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Competition between Reduction and Loss of Carbon Monoxide upon Photoexcitation of Cationic 2-Azaallenylidene Pentacarbonyl Complexes of Chromium and Tungsten

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The photochemistry of the cationic 2-azaallenylidene complexes $[(CO)_5M{=}C{=}N{=}CR_2]BF_4$ (M = Cr, W; R = Ph, Mes (Mes = 2,4,6-trimethylphenyl)) has been investigated at −55 °C in CH_2Cl_2. $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ undergoes photolysis with a 313-nm disappearance quantum yield of 0.1 ± 0.01. Irradiation at 366 nm or at longer wavelengths gives essentially no reaction. For R = Mes and M = Cr or W, two competitive photoreactions have been observed: CO loss to yield the complexes $BF_4(CO)_4M(CNCMes_2)$ and photoreduction to yield the isocyanide radical complexes $(CO)_5M{-}C{\equiv}N{-}\dot{C}Mes_2$. The latter complexes have also been prepared and isolated by the reduction of $[(CO)_5M{=}C{=}N{=}CMes_2]BF_4$ with $Fe(\eta^5\text{-}C_5H_5)_2$. For $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$, the relative importance of the photoreactions depends on the irradiation wavelength. At 313 nm CO loss is about two times more important than when irradiation is at 254 nm. This demonstrates that photoreduction and photodissociation occur from two different excited states. $BF_4(CO)_4Cr(CNCMes_2)$ reacts with $[n\text{-}Bu_4N]Br$ to yield *trans*-$Br(CO)_4Cr(CNCMes_2)$, the first substituted 2-azaallylidene complex of Cr. When complexes without bulky ligands, e.g., $[(CO)_5Cr{=}C{=}N{=}CPh_2]BF_4$, are irradiated, only products due to photoreduction are formed.

Introduction

The photochemistry of transition-metal carbonyl complexes with metal–carbon multiple bonds has been little studied.[1] Photoreactions of complexes with metal–carbon bonds are usually dominated by CO loss, but some interesting reactions involving the alkylidene or alkylidyne ligand, such as ligand isomerizations,[2-4] a carbyne–CO coupling reaction,[5] and an electrophilic addition to a carbyne ligand,[6] may proceed without prior CO loss. Hegedus's β-lactam synthesis[7] has also been claimed not to involve primary CO dissociation. To the best of our knowledge, the photochemistry of metallacumulene or -heterocumulene complexes, i.e., complexes that contain a metal–carbon multiple bond as part of a cumulene or heterocumulene system, has not been reported. However, the electron delocalization in these extended π-systems should significantly influence the photochemistry of these compounds and make photoreactions involving the unsaturated ligand more likely. In particular, the unusual ground-state properties of cationic 2-azaallenylidene complexes $[(CO)_5M{=}C{=}N{=}CR_2]BF_4$ (M = Cr, W) and the unexpected isolation of olefins $R_2C{=}CR_2$ from their exhaustive photolysis[8] prompted us to investigate the photochemistry of 2-azaallenylidene complexes.

Experimental Section

Instruments and Equipment. UV–vis spectra were recorded on a Cary 17 or a Hewlett-Packard 8451 A diode array spectrophotometer. IR spectra were recorded on a Nicolet 7199 or a Nicolet 60SX Fourier transform spectrometer. Low-temperature UV–vis and IR spectra were recorded with the samples being held in a Specac Model P/N 21.000 variable-temperature cell with CaF_2 windows using EtOH/dry ice as coolant. Before being loaded the cells were cooled with dry ice in a glovebag to avoid thermal decomposition of the 2-azaallenylidene complexes. NMR spectra were recorded on a Varian XL-300 Fourier transform spectrometer. Field desorption mass spectra were recorded on a Varian MAT 731 spectrometer.

Chemicals. All solvents used were reagent grade and were freshly distilled under Ar from appropriate drying agents (pentane and hexane from CaH_2 and CH_2Cl_2 and Na/Pb alloy). All reactions and manipulations of the organometallic compounds were carried out by using standard Schlenk techniques under an Ar atmosphere. $Fe(\eta^5\text{-}C_5H_5)_2$ was obtained from Aldrich and used as received. $AlBr_3$ was obtained from Fluka and freshly sublimed before use. BF_3 was obtained from Matheson. $[n\text{-}Bu_4N]Br$ was obtained from Eastman and used as received. The 2-azaallenylidene complexes $[(CO)_5M{=}C{=}N{=}CR_2]BF_4$ (M = Cr, W; R = Ph, Mes (Mes = 2,4,6-trimethylphenyl)) were prepared as described in ref 8. $[(CO)_5Cr{=}C{=}N{=}CMes_2]AlBr_4$ was prepared from $(CO)_5Cr[C(OEt)N{=}CMes_2]$[8b,9] and a threefold excess of $AlBr_3$ in CH_2Cl_2 at −10 °C. The resulting deep blue solution was used without further purification.

Preparation of $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$. At −20 °C a solution of 300 mg (1.6 mmol) of $Fe(\eta^5\text{-}C_5H_5)_2$ in 10 mL of CH_2Cl_2 was added to a solution of 1.2 g (1.9 mmol) of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4{\cdot}CH_2Cl_2$ in 10 mL of CH_2Cl_2. The color changed immediately from blue to purple. After the solution was stirred for 30 min, the solvent was evaporated in vacuo. The residue was extracted three times with 20 mL of pentane each. The combined extracts were chromatographed on SiO_2 at −20 °C by using pentane/CH_2Cl_2 (2/1, v/v) as the eluant. The solvent was evaporated in vacuo and the residue dissolved in a few milliliters of pentane and cooled to −78 °C to yield 400 mg (53%) of $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$. Identification was by spectroscopic comparison (IR, UV–vis) with an authentic sample.[10]

Preparation of $(CO)_5W{-}C{\equiv}N{-}\dot{C}Mes_2$. This complex was prepared in a manner analogous to that for the Cr species from 110 mg (0.59 mmol) of $Fe(\eta^5\text{-}C_5H_5)_2$ and 500 mg (0.65 mmol) of $[(CO)_5W{=}C{=}N{=}CMes_2]BF_4{\cdot}CH_2Cl_2$ at 50 °C; yield 180 mg (51%).

Preparation of $(CO)_5Cr{-}C{\equiv}N{-}CPh_2{-}CPh_2{-}N{\equiv}C{-}Cr(CO)_5$. BF_3 was slowly bubbled through a solution of 170 mg (0.40 mmol) of $(CO)_5Cr[C(OEt)N{=}CPh_2]$[11] in 10 mL of CH_2Cl_2 at −100 °C for 10 min. The solution was then stirred for 2 h at −60 °C, the solvent was removed in vacuo (−30 °C), and the residue was dried for several hours in vacuo at −30 °C to remove excess BF_3. The residue was redissolved in 5 mL of cold CH_2Cl_2. After the solution was cooled to −78 °C, 80 mg (0.43 mmol) of $Fe(\eta^5\text{-}C_5H_5)_2$ in 5 mL of CH_2Cl_2 was added dropwise. The solution turned immediately colorless. After the solution was warmed to 0 °C, the solvent was evaporated in vacuo, and the residue was extracted three times with 20 mL of pentane each. The combined extracts were filtered and reduced to 20 mL. Cooling the solution to −30 °C afforded 25 mg (8%) of colorless crystals. ^1H NMR (acetone-d_6 as solvent and standard): 7.4 ppm (m). MS (FD): *m/e* 768; calcd for $C_{38}H_{20}Cr_2N_2O_{10}$ 768.6.

Preparation of *trans*-$Br(CO)_4Cr(CNCMes_2)$. In a Pyrex Schlenk tube 140 mg (0.22 mmol) of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4{\cdot}CH_2Cl_2$ was dissolved in 50 mL of cold CH_2Cl_2. While the solution was purged with Ar, it was irradiated (with a 550-W Hanovia medium-pressure Hg lamp) until about 70% of the starting material was consumed (monitored by FTIR; approximately 4 h). $[n\text{-}Bu_4N]Br$ (50 mg, 0.16 mmol), dissolved in 5 mL of CH_2Cl_2, was added, the solvent was removed in vacuo (−20 °C), and the residue was extracted three times with 25 mL of pentane/CH_2Cl_2 (5/1, v/v) each. The product mixture was separated by chromatography on SiO_2 at −20 °C. After a purple band containing $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$ had been eluted with pentane/CH_2Cl_2 (5/1,

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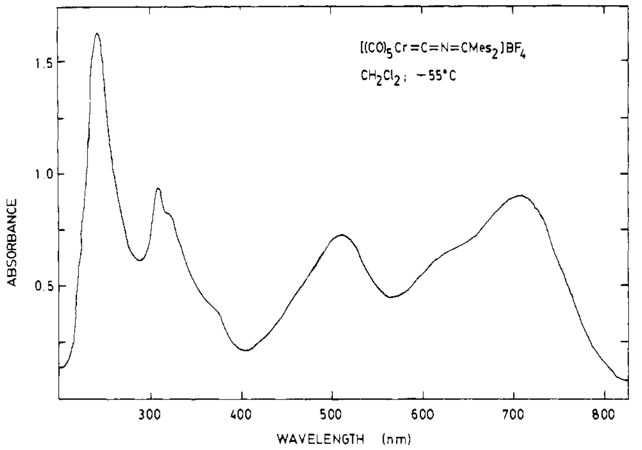

Figure 1. Electronic absorption spectrum of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ (2.5 mM in CH_2Cl_2; 0.2-mm path-length CaF_2 cell; −55 °C).

v/v), the product complex was eluted with CH_2Cl_2. The solvent was removed in vacuo and the product recrystallized from Et_2O yielded red crystals; yield 40 mg (35%). ^1H NMR (CD_2Cl_2 as solvent and standard): 2.11 (s, 12 H), 2.18 (s, 6 H), 6.85 ppm (s, 4 H). MS (FD): *m/e* 519/521; calcd for $C_{24}H_{22}BrCrNO_4$ 520.3.

Irradiations. A Bausch and Lomb SP200 high-pressure Hg lamp (output filtered by a 10-cm H_2O filter with Pyrex windows) was used as the light source for IR and UV–vis studies. For quantum yield determinations, 3-mL portions of 1.5 mM solutions of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ in CH_2Cl_2 were loaded into a 1-cm quartz cell, which was placed in a copper block with appropriate holes that allowed irradiation of the solution. The copper block was placed in a Dewar equipped with quartz windows and cooled with dry ice. The temperature reached was −55 ± 5 °C. The system was calibrated at 25 °C by ferrioxalate actinometry[12] before and after the measurements. Great care was taken to make sure that the geometrical arrangement was the same for each measurement and the calibrations. The light source for quantum yield determinations was a 550-W Hanovia medium-pressure Hg lamp. The light was filtered through Corning glass filters for irradiation at 366 nm and through Corning glass filters and a solution of K_2CrO_4/K_2CO_3 for 313 nm. The excitation rate was typically 5×10^{-8} einstein/min.

For measuring the photoproduct ratios [*cis*-$BF_4(CO)_4Cr(CNCMes_2)$]/[$(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$], 0.01 M solutions of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ were used. An unfiltered Ultraviolet Products Inc. Model PCQ-X1 low-pressure Hg lamp was used for 254-nm irradiation. For 313-nm irradiation, the light of a Bausch and Lomb SP200 high-pressure Hg lamp was filtered through a 10-cm H_2O filter with Pyrex windows and through 1 cm of a K_2CrO_4/K_2CO_3 solution. The product ratios were determined at less than 10% conversion to minimize effects of secondary photolysis. Since both IR bands of *cis*-$BF_4(CO)_4Cr(CNCMes_2)$ overlap strongly with bands of the starting complex, the intensities of these bands could not be measured directly but were calculated in the following way. From the decrease of the 1890 cm^{-1} band of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ and the known extinction coefficients of this complex, a theoretical decrease for the 2104 cm^{-1} band can be calculated. The difference between the measured and the calculated absorptions at 2104 cm^{-1} is the increase in absorption due to formation of *cis*-$BF_4(CO)_4Cr(CNCMes_2)$. The ratio of this difference to the increase at 1956 cm^{-1} (due to $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$) is proportional to the product ratio [*cis*-$BF_4(CO)_4Cr(CNCMes_2)$]/[$(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$].

Results

Electronic Absorption Spectra of 2-Azaallenylidene Complexes. The UV–vis spectrum of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ (Mes = 2,4,6-trimethylphenyl) in Figure 1 serves as a representative example for all 2-azaallenylidene complexes with aromatic substituents. They invariably display two overlapping bands in the region between 600 and 720 nm for the Cr complexes and between 560 and 660 nm for the W complexes. These two bands can be assigned to MLCT (metal to ligand charge transfer) transitions from nondegenerate d orbitals into the LUMO of the 2-azaallenylidene ligand.[8] The orbital of termination has π-symmetry and consists basically of p orbitals of the two carbon atoms of the heterocumulene system. Consistent with the assignment as MLCT transitions, increasing donor capacity of the 2-azaallenylidene ligand results in shifts of these bands to higher energy. A third band in the region between 370 and 520 nm can be assigned to an intraligand transition from the π-orbitals of the aromatic rings into the LUMO of the 2-azaallenylidene ligand. This third band is not found in 2-azaallenylidene complexes with aliphatic substituents. A similar band has been reported for 2-azaallenium salts $[R_2C{=}N{=}CR_2]^+$ with aromatic R.[13] Additional arguments for this assignment are the insensitivity of the position of this band toward variation of the metal and, despite the dependence of its energy on the aromatic substituents, the lack of a correlation between their donor capacity and the transition energy. The complexes absorb strongly ($\epsilon > 10^4\ M^{-1}\ cm^{-1}$) below 350 nm with maxima around 250 and 310 nm. Shoulders indicate the presence of additional transitions. In this spectral region the following transitions are to be expected: MLCT transitions into the π*-orbitals of the carbonyl ligands; a MLCT transition into an unoccupied π-orbital of the 2-azaallenylidene ligand, which is orthogonal to the LUMO; aromatic π → π* transitions; and ligand field transitions. Ligand field (d–d) transitions for the Cr and W complexes are expected to be at energies higher than 350 nm on the basis of the absorption spectrum of the $M(CO)_6$ complexes.[14]

Irradiation of $[(CO)_5Cr{=}C{=}N{=}CMes_2]X$ (X = BF_4, $AlBr_4$). Upon irradiation of a 0.01 M solution of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ in CH_2Cl_2 at −55 °C with near-UV light, a rapid photochemical reaction takes place. The disappearance quantum yield at 313 nm is 0.1 ± 0.01. At 366 nm the disappearance quantum yield is at least 1 order of magnitude smaller. If the incident light is filtered through a 370-nm cutoff filter, essentially no photoreaction is observed. Obviously neither the MLCT transitions at 625 and 700 nm nor the intraligand transition at 510 nm are photoactive. Since population of these nonreactive excited states from the higher excited states should provide an efficient pathway for radiationless deactivation of the reactive states, one would expect a much lower quantum yield than the 0.1 found. For instance, $(CO)_5W[C(OMe)Ph]$ has a nonreactive MLCT state as the lowest excited state. At higher energy is a LF excited state, which can undergo CO loss. However, since the conversion of the LF state to the MLCT state is fast, the quantum yield for CO loss is low, $\Phi_{313} = 0.011$.[15] Of course, radiationless deactivation of the photoactive states is important in $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$, too, but is significantly less efficient, probably because of several effects: (1) the energy gap between the photoactive excited states and the intraligand excited state corresponding to the 510-nm band is considerably larger; (2) the orbitals involved in this intraligand excitation are localized on different parts of the molecule, resulting in poor overlap of the wavefunctions describing the respective excited states and low transition probability between them; (3) the ground-state reactivity of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ is very high, and thus the consumption of starting material upon irradiation could, at least partially, be due to a hot ground-state reaction.

Exhaustive photolysis of 0.01 M solutions of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ in CH_2Cl_2 at −55 °C gives a solution showing the IR spectrum of Figure 2b compared to the spectrum for the unirradiated solution shown in Figure 2a. The main absorptions in Figure 2b are due to two different complexes, as was shown by warm-up experiments. The band at 1956 cm^{-1} and the shoulder at 2086 cm^{-1} can be assigned to the isocyanide radical complex $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$ (Table I). These radicals are C-centered radicals as established by data previously obtained.[10] Besides the IR spectrum, this assignment is confirmed by an absorption in the UV–vis spectrum at 560 nm (Table II) which is identical with that of an independently prepared sample of $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$. This complex had been previously

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Table I. IR Spectroscopic Data for Relevant Complexes

complex	band maxima[a]	ref
$[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$	2104 s, 2032 s, 2005 vs, 1890 vs[b]	8b
$[(CO)_5W{=}C{=}N{=}CMes_2]BF_4$	2115 s, 2020 s, 1997 vs, 1881 vs[b]	8b
$[(CO)_5Cr{=}C{=}N{=}CPh_2]BF_4$	2103 vs, 2031 s, 2008 s, 1888 m[b]	8b
$(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$	2148 vw, 2084 w, 1964 sh, 1962 vs[c]	10
	2086 w, 1956 vs[b]	*d*
$(CO)_5W{-}C{\equiv}N{-}\dot{C}Mes_2$	2153 vw, 2088 w, 1960 sh, 1957 vs[c]	*d*
	2089 w, 1950 vs[b]	*d*
cis-$BF_4(CO)_4Cr(CNCMes_2)$	2102 m, 1993 s[b]	*d*
trans-$BF_4(CO)_4Cr(CNCMes_2)$	2104 m, 2051 s[e]	*d*
trans-$Br(CO)_4Cr(CNCMes_2)$	2090 m, 2039 s[c]	*d*
trans-$BF_4(CO)_4W(CNCMes_2)$	2107 m, 2025 s[b]	*d*
trans-$Br(CO)_4W(CNCMes_2)$	2103 m, 2016 s[c]	9
trans-$Cl(CO)_4W(CNCMes_2)$	2104 m, 2014 s[e]*d*	*d*
$[(CO)_5Cr{-}C{\equiv}N{-}CPh_2]_2$	2141 w, 2053 m, 1964 vs[c]	*d*
	2148 w, 2058 m, 1958 vs[b]	*d*
$[(CO)_5W{-}C{\equiv}N{-}CPh_2]_2$	2142 w, 2053 m, 1960 vs[c]	9

[a] Wavenumbers in cm^{-1}. [b] Conditions: CH_2Cl_2, −55 °C. [c] Conditions: hexanes, ambient temperature. [d] This work. [e] Conditions: CH_2Cl_2, ambient temperature.

Table II. UV–Vis Spectroscopic Data for Relevant Complexes

complex	band maxima[a]	ref
$[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$	696, 625, 506[b]	8b
$[(CO)_5W{=}C{=}N{=}CMes_2]BF_4$	644, 608, 504[b]	8b
$[(CO)_5Cr{=}C{=}N{=}CPh_2]BF_4$	700, 630, 417[b]	8b
$(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$	568 (3.77), 358 (4.17)[c]	10
$(CO)_5W{-}C{\equiv}N{-}\dot{C}Mes_2$	549 (3.90), 411 (3.95), 360 (4.45), 345 (4.39), 323 (4.35)[c]	*d*
cis-$BF_4(CO)_4Cr(CNCMes_2)$	460[e]	*d*
trans-$Br(CO)_4Cr(CNCMes_2)$	520, 410 (sh), 340 (sh), 305[f]	*d*
trans-$BF_4(CO)_4W(CNCMes_2)$	460[e]	*d*
trans-$Br(CO)_4W(CNCMes_2)$	455, 470 (4.03)[c]	9

[a] Wavelength in nm; log ϵ in parentheses. [b] Conditions: CH_2Cl_2, −20 °C. [c] Conditions: hexanes, ambient temperature. [d] This work. [e] Conditions: CH_2Cl_2, −55 °C. [f] Conditions: CH_2Cl_2, ambient temperature.

obtained from the reaction of $[(CO)_5Cr{=}C{=}N{=}CMes_2]AlBr_4$ with tetrahydrofuran,[10] probably via reaction with Br^- liberated from $AlBr_4^-$. We developed a more efficient synthesis of $(CO)_5Cr{-}C{\equiv}N{-}\dot{C}Mes_2$, which we needed for spectroscopic comparison: $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ reacts with $Fe(\eta^5\text{-}C_5H_5)_2$ in CH_2Cl_2 to form the isocyanide radical complex in good yield. In the photoreduction, an excited molecule of $[(CO)_5Cr{=}C{=}N{=}CMes_2]^+$ probably reacts with the solvent, the solvent giving unidentified products. We cannot completely rule out that another metal complex or an impurity acts as the reductant, but in view of the large (at least 1500 fold in the solutions employed) excess of CH_2Cl_2 over any metal complex possibly present in the solution and the high reactivity that the excited complex will have, this possibility seems less likely.

The positions and relative intensities of the remaining two strong bands in Figure 2b are indicative of a tetracarbonyl complex as the second photoproduct. That CO loss from $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ occurs is also evident from a weak absorption due to free CO at 2135 cm^{-1}. Since among all the species present in the solution, BF_4^- has obviously the best ligating properties toward a positively charged, coordinatively unsaturated metal fragment, we ascribe the tetracarbonyl complex the formula $BF_4(CO)_4Cr(CNCMes_2)$. A similar, albeit thermal, exchange of CO for BF_4^- has been reported for $[(CO)_5W{\equiv}CNEt_2]BF_4$ to give *trans*-$BF_4(CO)_4W{\equiv}CNEt_2$.[16] Several other complexes with BF_4^- acting as a ligand are known.[17] $BF_4(CO)_4Cr(CNCMes_2)$ can have cis or trans geometry around the metal. Surprisingly, the primary photoproduct seems to be the cis complex (compared to *trans*-$BF_4(CO)_4W(CNCMes_2)$ the IR bands are at lower energy, which makes a trans geometry very unlikely; cf. Table I). On prolonged irradiation at −40 °C or upon warming, *cis*-$BF_4(CO)_4Cr(CNCMes_2)$ undergoes isomerization to give *trans*-$BF_4(CO)_4Cr(CNCMes_2)$; cf. Table I and Figure 2b. At 298 K the tetracarbonyl photoproduct is rapidly decomposed. Since the heterocumulene band of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ at 1897 cm^{-1} disappears on irradiation, the Cr—C—N—C system in both *cis*- and *trans*-$BF_4(CO)_4Cr(CNCMes_2)$ is probably bent as in 2-azaallylidene tungsten complexes.[9,18] A band in the electronic absorption spectrum at 460 nm is also consistent with the presence of a bent 2-azaallylidene ligand (cf. Table II).

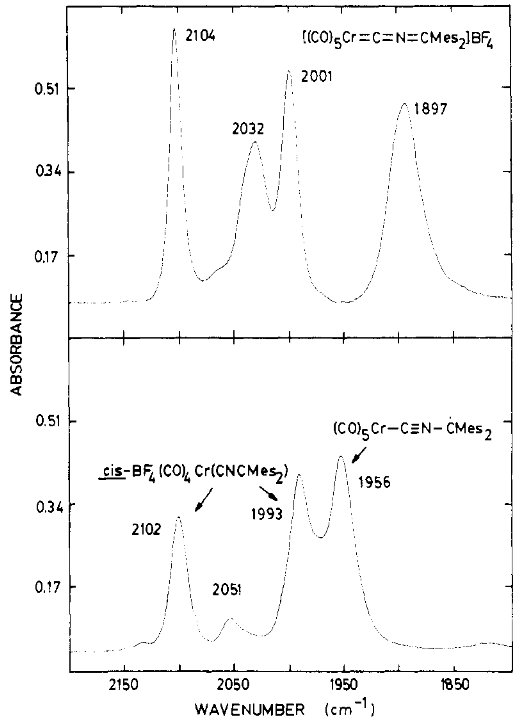

Figure 2. Top: IR spectrum of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ (10^{-2} M in CH_2Cl_2; 0.2-mm path-length CaF_2 cell; −55 °C). Bottom: IR spectrum of a completely photolyzed ($\lambda > 300$ nm) solution of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$ (10^{-2} M in CH_2Cl_2; 0.2-mm path-length CaF_2 cell; −55 °C).

The complexes $BF_4(CO)_4Cr(CNCMes_2)$ should easily substitute BF_4^- for more strongly coordinating ligands, as has been observed for other BF_4^- complexes.[16,17] Indeed, the addition of $[n\text{-}Bu_4N]Br$ to a solution of *trans*-$BF_4(CO)_4Cr(CNCMes_2)$ even at −78 °C immediately affords *trans*-$Br(CO)_4Cr(CNCMes_2)$, which can be isolated by low-temperature chromatography. The good agreement of the IR (Table I) and UV–vis spectra (Table II) with those of 2-azaallylidene tungsten complexes indicates a similar geometry of the ligand. For *trans*-$Br(CO)_4W(CNCPh_2)$ an X-ray diffraction analysis showed that the W-C-N-C system is strongly bent at the nitrogen.[9,18] Although we have not yet been able to obtain crystals suitable for X-ray analysis, we therefore propose a similarly bent structure for *trans*-$Br(CO)_4Cr(CNCMes_2)$ as well. Additional evidence for a bent ligand is a strong band in the IR spectrum at 1600 cm^{-1} (KBr pellet). The stretching frequencies of bent 2-azaallyl systems are typically found in this region.[9,18,19]

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The ratio of photosubstitution vs. photoreduction can be controlled by the reaction conditions. If the irradiation is carried out in a CO-saturated solution, the product ratio is shifted in favor of $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$, but some $BF_4(CO)_4Cr(CNCMes_2)$ is also formed. Conversely, the photoreduction can be completely suppressed, if $[(CO)_5Cr=C=N=CMes_2]AlBr_4$ is irradiated in a solution containing excess $AlBr_3$. No net photoreduction is observed in this case, probably because $AlBr_3/CH_2Cl_2$ reoxidizes any $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$ formed. $AlCl_3/CH_2Cl_2$ is a known oxidizing agent.[20] We were able to establish this possibility by treating a solution of $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$ in CH_2Cl_2 with $AlBr_3$. It reacted immediately to form $[(CO)_5Cr=C=N=CMes_2]^+$ as the only metal carbonyl product. The most interesting way to control the product ratio is by variation of the irradiation energy. Upon irradiation of $[(CO)_5Cr=C=N=CMes_2]BF_4$ at 254 nm, approximately two-thirds of the consumed starting material is converted to the photoreduction product $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$ and about one-third of the consumed starting complex undergoes CO loss. At 313 nm the product ratio [*cis*-$BF_4(CO)_4Cr(CNCMes_2)]/[(CO)_5Cr-C\equiv N-\dot{C}Mes_2]$ is shifted by a factor of at least 2 in favor of the CO substitution product. Thus, photoreduction and photosubstitution clearly occur from two different excited states.

Irradiation of $[(CO)_5W=C=N=CMes_2]BF_4$. $[(CO)_5W=C=N=CMes_2]BF_4$ undergoes essentially the same photochemistry as the Cr analogue to yield $(CO)_5W-C\equiv N-\dot{C}Mes_2$ and *trans*-$BF_4(CO)_4W(CNCMes_2)$. No cis isomer was observed in this case. The reduction product has been previously reported as a minor byproduct in the reaction of $[(CO)_5W=C=N=CMes_2]BF_4$ with $[n\text{-}Bu_4N]Br$.[10] As with $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$, we prepared $(CO)_5W-C\equiv N-\dot{C}Mes_2$ in good yield by reduction of $[(CO)_5W=C=N=CMes_2]BF_4$ with $Fe(\eta^5\text{-}C_5H_5)_2$. The product from reduction gives spectroscopic data in good agreement with those reported for the analogous Cr complex.[10] A low-energy band is observed in the UV–vis spectrum at 549 nm with a shoulder at 590 nm (in methylcyclohexane, Table II). The band pattern of the EPR spectrum closely resembles that of the Cr complex.

In contrast to $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$, the isocyanide radical W complex is very photolabile. Therefore only minor amounts of it are detectable in an irradiated solution of $[(CO)_5W=C=N=CMes_2]BF_4$. Photolysis of $(CO)_5W-C\equiv N-\dot{C}Mes_2$ in CH_2Cl_2 yields a complex with bands at 2088 and 1969 cm^{-1}. The same bands are also observed in an irradiated solution of $[(CO)_5W=C=N=CMes_2]BF_4$, consistent with the conclusion that $(CO)_5W-C\equiv N-\dot{C}Mes_2$ is initially formed in much higher yield but subsequently undergoes photolysis. The photolysis product of $(CO)_5W-C\equiv N-\dot{C}Mes_2$ can be tentatively assigned the structure $(CH_2Cl_2)(CO)_4W(CNCMes_2)$. The IR spectral changes are inconsistent with loss of the organic radical to yield a derivative of $W(CO)_5$. The formation of $(CO)_5W-C\equiv N-\dot{C}Mes_2$ (by back reaction with CO) and of *trans*-$Cl(CO)_4W(CNCMes_2)$ (by reaction with solvent) on warming the species formulated as $(CH_2Cl_2)(CO)_4W(CNCMes_2)$ to 298 K are consistent with this assignment. A similar activation of CH_2Cl_2 upon coordination has been recently postulated to occur in the reaction of $[(\eta^5\text{-}C_5H_5)_2W(CH_2Ph)(CH_2Cl_2)]PF_6$ with trityl radical to give $[(\eta^5\text{-}C_5H_5)_2W(CH_2Ph)Cl]PF_6$.[21] The addition of $[n\text{-}Bu_4N]Br$ to a completely photolyzed solution of $[(CO)_5W=C=N=CMes_2]BF_4$ yields the known[9] complex *trans*-$Br(CO)_4W(CNCMes_2)$. This result is additional evidence for the assignment of the substitution photoproduct as *trans*-$BF_4(CO)_4W(CNCMes_2)$.

Irradiation of $[(CO)_5Cr=C=N=CPh_2]BF_4$. Irradiation at −55 °C of a CH_2Cl_2 solution of $[(CO)_5Cr=C=N=CPh_2]BF_4$ using $\lambda > 300$ nm rapidly decomposes the starting complex. No product bands, however, can be observed. When a 370-nm cutoff filter is used, which requires much longer irradiation times, bands consistent with the formation of an isocyanide complex are observed. A completely photolyzed solution is colorless. The same isocyanide complex can be isolated, albeit in low yield, from the reaction of $[(CO)_5Cr=C=N=CPh_2]BF_4$ with $Fe(\eta^5\text{-}C_5H_5)_2$. Since a low-energy absorption in the electronic spectrum is missing, this complex cannot be analogous with the isocyanide radical complex $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$. The intermediate formation of $(CO)_5Cr-C\equiv N-\dot{C}Ph_2$, however, seems very likely both in the photoreaction and in the reduction with $Fe(\eta^5\text{-}C_5H_5)_2$. Unlike its mesityl analogue, due to the lack of steric hindrance this isocyanide radical complex is not stable and dimerizes to give $(CO)_5Cr-C\equiv N-CPh_2-CPh_2-N\equiv C-Cr(CO)_5$. The analogous W complex has been previously prepared and shows a very similar IR spectrum[9,18] (Table I). When $(CO)_5Cr-C\equiv N\text{-}CPh_2-CPh_2-N\equiv C-Cr(CO)_5$ is irradiated by using $\lambda > 300$ nm, it decomposes rapidly. This explains why no metal carbonyl products are observed when $[(CO)_5Cr=C=N=CPh_2]BF_4$ is irradiated at this energy. The binuclear isocyanide complex is apparently the source of the $Ph_2C=CPh_2$ that can be isolated from exhaustively photolyzed solutions of $[(CO)_5Cr=C=N=CPh_2]BF_4$.[8]

A remarkable fact about the photochemistry of $[(CO)_5Cr=C=N=CPh_2]BF_4$ is the inability to detect CO loss products. To attempt to exclude the possibility that this merely reflects the instability of products like $BF_4(CO)_4Cr(CNCPh_2)$, we repeated the irradiation of $[(CO)_5Cr=C=N=CPh_2]BF_4$ in a CO saturated solution. We find no difference in the rate for the disappearance of the cationic complex. Therefore, $[(CO)_5Cr=C=N=CPh_2]BF_4$ appears to undergo only reduction on photolysis. However, given the similarity of the electronic structure of the cationic $[(CO)_5Cr=C=N=CR_2]^+$ complexes with R = Mes and R = Ph, it seems likely that CO loss does occur for R = Ph, but the net quantum yield must be smaller for R = Ph than for R = Mes.[9]

Discussion

By far the most important type of photoreaction of metal carbonyl complexes is ligand dissociation.[22] With a few exceptions, this is also true for complexes with metal–carbon multiple bonds.[1] The cationic 2-azaallenylidene complexes $[(CO)_5M=C=N=CR_2]^+$, however, are a class of compounds, where both CO loss and reduction can be observed upon photoexcitation. Photoreduction gives the isocyanide radical complexes $(CO)_5M-C\equiv N-\dot{C}R_2$, and CO loss gives 16e fragments, which are stabilized by coordination of BF_4^- to give $BF_4(CO)_4M(CNCR_2)$. The relative importance of the net photoreactions depends on a variety of parameters. Unless R is a bulky substituent like mesityl, the photoreduction product dominates. Thus, for $[(CO)_5Cr=C=N=CPh_2]BF_4$ we find no photosubstitution products. Likewise, CO substitution is not observed for $[(CO)_5W=C=N=CPh_2]BF_4$ and $[(CO)_5Cr=C=N=C(C_6H_4)_2O]BF_4$, whereas photoreduction does occur. Solution additives affect the product distribution. For $[(CO)_5Cr=C=N=CMes_2]BF_4$ external CO suppresses the photodissociation reaction to some extent. The redox potential of the solution is also an important factor. In an oxidizing solution, e.g., in the presence of excess $AlBr_3$, no photoreduction product could be obtained. This is apparently due to reoxidation of $(CO)_5Cr-C\equiv N-\dot{C}Mes_2$ with $AlBr_3$. For $[(CO)_5Cr=C=N=CMes_2]BF_4$ variation in the excitation wavelength also affects the product ratio. The ratio of photodissociation vs. photoreduction is at least two times higher at 313 nm than when irradiation is at 254 nm. Therefore, photoreduction and photodissociation clearly occur from two different excited states, with the excited state causing reduction being at somewhat higher energy. Ligand dissociation, in our case CO loss, is commonly associated with LF excited states.[22] The same assignment is certainly true for $[(CO)_5Cr=C=N=CMes_2]BF_4$ as well. The strong dependence of the photodissociation/photoreduction ratio on the steric demand of the substituents R could indicate that the reduction requires prior coordination of the reducing molecule to the 2-azaallenylidene ligand. This would

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then point to a LMCT or intraligand state as the excited state associated with reduction. However, our knowledge about the electronic structure of these complexes is insufficient for definitive conclusions. An interesting point is that the dominant, assigned electronic absorptions (Figure 1 and Table II) do not provide a rationale for the photochemistry of $[(CO)_5M{=}C{=}N{=}CR_2]^+$. The optically silent ligand field states are likely responsible for loss of CO, while a high-energy charge-transfer state leads to reduction products.

Whereas the W complex $[(CO)_5W{=}C{=}N{=}CMes_2]BF_4$ undergoes thermal as well as photochemical CO loss, the same is not true of $[(CO)_5Cr{=}C{=}N{=}CMes_2]BF_4$. Therefore, the photochemical conversion constitutes the only path to $BF_4(CO)_4Cr(CNCMes_2)$. As evidenced by our synthesis of *trans*-$Br(CO)_4Cr(CNCMes_2)$, the complexes $BF_4(CO)_4M(CNCMes_2)$ are valuable starting materials for the synthesis of complexes of the type $X(CO)_4M(CNCMes_2)$. These have hitherto been completely unknown for M = Cr and were restricted to X = Cl, Br, and I for M = W. Moreover, attempts to substitute Br^- in *trans*-$Br(CO)_4Cr(CNCMes_2)$ directly by X^- had proven unsuccessful. The reaction of $BF_4(CO)_4M(CNCMes_2)$ with X^- now makes a large number of complexes $X(CO)_4M(CNCMes_2)$ accessible.

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Registry No. $(CO)_5Cr(CNCMes_2)$, 103671-32-5; $(CO)_5W(CNCMes_2)$, 103671-33-6; $Fe(\eta^5\text{-}C_5H_5)_2$, 102-54-5; $[(CO)_5Cr(CNCMes_2)]BF_4$, 105472-37-5; $[(CO)_5W(CNCMes_2)]BF_4$, 103671-29-0; $(CO)_5CrCNC(Ph)_2C(Ph)_2NCCr(CO)_5$, 105472-38-6; $(CO)_5Cr[C(OEt)NCPh_2]$, 54330-36-8; *trans*-$Br(CO)_4Cr(CNCMes_2)$, 105472-39-7; $[(CO)_5Cr(CNCPh_2)]BF_4$, 94598-03-5; *trans*-$BF_4(CO)_4W(CNCMes_2)$, 105472-40-0; $(CH_2Cl_2)(CO)_4W(CNCMes_2)$, 105472-41-1; *cis*-$BF_4(CO)_4Cr(CNCMes_2)$, 105472-42-2; *trans*-$BF_4(CO)_4Cr(CNCMes_2)$, 105561-14-6; *trans*-$Cl(CO)_4W(CNCMes_2)$, 105472-43-3.

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Four Bridging Bis Chelate Ligands with Very Low Lying π* Orbitals. MO Perturbation Calculations, Electrochemistry, and Spectroscopy of Mononuclear and Binuclear Group 6 Metal Tetracarbonyl Complexes

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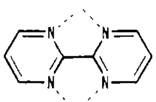
Coordination characteristics of the four bridging, π-delocalized bis chelate ligands 2,2′-bipyrimidine (bpym), 2,5-bis(2-pyridyl)pyrazine (bppz), 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz), and azo-2,2′-bipyridine (abpy) were evaluated with use of π molecular orbital perturbation calculations and were studied experimentally by example of mononuclear and binuclear complexes with the fragments $M(CO)_4$, M = Cr, Mo, W. The substantial stabilization of the π* (LUMO) levels in the order bpym, bppz, bptz, abpy strongly facilitates reduction of the complexes and causes shifts of the intense MLCT absorption bands out into the near-infrared region. Despite a notable activation barrier for the formation of binuclear abpy complexes with six-coordinate metals, the compound $(abpy)[Mo(CO)_4]_2$ was prepared and was shown to exhibit most remarkable spectral properties such as an intense yet rather narrow and little solvent sensitive MLCT absorption band at 11 000 cm^{-1}, with the next detectable absorption maximum lying above 30 000 cm^{-1}, a reduction potential close to that of the reference electrode, SCE, and closely spaced yet well-resolved CO stretching frequencies in the IR spectrum. All these spectral results can be correlated to π MO calculation data, which strongly suggest the use of bptz and abpy for studies concerned with ligand-mediated electronic interactions between metal centers. A particular asset of binuclear abpy complexes is the unusually short metal–metal distance caused by their coordination-induced "S-frame" conformation.

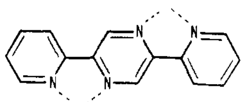
Introduction

Ligands that can serve as molecular bridges between metal centers and that also contain a delocalized π system have received considerable attention in recent years as potential electron "propagating" components (1) for inner-sphere electron-transfer reactions between metals,[1] (2) in magnetically coupled polynuclear systems ("superexchange"),[2] (3) in models for binuclear arrangements occurring in metalloenzymes,[3] and (4) in low-dimensional conducting coordination polymers.[4] Other conceivable applications of such bridged complexes include their use in multielectron storage systems for the activation of small molecules[2h] and as light-capturing antennas via charge-transfer (CT) transitions in the long-wavelength (near-infrared) region of the spectrum.[5a,6] Double coordination of metal fragments to such binucleating ligands is known to cause a particularly strong perturbation of the ligand π system, as is evident from pronounced spectroscopic effects.[5] Unfortunately, however, the dissociative stability of binuclear species is frequently diminished because of the reduced σ-donor strength of mononuclear complexes with respect to a second coordination; this effect is typically illustrated by the coordination behavior of *doubly monodentate* bridging

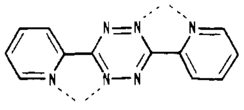
Chart I



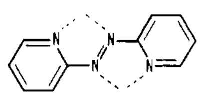
bpym



bppz



bptz



abpy

[†] Karl Winnacker Fellow, 1982–1987.

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