-DAB ligand as in reaction 6.

Reaction 7 was only observed for the reaction of I with tBu-DAB, i.e. when reaction 6 gave rise to back-formation of the parent complex only. In the case of R ≠ Bu, reaction 6a dominated completely. The photoproduct of reaction 7 was thermally not stable above 200 K. It then converted slowly into Ni(tBu-DAB)₂ (λ_{max} = 470 nm). Apparently, the barrier for chelation of the second tBu-DAB ligand could be overcome at this temperature.

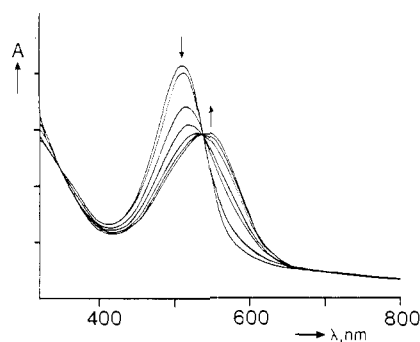
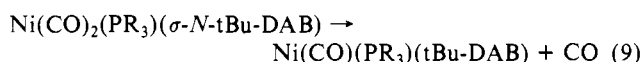
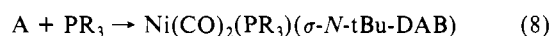


Figure 5. UV/visible spectral changes accompanying the photochemical reaction of complex I with P(nBu)₃ upon irradiation with λ = 514.5 nm in toluene at 190 K.

When such a low-temperature solution of I was instead irradiated in the presence of excess PR₃ (R = Ph, OPh, cHex, nBu), CO was photosubstituted by PR₃ according to reactions 1, 8, and 9. The UV/vis spectral changes accompanying the reaction with P(nBu)₃ in toluene are shown in Figure 5.



The MLCT band shifts to lower energy in accordance with the photosubstitution of an electron-withdrawing CO group by the basic P(nBu)₃ ligand. Similar effects were observed for the reactions of M(CO)₄(R-DAB) (M = Cr, Mo, W)³¹ and Fe(CO)₃(R-DAB)^{9,32} with phosphines. The quantum yield of the reaction with P(nBu)₃ was about 5 × 10⁻³ mol/einstein, which value is much lower than those obtained by irradiation into the MLCT band of the corresponding d⁸-Fe(CO)₃(R-DAB) complexes (φ = 0.1–0.2 mol/einstein).⁹ For these latter complexes the reaction takes, however, place from a close-lying reactive ³LF state, not present in the d¹⁰ complexes under study.

Due to the high thermal reactivity of I with respect to phosphines, the photochemical reactions with these ligands could only be followed by IR spectroscopy for PPh₃, P(OPh)₃, and P(cHex)₃ but not for P(nBu)₃. The IR spectra of the photoproducts showed only one CO-stretching vibration at lower frequency (Table I), in agreement with the formation of Ni(CO)(PR₃)(tBu-DAB). All these photoproducts decomposed upon raising the temperature of the solution.

Reactions 9 and 7 are completely similar. Apparently, rechelation of the tBu-DAB ligand with concomitant loss of CO is a more likely process here than substitution of the σ-N-coordinated tBu-DAB ligand in Ni(CO)₂(PR₃)(σ-N-tBu-DAB) by PR₃ or CO. This is, however, only the case when the R group is not too bulky. When the above reaction was performed in the presence of P(cHex)₃, Ni(CO)₃(P(cHex)₃) was formed as a side product with CO-stretching modes at 2057 and 1977 cm⁻¹, respectively.³³ Rechelation of the σ-N-tBu-DAB ligand according to reaction 9 is then partly inhibited by the steric hindrance between the cHex and tBu groups. The tBu-DAB ligand may then be released instead and substituted by CO from the solution. Substitution by P(cHex)₃ to give Ni(CO)₂(P(cHex)₃)₂ will be prevented by the bulkiness of the phosphine ligand. A similar influence of steric hindrance was observed for the reaction of complex I with tBu-DAB (vide supra), which gave rise not only to reaction 7 but also to the formation of Ni(CO)₃(σ-N-tBu-DAB) as a side product.

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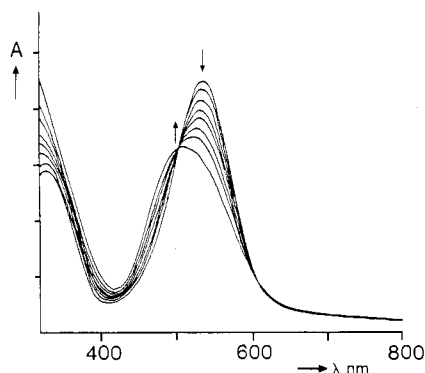


Figure 6. UV/visible spectral changes accompanying the photochemical reaction of complex II with 2,6-*i*Pr₂Ph-DAB upon irradiation with $\lambda = 514.5$ nm in toluene at 203 K.

The mechanism of the above reaction proceeding via eq 1, 8, and 9 is similar to that proposed for the photosubstitution of CO by PR₃ in Fe(CO)₃(tBu-DAB).⁹ In that case, however, complexes Fe(CO)₃(PR₃)(σ -*N*-tBu-DAB) could be identified as stable intermediates at low temperature (170–200 K). Raising the temperature caused the formation of Fe(CO)₂(PR₃)(tBu-DAB), analogous to reaction 9 of complex I.

From the above results it can be concluded that irradiation of complex I into its MLCT band causes the breakage of a Ni–N bond with formation of A as the primary photoproduct (reaction 1). All photoproducts are the result of (a) secondary thermal reaction(s) of this intermediate A, and this is shown in Scheme I. Irradiation into the UV absorption bands of I caused instead release of CO as the primary photoproduct.

Ni(CO)₂(2,6-*i*Pr₂Ph-DAB) (II). Reactions in the Absence of a Substituting Ligand. Irradiation of II in *n*-pentane at 170 K into its MLCT band only caused photodecomposition with Ni(CO)₄ as the main decomposition product. Neither a Ni(CO)₃ species with a σ -N monodentate 2,6-*i*Pr₂Ph-DAB ligand nor a dinuclear species as for I appeared to be formed. Just as for I, no reaction was observed upon irradiation in 2-MeTHF at 150 K. Because of its low volatility, complex II could not be dissolved in an inert-gas matrix.

More information about the photochemistry of this complex and the mechanisms involved could therefore only be obtained by studying the reactions with nucleophiles.

Reactions with R-DAB and PR₃. A low-temperature (ca. 200 K) solution of II was irradiated into its MLCT band in the presence of excess R-DAB (R = cHex, *i*Pr, 4Me-Ph, 2,6-*i*Pr₂Ph). As an example, Figure 6 shows the UV/vis spectral changes during the reaction of II with excess 2,6-*i*Pr₂Ph-DAB (toluene, 203 K). The characteristic MLCT band of II at 534 nm disappears, and two new bands show up at 491 and 751 nm, respectively. The positions and intensities of these bands are characteristic for a Ni(R-DAB)₂ complex with a pseudoplanar geometry^{34,35} and they are therefore assigned to Ni(2,6-*i*Pr₂Ph-DAB)₂. In contrast with this the IR spectrum showed a new ν (CO) band at 1957 cm⁻¹ belonging to the intermediate species Ni(CO)(σ -*N*-2,6-*i*Pr₂Ph-DAB)(2,6-*i*Pr₂Ph-DAB). The apparent discrepancy between the reactions observed in UV/vis and IR spectra is connected with the diffusion of CO from the sample solution. In the UV/vis sample cell this diffusion is rather fast; in the IR cell this process is nearly inhibited. Apparently, chelation of the second 2,6-*i*Pr₂Ph-DAB is prevented in the presence of CO. Raising the temperature of the IR solution caused a thermal back-reaction of the monocarbonyl species with CO to the parent complex II.

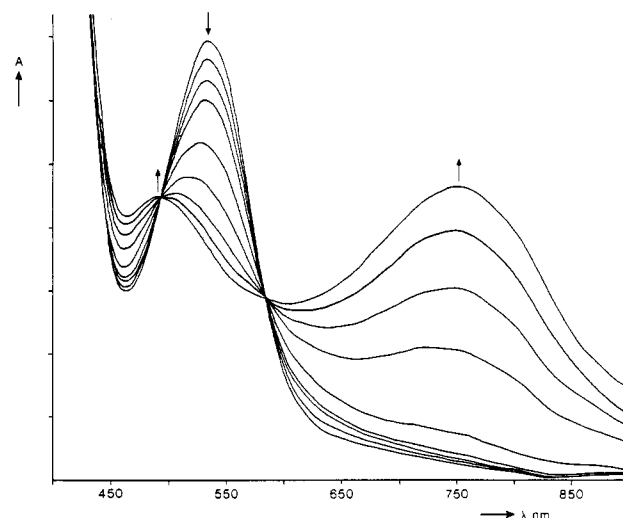
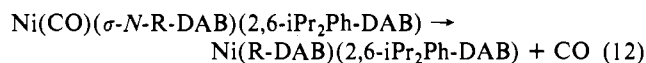
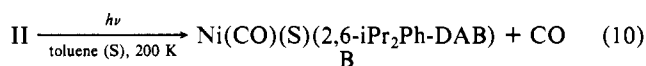


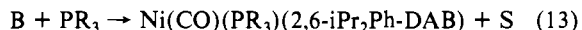
Figure 7. UV/visible spectral changes accompanying the photochemical reaction of complex II with P(*n*Bu)₃ upon irradiation with $\lambda = 514.5$ nm in toluene at 213 K.

On the basis of these results the following mechanism is proposed for this reaction:



The same reaction was observed in the presence of other R-DAB ligands. Thus, irradiation of II with cHex-DAB in 2-MeTHF at 200 K gave rise to two new absorption bands at 468 and 728 nm, not present in the spectra of either Ni(cHex-DAB)₂ or Ni(2,6-*i*Pr₂Ph-DAB)₂. They are therefore assigned to the mixed-ligand complex Ni(cHex-DAB)(2,6-*i*Pr₂Ph-DAB). The occurrence of the 728-nm band points to a distortion of the complex from a tetrahedral geometry.^{34,35} Unfortunately, these complexes could not be isolated due to the thermal instability of their solutions, producing a mixture of complex II and Ni(CO)₂(R-DAB). Upon reaction with tBu-DAB no mixed R-DAB complex was obtained but instead Ni(CO)₂(tBu-DAB) (I) was formed as the only photoproduct. This reaction cannot easily be explained with the mechanism of reactions 10–12. At the end of this section more attention will be paid to this special case.

Irradiation of II in the presence of PR₃ caused the substitution of CO by PR₃. This reaction will proceed via the same primary photoproduct B as the reaction of II with R-DAB (eq 10 and 13).



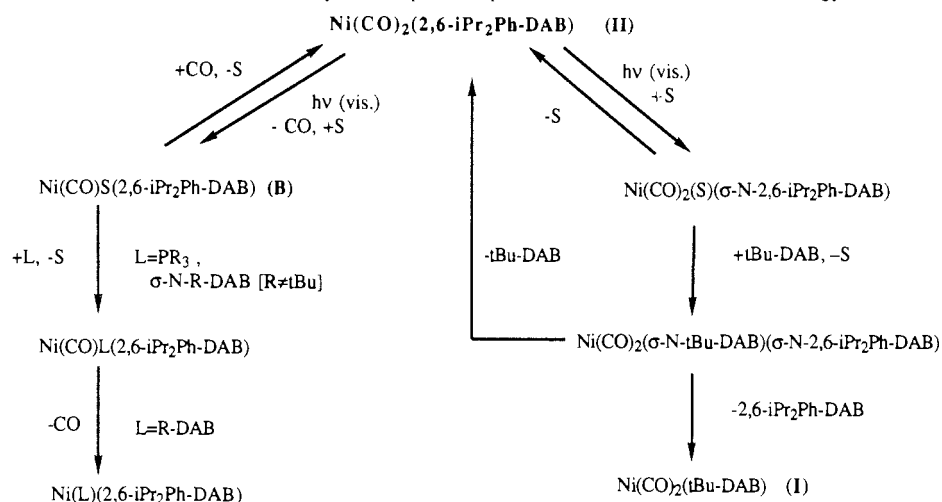
Unfortunately, these reactions could not be followed with IR spectroscopy because of the high thermal reactivity of II with respect to these PR₃ ligands. Figure 7 shows the UV/vis spectral changes accompanying the reaction with P(*n*Bu)₃. The photoproduct still contains an intense MLCT band in accordance with a substitution of CO by P(*n*Bu)₃. In contrast with the reaction of complex I with this ligand (Figure 5), the MLCT band shifts, however, to higher energy. A similar effect was observed for the reaction with P(cHex)₃ but not with PPh₃ or P(OPh)₃ (Table I). For the latter two ligands the MLCT band shifts to lower energy. This shift is closely related to the extent of mixing between the metal d and ligand π^* orbitals involved in this transition. If this mixing is not too strong, photosubstitution of CO by PR₃ merely destabilizes the metal d orbitals causing a shift of the MLCT band to lower energy. This effect was observed for all reactions of I. It has been shown in the preceding article on the spectroscopic properties of these complexes¹ that the HOMO and LUMO of

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Scheme II. Proposed Mechanism for the Photochemistry of Complex II upon Irradiation into Its Lowest Energy MLCT Transition



complex II, responsible for the MLCT transition, have strongly mixed metal d_{yz} , R-DAB π^* , and CO π^* character. In this complex substitution of CO by PR_3 not only destabilizes the metal d orbitals but also increases the mixing between the d_{yz} and π^* orbitals. This in turn causes an increase of the energy difference between the HOMO and LUMO and a concomitant shift of the MLCT band to higher energy. This effect will of course be most pronounced for the basic phosphines.

Although there is no direct evidence for the primary photoprocess of II (reaction 10) from matrix or flash-photolysis experiments, indirect information about this mechanism is provided by the analogy with the UV photochemistry of I. In both cases $\text{Ni}(\text{CO})_4$ was the only photoproduct upon low-temperature photolysis in the absence of a substituting ligand. Irradiation in the presence of PR_3 produced similar photoproducts $\text{Ni}(\text{CO})(\text{PR}_3)(\text{R-DAB})$ for both complexes. Moreover, UV irradiation of I in the presence of tBu-DAB produced $\text{Ni}(\text{CO})(\sigma\text{-N-tBu-DAB})(\text{tBu-DAB})$, while a similar product $\text{Ni}(\text{CO})(\sigma\text{-N-2,6-iPr}_2\text{Ph-DAB})(2,6\text{-iPr}_2\text{Ph-DAB})$ was obtained as an intermediate upon irradiation of II in the presence of 2,6-iPr₂Ph-DAB (reaction 11). In view of the close analogy between the above reactions, we conclude that the primary photoprocess of II upon excitation into the MLCT band is release of CO just as for I upon UV irradiation. This conclusion is supported by the photolysis of II with other R-DAB ligands, leading to the formation of mixed-ligand $\text{Ni}(\text{R-DAB})(2,6\text{-iPr}_2\text{Ph-DAB})$ complexes. Thus, the above products are derived from the primary photoproduct $\text{Ni}(\text{CO})(\text{S})(2,6\text{-iPr}_2\text{Ph-DAB})$ (B), and this is shown in Scheme II.

In this scheme the reaction of II with tBu-DAB is presented separately. This reaction cannot be explained in terms of the same primary photoprocess, since $\text{Ni}(\text{CO})_2(\text{tBu-DAB})$ (I) is formed, although with low quantum yield, instead of $\text{Ni}(\text{CO})(\sigma\text{-N-tBu-DAB})(2,6\text{-iPr}_2\text{Ph-DAB})$ and $\text{Ni}(\text{tBu-DAB})(2,6\text{-iPr}_2\text{Ph-DAB})$. With CPK molecular models it can, however, be shown that the steric properties of the tBu groups prevent the formation of such complexes. Since B cannot form a stable complex with tBu-DAB, II can only react via the alternative, less effective photoprocess, viz. breaking of a metal–nitrogen bond. $\text{Ni}(\text{CO})_2(\text{tBu-DAB})$ is then formed as the only photoproduct.

The only difference between the UV photochemistry of I and the MLCT photochemistry of II concerns the formation of $\text{Ni}(\text{CO})_3\text{L}$ [$\text{L} = \text{P}(\text{cHex})_3, \sigma\text{-N-tBu-DAB}$] in the case of I only. Since these $\text{Ni}(\text{CO})_3\text{L}$ complexes are in this case photoproducts of $\text{Ni}(\text{CO})_4$, they will only be formed by irradiation with UV light.

Primary Photoprocesses and Excited-State Properties. The most important result from this study is that different primary photoprocesses take place for complexes I and II upon irradiation into the lowest MLCT band. This difference in behavior is a consequence of the change of molecular structure upon going from I to II. In the preceding article on the bonding and spectroscopic properties of these complexes,¹ it has been demonstrated that this

change of structure is accompanied by a drastic change of character for the lowest energy electronic transition. In the tetrahedral complex I this transition is accompanied by charge transfer from the metal to the tBu-DAB ligand. Population of the corresponding ³MLCT state by irradiation into this low-energy band does not lead to a drastic weakening of any of the metal–ligand bonds, since the resonance Raman effects of the symmetric metal–ligand vibrations are only weak. As a result, a Ni–N bond is preferably broken in the ³MLCT state, since it is already the weaker one in the ground state. Thus, all thermal reactions of I with Lewis bases (L) lead to the formation of $\text{Ni}(\text{CO})_2\text{L}_2$. UV excitation takes place into metal to $\pi^*(\text{CO})$ transitions and causes release of CO.

Complex II has a pseudoplanar conformation with a HOMO and LUMO that have now strongly mixed metal d , R-DAB, π^* , and CO π^* character. As a result, the lowest energy transition has no MLCT character. It is instead a metal–ligand bonding to antibonding transition with respect to both the metal–R-DAB and metal–CO bonds. Irradiation into this transition is expected to weaken all metal–ligand bonds but in particular the metal–CO bonds because of the much stronger resonance Raman effect observed for $\nu_s(\text{Ni-C})$ than for $\nu_s(\text{Ni-N})$.¹ This explains the release of CO as the primary photoprocess for complex II. Only in the case that this reaction did not lead to a stable photoproduct was breaking of a metal–nitrogen bond observed as a much less effective photoprocess.

Conclusion

The above results show that the photochemical behavior of the complexes $\text{Ni}(\text{CO})_2(\text{R-DAB})$ is in close agreement with their theoretical and spectroscopic properties, which have been described in the preceding article. The change of character of the MLCT transition, induced by the change of structure upon going from complex I to complex II, also invokes a change of the primary photoprocess. For the tetrahedral complex I, a metal–nitrogen bond is broken by irradiation into the MLCT band, while the pseudoplanar complex II loses CO.

Acknowledgment. W. G. J. de Lange is thanked for his skillful synthesis of the complexes. The Laboratory of Organic Chemistry of the University of Amsterdam is thanked for putting at our disposal the flash-photolysis equipment. A. Terpstra and R. J. van Raamsdonk are thanked for their technical assistance during the measurements. Thanks are due to the Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for the Advancement of Pure Research (NWO) for their financial support.

Registry No. I, 98756-63-9; II, 116917-18-1; $\text{Ni}(\text{CO})_4$, 13463-39-3; $\text{Ni}(\text{CO})_3(\text{P}(\text{cHex})_3)$, 18475-08-6; $\text{Ni}(\text{CO})_3((\sigma\text{-N},\sigma\text{-N'})\text{tBu-DAB})\text{Ni}(\text{CO})(\text{tBu-DAB})$, 119878-58-9; $\text{Ni}(\text{CO})_2(\text{cHex-DAB})$, 119679-76-4; $\text{Ni}(\text{CO})(\text{P}(\text{cHex})_3)(\text{tBu-DAB})$, 119878-60-3; $\text{Ni}(\text{CO})(\text{PPh}_3)(\text{tBu-DAB})$, 119878-61-4; $\text{Ni}(\text{CO})(\text{P}(\text{OPh})_3)(\text{tBu-DAB})$, 119907-59-4; $\text{Ni}(\text{CO})(\text{P}$

(nBu)₃(tBu-DAB), 119878-62-5; Ni(CO)(P(nBu)₃)(cHex-DAB), 119878-66-9; Ni(CO)(P(nBu)₃)(2,6-iPr₂Ph-DAB), 119878-64-7; Ni(CO)(PPh₃)(2,6-iPr₂Ph-DAB), 119907-57-2; Ni(CO)(P(OPh)₃)(2,6-iPr₂Ph-DAB), 119878-67-0; Ni(CO)(P(cHex)₃)(2,6-iPr₂Ph-DAB), 119878-65-8; Ni(CO)(σ-N-tBu-DAB)(tBu-DAB), 119878-59-0; Ni(CO)(σ-N-2,6-iPr₂Ph-DAB)(2,6-iPr₂Ph-DAB), 119907-58-3; Ni(tBu-

DAB)₂, 63576-87-4; Ni(2,6-iPr₂Ph-DAB)₂, 78802-17-2; Ni(cHex-DAB)(2,6-iPr₂Ph-DAB), 119878-63-6; cHex-DAB, 3673-06-1; iPr-DAB, 24764-90-7; 2,6-iPr₂Ph-DAB, 74663-75-5; Ni(CO)₂(iPr-DAB), 119679-77-5; Ni(CO)₃(σ-N-tBu-DAB), 119878-57-8; PPh₃, 603-35-0; P(OPh)₃, 101-02-0; P(cHex)₃, 2622-14-2; P(nBu)₃, 998-40-3; CO, 630-08-0.

Contribution from the Chemistry Departments, University of Virginia, Charlottesville, Virginia 22901, and James Madison University, Harrisonburg, Virginia 22807

Intramolecular Excited-State Interactions of Surfactant-Active Osmium(II) Photosensitizers

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A new class of luminescent surfactant-active complexes, *cis*-OsL₂(CO)NC(CH₂)_nCH₃²⁺ (*n* = 0-19; L = 2,2'-bipyridine and 1,10-phenanthroline), were synthesized and characterized. They represent another example of an intramolecular perturbation of excited-state properties by what would normally be considered an electronically passive alkyl ligand. The effect is smaller in the Os(II) case and has a different *n* dependence than was observed in the *fac*-ReL(CO)₃NC(CH₂)_nCH₃⁺ system. The differences arise from varied geometric constraints on the foldback and the orbital parentage of the emitting state. Foldback must be directly to ligands involved in the emission process in order to perturb the emission. The osmium(II) center highly activates the bound nitrile to thermal nucleophilic attack, and luminescent adducts are formed with alcohols and aliphatic and aromatic amines. Such activation has not been previously observed in complexes with α-diimine ligands. The complexes also photodecompose by labilization of the nitrile.

Introduction

Luminescent transition-metal complexes are used as probes of macromolecular structures¹ and heterogeneous media² and as photosensitizers for solar energy conversion³ and electron-transfer reactions.⁴ While Ru(II) complexes, in particular, have found broad application, the excited-state properties of complexes of Re(I),^{5,6} Ir(III),⁷ Mo(0), W(0),⁸ and Os(II)⁹ are being increasingly investigated. The metal, ligands, and solvent environment can affect excited-state properties, and variations of one or more of these constituents can "tune" the photophysical and photochemical properties.¹⁰⁻¹² We recently studied the series *fac*-Re(bpy)(CO)₃NC(CH₂)_nCH₃⁺ (*n* = 0-17). Surprisingly, the emission properties are strongly perturbed by variations in *n*. We demonstrated that this effect is caused by intramolecular foldback of the alkyl chain onto the face of a bipyridine ligand.¹³ The resulting change in solvent environment around the excited portion of the molecule alters the excited-state properties. To further investigate these intramolecular interactions, we synthesized *cis*-OsL₂(CO)NC(CH₂)_nCH₃²⁺ (*n* = 0-19), where L = 2,2'-bipyridine (bpy) or 1,10-phenanthroline (phen). This allows one to examine foldback in other systems and to determine the effect of differing geometries and energy-level patterns. While foldback does occur, we rationalize the significant differences in the foldback impact.

Experimental Section

Syntheses. Materials and syntheses are described in the supplementary material, *cis*-Os(bpy)₂Cl₂¹⁴ was converted to *cis*-[Os(bpy)₂(CO)-Cl]PF₆ by using formic acid.¹⁵ The carbonyl was reacted with CF₃SO₃H to yield *cis*-[Os(bpy)₂(CO)(CF₃SO₃)](CF₃SO₃), which was converted to the nitriles.¹⁵

Equipment and Procedures. Absorption spectra and kinetics used a Hewlett-Packard 8452 spectrophotometer. Emission and excitation spectra were recorded as described earlier.¹³ Emission spectra were instrument and background corrected, while excitation spectra were only background corrected. Room-temperature emission spectra were typically from aerated solutions (λ_{ex} = 400 nm). Low-temperature, 77 K, spectra were measured by using EPA (5:5:2 diethyl ether-isopentane-ethanol), absolute EtOH, 9:2 DMF-CH₂Cl₂, 4:1 MeOH-H₂O, or 5:4 butyronitrile-propionitrile glasses (λ_{ex} = 300 and 400 nm).

We show a powerful, simple method for assessing emission inhomogeneity. Two uncorrected sample excitation spectra are measured at

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