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Contribution from the Anorganisch Chemisch Laboratorium,
J. H. van't Hoff Instituut, 1018 WV Amsterdam, The Netherlands

Photochemistry of Metal-Metal-Bonded Complexes. 2. MLCT Photochemistry of (CO)$_5$MM′(CO)$_3$(R-DAB) (M, M′ = Mn, Re; DAB = 1,4-Diaza-1,3-butadiene) in Inert-Gas Matrices at 10 K and in PVC Film at 193 and 293 K

MAARTEN W. KOKKES, DERK J. STUFKENS,* and AD OSKAM

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The photolysis of (CO)$_5$MM′(CO)$_3$(R-DAB) (M, M′ = Mn, Re; R-DAB = R-substituted 1,4-diaza-1,3-butadiene, RN=CH—CH=NR) is reported in inert-gas matrices at 10 K and in PVC films at 193 and 293 K. It is shown that photolysis of (CO)$_5$MM′(CO)$_3$(*i*-Pr-DAB) with visible light (λ = 514.5 nm) in an inert-gas matrix at 10 K results in release of two carbonyl ligands from the Mn(CO)$_5$ moiety followed by a changeover of the *i*-Pr-DAB ligand from a σ,σ-chelate (4e) to $\sigma,\sigma,\eta'^2,\eta'^2$-bridging (8e). Matrix photolysis of other (CO)$_5$MM′(CO)$_3$(*i*-Pr-DAB) complexes does not show this reaction. However, when (CO)$_5$MnMn(CO)$_3$(R-DAB) (R = *i*-Pr, *p*-Tol) is photolyzed with visible light (λ = 514.5 nm) and (CO)$_5$MnRe(CO)$_3$(R-DAB) and (CO)$_5$ReMn(CO)$_3$(R-DAB) (R = *i*-Pr, *p*-Tol) are photolyzed with UV light in a PVC film at 293 K, the same change of coordination of the R-DAB ligand is observed. Photolysis of (CO)$_5$MnRe(CO)$_3$(*i*-Pr-DAB) with visible light (λ = 514.5 nm) in a PVC film results in another reaction different from that observed in a matrix at 10 K. At 193 K (CO)$_5$MnRe(CO)$_3$(σ-N-*i*-Pr-DAB)(THF) is then formed, in which the R-DAB ligand is monodentately coordinated and the open site is occupied by a THF molecule, present in the film. These reactions are discussed, considering two different close-lying excited states, $^3\sigma_b\pi^*$ and $^3d_\pi\pi^*$, respectively.

Introduction

Much attention has been paid recently to the coordinating properties of α-diimine ligands[1] and to the chemical[1] spectroscopic[1-5] and photochemical[2b,6-12] properties of their low-valence metal complexes.

Contrary to 2,2′-bipyridine and 1,10-phenanthroline, the 1,4-diaza-1,3-butadiene ligands (R-DAB(R′, R″); RN=C(R′)—(R″)C=NR[13] show many modes of coordination, viz. σ-monodentate (2e), σ,σ-chelate (4e), σ,σ'-bridging (4e), η^2,η^2-chelate (4e), σ,σ,η'^2 (6e), and $\sigma,\sigma,\eta'^2,\eta'^2$ (8e).[1] Several reactions have been reported during which the R-DAB ligand changes its coordination or undergoes a chemical change while bonded to the metal.[1] The most common photochemical reaction is breaking of a metal–nitrogen bond by which the α-diimine ligand changes its coordination from σ,σ-chelate (4e) into σ-monodentate (2e).[6,9,10,12]

Quite recently, however, another change of coordination has been shown to occur photochemically in complexes of the type Fe(CO)$_3$(R-DAB).[6a,14] The R-DAB ligand appears to change its coordination from σ,σ-chelate (4e) to η^2,η^2-chelate (4e) in a rare-gas matrix at 10 K. In this article we report quite another kind of photochemical reaction of coordinated R-DAB ligands taking place in (CO)$_5$MnM′(CO)$_3$(R-DAB) (M′ = Mn, Re) complexes (see Figure 1) upon photolysis in inert-gas matrices at 10 K and in PVC films.

Just as Mn$_2$(CO)$_{10}$, the complexes (CO)$_5$MM′(CO)$_3$(α-diimine) (M, M′ = Mn, Re) possess a metal–metal bond. The latter complexes all exhibit a low-energy absorption band between 500 and 600 nm, which has been assigned by Wrighton et al. to a transition from the metal–metal bonding orbital (σ_b) to the lowest π^* orbital of the α-diimine ligand ($\sigma_b \rightarrow \pi^*$).[11] This assignment was based on the observation that the metal–metal bond is broken homolytically upon irradiation into this band.

However, in recent articles[12,5b] we have assigned this band to an electronic transition from a metal-d$_\pi$ orbital, not involved in the metal–metal bond (d$_\pi$(M′)) to the π^* orbital of the α-diimine ligand (d$_\pi$(M′) $\rightarrow \pi^*$). This assignment was based on the close analogy between the absorption and resonance Raman (RR) spectra of these complexes and those of the d^6-complexes (M(CO)$_4$(α-diimine) (M = Cr, Mo, W)[2a,b] and M′(CO)$_3$X(α-diimine) (M′ = Mn, Re; X = Cl, Br)[4c] and the d^8-complexes M(CO)$_3$(α-diimine) (M = Fe, Ru),[5b] which do not possess a metal–metal bond. The electronic transition will therefore be directed to the $^1d_\pi\pi^*$ state, and from this state intersystem crossing to the $^3d_\pi\pi^*$ state will occur, although in the case of M′ = Re the meaning of the spin label is questionable. However, although the $^1d_\pi\pi^*$ state and not the $^1\sigma_b\pi^*$ state becomes occupied during the electronic transition, intersystem crossing may also occur to the $^3\sigma_b\pi^*$ state. This is shown schematically in Figure 2. From both triplet states a photochemical reaction can occur. In a recent article[12] we have shown that the reaction from the $^3\sigma_b\pi^*$ state is the main reaction for the (CO)$_5$MnM′(CO)$_3$(α-diimine) (M′ = Mn, Re) complexes in 2-MeTHF at $T \geq 200$ K and that it leads to homolytic splitting of the metal–metal bond. The reaction from the $^3d_\pi\pi^*$ state has been observed for several complexes at 133

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* To whom correspondence should be addressed.

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(5) Some spectroscopic studies of the dinuclear metal complexes (CO)$_5$MM′(CO)$_3$(α-diimine) (M, M′ = Mn, Re) are: (a) Staal, L. H.; van Koten, G.; Vrieze, K. *J. Organomet. Chem.* **1979**, *175*, 73. (b) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *J. Mol. Struct.*, in press.

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(13) Most 1,4-diaza-1,3-butadienes have the general formula RN=C(R′)-—C(R″)=NR, an important subgroup of this class being RN=CH—CH=NR (R-DAB(H H)). For economy of space, if the R grouping is specifically stated, then the form R(substituent)-DAB is used and this implies proton substitution at the α-diimine carbon atoms, e.g. *i*-PrN=CH—CH=N-*i*-Pr becomes *i*-Pr-DAB. Abbreviations for the R groups in R-DAB are *i*-Pr = isopropyl, *t*-Bu = *tert*-butyl and *p*-Tol = *p*-tolyl. See also ref 1.

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Table I. CO Stretching Frequencies of Several $(CO)_3M(R\text{-}DAB)M'(CO)_3$ (M, M′ = Mn, Re) Complexes

compd	CO stretching freq,[a] cm^{-1}						
$(CO)_3Mn(Me\text{-}DAB[CH_3, CH_3])Mn(CO)_3$[c,e]	2035 (m)	1998 (s)	1940 (s)		1935 (s)	1926 (m)	1917 (s)
$(CO)_3Mn(t\text{-}Bu\text{-}DAB)Mn(CO)_3$[c]	2025 (m)	1996 (s)		1938 (s)		1932 (s)	1918 (s)
$(CO)_3Mn(i\text{-}Pr\text{-}DAB)Re(CO)_3$[b]	2034 (m)	2004 (s)		1940 (s)		1925 (m)	1908 (m)
$(CO)_3Mn(i\text{-}Pr\text{-}DAB)Re(CO)_3$[d]	2029 (m)	2001 (s)			~1926 (s, br)		1918 (sh)
$(CO)_3Mn(p\text{-}Tol\text{-}DAB)Re(CO)_3$[d]	2025 (m)	2010 (s)			~1928 (s, br)		
$(CO)_3Mn(i\text{-}Pr\text{-}DAB)Mn(CO)_3$[d]	2029 (m)	1995 (s)			~1929 (s, br)		1911 (m)
$(CO)_3Mn(p\text{-}Tol\text{-}DAB)Mn(CO)_3$[d]	2036 (m)	2003 (s)			~1940 (s, br)		1915 (sh)
$(CO)_3Re(i\text{-}Pr\text{-}DAB)Mn(CO)_3$[d]	2029 (m)	2003 (s)			1929 (s, br)		1907 (m)
$(CO)_3Re(p\text{-}Tol\text{-}DAB)Mn(CO)_3$[d]	2037 (m)	2010 (s)			1939 (s, br)		

[a] Relative intensities are m = medium, s = strong, sh = shoulder, and br = broad. [b] Measured in a CH_4 matrix at 10 K. [c] Measured in *n*-hexane. [d] Measured in a PVC film, cast from THF, at 293 K. [e] Values according to Adams.[22]

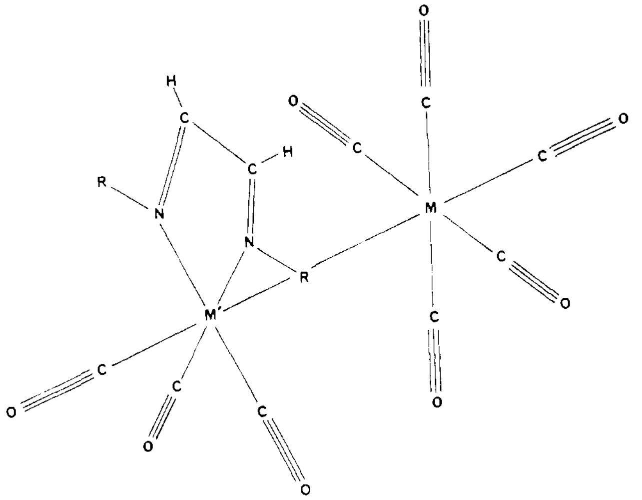

Figure 1. Structure of $(CO)_5MM'(CO)_3(R\text{-}DAB)$ (M, M′ = Mn, Re).

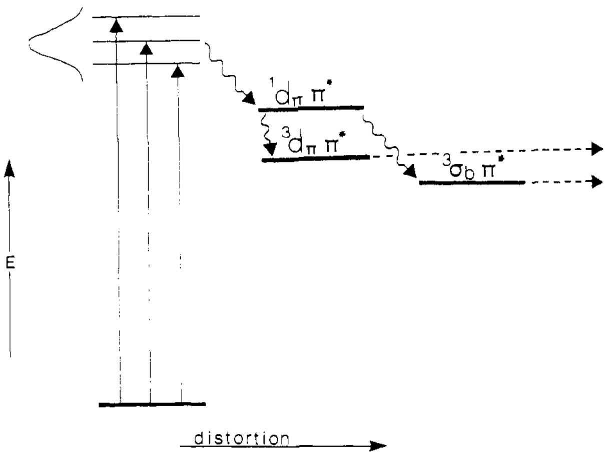

Figure 2. Energy vs. distortion diagram for $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M′ = Mn, Re).

K. The primary photoprocess is breaking of a metal–nitrogen bond, which is followed by release of CO and re-formation of the metal–nitrogen chelate bond just as in the case of the $Fe(CO)_3(R\text{-}DAB)$ complexes.[6a] Raising the temperature led to disproportion of this photoproduct into $[Mn(CO)_5]^-$ and $[M'(CO)_2(2\text{-}MeTHF)_2(\alpha\text{-diimine})]^+$ or $[M'(CO)_3(2\text{-}MeTHF)(\alpha\text{-diimine})]^+$.

Now, if this photolysis takes place in a rigid medium such as an inert-gas matrix at 10 K, both reactions are not expected to occur. The radicals formed by homolysis of the metal–metal bond can not diffuse from the matrix site and will therefore recombine to the parent compound. Similarly, breaking of a metal–nitrogen bond will not give a photoproduct since the ligand cannot rotate freely within the matrix and therefore will recoordinate to the metal. If therefore a photochemical reaction takes place at all in these matrices, it has to be quite different from what has been observed in 2-Me-THF solutions.

In this article we present evidence of a remarkable photochemical reaction in matrices, which can however still be understood within the scheme of Figure 2. For comparison also photolysis experiments have been performed in a PVC film, which medium is less rigid than the matrices, especially at higher temperatures.

Experimental Section

The R-DAB ligands[15] and binuclear metal carbonyl complexes[5a,16] were synthesized according to published methods.

The matrix isolation equipment, a modified Air Products Displex Model CSW-202 B closed-cycle helium refrigerator, has been described in detail before.[17] The sample window of CaF_2 had a temperature of 10 K during deposition and the vacuum was better than 10^{-6} torr. $(CO)_5MnMn(CO)_3(i\text{-}Pr\text{-}DAB)$ was sublimed at 50 °C, $(CO)_5MnRe(CO)_3(i\text{-}Pr\text{-}DAB)$ at 70 °C, $(CO)_5ReMn(CO)_3(i\text{-}Pr\text{-}DAB)$ at 80 °C, and $(CO)_5ReRe(CO)_3(i\text{-}Pr\text{-}DAB)$ at 90 °C, and gas mixtures were made by adding Ar, CH_4, N_2, or CO (purity 99.999%) to the vapor of the samples.[18] Attempts to prepare matrices of $(CO)_5MM'(CO)_3(p\text{-}Tol\text{-}DAB)$ and $(CO)_5MM'(CO)_3(phen)$ failed. The vapor pressure of these complexes proved to be too low.

The PVC films in this study were prepared by using a solvent-casting technique.[19,20] A 500-mg sample of PVC (Corvic D60/11, obtained from ICI) was dissolved in 25 mL of freshly distilled THF at 25 °C with rapid stirring. A 4-mg sample of the binuclear complex was then added, and the resulting solution was poured into a petri dish (10-cm diameter), which was kept horizontal on a mercury bath. The solution was allowed to evaporate overnight, and the polymer (thickness ca. 40 μm) was then taken out of the dish. Special care was taken to exclude all light during these manipulations. This technique enabled us to obtain a polymer matrix in which the concentration of the complex was uniform throughout. A piece of the polymer film was evenly clamped between two CaF_2 windows (diameter 25 mm) and brought into an IR cell that could be cooled. For our experiments a mixture of solid carbon dioxide and acetone was used to get a temperature of about 193 K.

Electronic absorption spectra were measured on Cary-14 or Perkin-Elmer Lambda 5 spectrophotometers and IR spectra on a Nicolet 7199 B FT-IR interferometer with a liquid-nitrogen-cooled Hg, Cd, Te-detector (32 scans, resolution 0.5 cm^{-1}).

As light source for the photolysis experiments a Coherent CR 8 Ar ion laser was used. The laser power was 30–50 mW, and the laser beam was defocused before entering the sample.

Results and Discussion

Photolysis of $(CO)_5MM'(CO)_3(i\text{-}Pr\text{-}DAB)$ (M, M′ = Mn, Re) in Inert-Gas Matrices at 10 K. The complex $(CO)_5MnRe(CO)_3(i\text{-}Pr\text{-}DAB)$ has been photolyzed in a CH_4 matrix at 10 K with the green line (λ = 514.5 nm) of an argon ion laser close to the maximum of its absorption band (λ_{max} = 541 nm and ϵ_{max} = 11.500 dm^3 mol^{-1} cm^{-1} measured in *n*-hexane). The CO vibrations of the parent compound then disappear, and five new bands show up with simultaneous release of CO (ν(CO) = 2138

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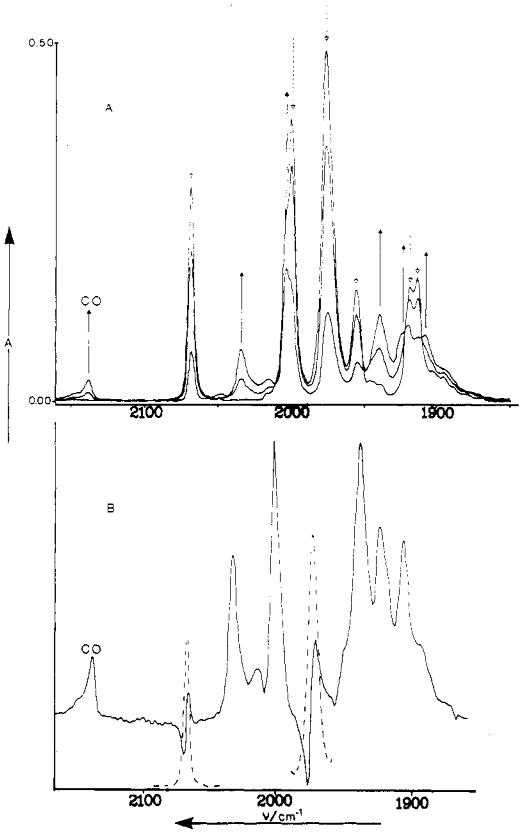

Figure 3. (A) IR spectral changes in the CO stretching region upon photolysis of $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB) with $\lambda = 514.5$ nm (30 mW) in a CH_4 matrix at 10 K. The irradiation times are 0, 1, and 5 h, respectively. (B) IR spectrum of the photoproduct obtained by subtracting the spectrum of the parent compound from the spectrum taken after 5 h of photolysis. The oscillations at 2070 and 1977 cm^{-1}, respectively, are due to a site preference. The CO bands of the parent compound are drawn as dotted lines over these oscillations to show that they are centered at the same wavenumber.

cm^{-1}). Figure 3a shows that the IR spectral changes in the CO stretching region are accompanied by several isosbestic points, which indicate a well-defined clean reaction. From this spectrum the frequencies and relative intensities of the photoproduct have been obtained by substracting the spectrum of the parent compound (Figure 3b, Table I). In the absorption spectrum the band at 528 nm disappears, and no new absorption band shows up in the visible region. Annealing a CO matrix after the photolysis reaction did not show any back-reaction to the parent compound, which means that the photoproduct is coordinatively saturated. Such a coordinatively saturated complex might be formed after release of CO by a bridging carbonyl or R-DAB ligand. The photoproduct does however not contain a bridging CO group since no CO vibration is found in that particular region.

Bridging R-DAB ligands have been shown to be present in several complexes as σ,σ' (4e), σ,σ,η'^2 (6e), or $\sigma,\sigma,\eta'^2,\eta'^2$ (8e) coordinating ligands.[1] A σ,σ'-bridging (4e) coordination of the *i*-Pr-DAB ligand is very improbably here since in that case the ligand would have changed its coordination from σ,σ-chelate (4e) into σ,σ-bridging (4e), resulting in a coordinatively unsaturated photoproduct. This does not agree with the result of the annealing experiment (vide supra). In principle both σ,σ,η'^2 (6e) and $\sigma,\sigma,\eta'^2,\eta'^2$ (8e) coordination, in which the η'^2 coordination takes place via a C=N bond of the ligand, are possible here. They are both in agreement with the disappearance of the $d_\pi(Re) \rightarrow \pi^*$(R-DAB) electronic transition due to the involvement of the π^* orbital in the bonding. However, in the case of σ,σ,η'^2-bonding (6e), only one of the CN bonds will be affected, while in the case of $\sigma,\sigma,\eta'^2,\eta'^2$-coordination (8e) both CN bonds will be affected. This will be reflected in the occurrence of two or one CN stretching modes, respectively. In this connection it has to be mentioned that for the complexes $Fe(CO)_3(\eta^2,\eta^2$-R-DAB), which have been obtained as photoproducts of $Fe(CO)_3(\sigma,\sigma$-R-DAB) in rare-gas matrices at 10 K, only one ν_s(CN) band was found, which was shifted by about 100 cm^{-1} to lower frequency with respect to the corresponding vibration of the parent compound. Figure 4 shows the IR spectra in the 1200–1500-cm^{-1} region for both the parent compound and the photoproduct.

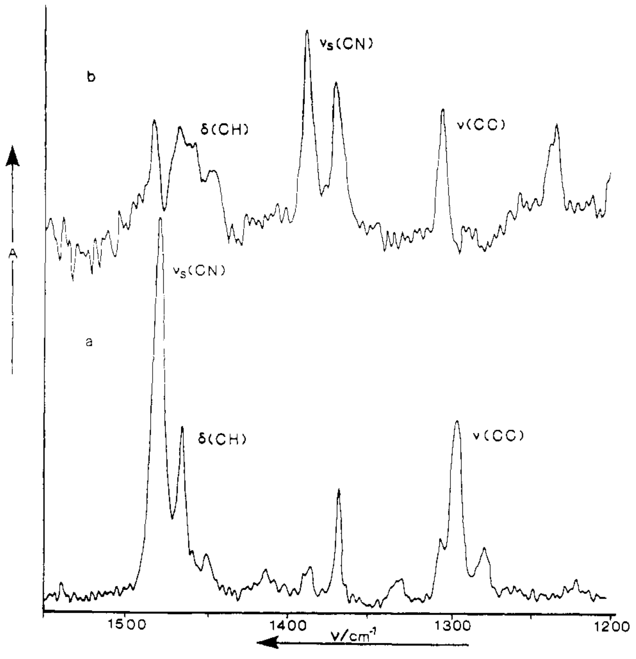

Figure 4. IR spectra (1200–1500 cm^{-1}) of $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB) (a) and of its photoproduct (b) in a CO matrix at 10 K. Spectrum b is obtained by subtracting the spectrum of the parent compound from a spectrum taken after 5 h of photolysis.

On the basis of the RR spectrum[5b] the 1479-cm^{-1} band of the parent compound is assigned to ν_s(CN) and the 1294-cm^{-1} band to ν(CC). The bands at 1465 and 1367 cm^{-1} belong to C–H bending modes of the *i*-Pr-DAB ligand. In the spectrum of the photoproduct the bands belonging to ν_s(CN) and ν(CC) have disappeared whereas those at 1465 and 1367 cm^{-1} only show a minor shift. The two new bands at 1389 and 1304 cm^{-1} are assigned to ν_s(CN) and ν(CC), respectively. The presence of only one CN stretching mode shifted by 90 cm^{-1} to lower frequency with respect to the parent compound agrees with the η^2,η^2-coordination present in $Fe(CO)_3(\eta^2,\eta^2$-R-DAB) and points to a $\sigma,\sigma,\eta'^2,\eta'^2$-coordination (8e) of the R-DAB ligand. The large shift of ν_s(CN) to lower frequency and the small shift of ν(CC) to higher frequency going from σ,σ-chelate (4e) to $\sigma,\sigma,\eta'^2,\eta'^2$-bridging (8e) agrees with the fact that the π^* orbital of the R-DAB ligands is strongly antibonding between C and N and weakly bonding between the central C atoms.

On the basis of these results, we propose that upon photolysis the complex $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$[21] is formed, shown in Figure 5, in which the *i*-Pr-DAB ligand is σ,σ-coordinated to Re and η'^2,η'^2-coordinated to Mn. This proposition is strongly supported by the observations of Adams[22] and Keysper.[23] Adams accidentally synthesized the compound $(CO)_3Mn(Me\text{-}DAB(CH_3,CH_3))Mn(CO)_3$ while investigating the reaction of $[Mn(CO)_4(CNCH_3)]^-$ with CH_3I. He established the structure by X-ray diffraction. Keysper synthesized in low yield an analogous complex $(CO)_3Mn$(*t*-Bu-DAB)$Mn(CO)_3$ by treating $Mn(CO)_3$(*t*-Bu-DAB)Br with $[CpFe(CO)_2]^-$ (Cp = cyclopentadienyl). As can be seen from Table I, the CO stretching frequencies of these complexes agree well with those of our photoproduct $(CO)_3Mn$-

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[21] To avoid possible uncertainties we adapt the notation $(CO)_3M$(R-DAB)$M'(CO)_3$ for those complexes in which the DAB-ligand is η^2-CN, η^2-CN coordinated to M and σ-N, σ-N coordinated to M′.

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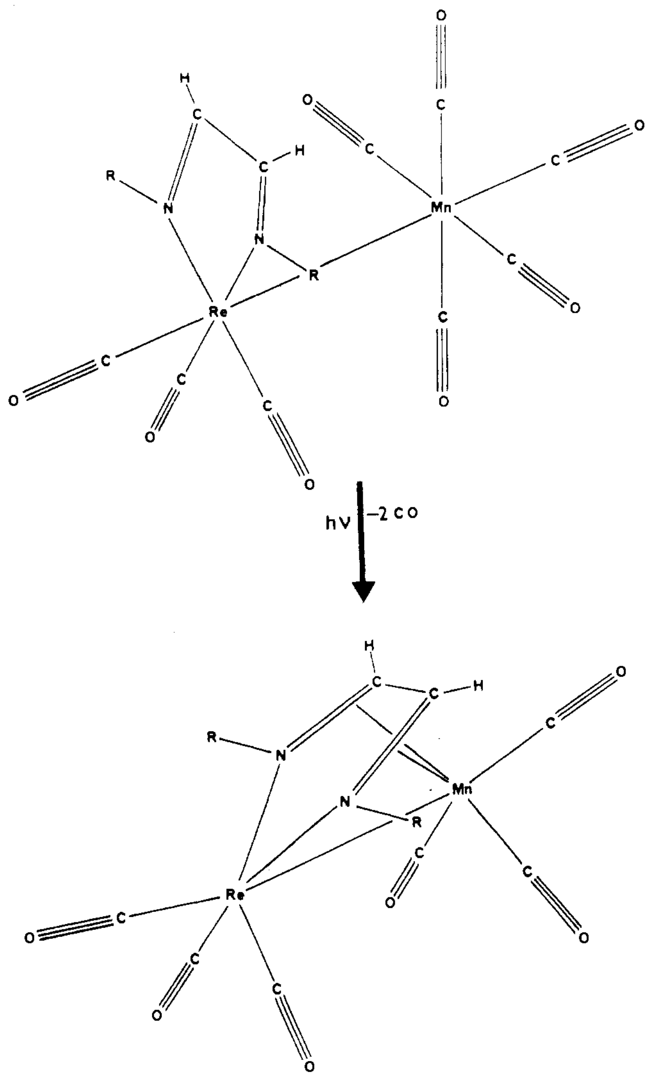

Figure 5. Proposed reaction for the photolysis of $(CO)_5MnRe(CO)_3$(R-DAB) in a matrix at 10 K (R = *i*-Pr).

(*i*-Pr-DAB)$Re(CO)_3$. The CO-stretching frequencies belonging to the $Re(CO)_3$ moiety of the latter complex will not differ much from those of the same group in the parent compound $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB). Indeed, three CO frequencies are hardly shifted (2004, 1925, and 1908 cm^{-1} for the photoproduct and 2004, 1919, and 1913 cm^{-1} for the parent compound). The CO stretching frequencies belonging to the $Mn(CO)_3$ moiety on the other hand, will be shifted to lower frequency with respect to those of the $Mn(CO)_5$ group of the parent compound. The metal–carbonyl bonds of the $Mn(CO)_3$ group will be strengthened greater by the loss of two CO groups than weakened by the η'^2,η'^2-coordination of the *i*-Pr-DAB ligand. So a shift is observed for these CO stretching frequencies from 2070, 2000, 1977, and 1957 cm^{-1} for the parent compound to 2040 and 1940 cm^{-1} for $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$.

Photolysis of the other $(CO)_5MM'(CO)_3$(*i*-Pr-DAB) (M, M′ = Mn, Re) complexes in inert-gas matrices at 10 K did not lead to the formation of $(CO)_3M$(*i*-Pr-DAB)$M'(CO)_3$. Instead, photolysis of $(CO)_5M'Mn(CO)_3$(*i*-Pr-DAB) (M′ = Mn, Re) with visible light caused the disappearance of the CO bands of the parent compound while an intensive band showed up at 1900–1960 cm^{-1}, consisting of several partly overlapping CO frequencies. Furthermore, several weak bands appeared at higher frequencies together with a large amount of free CO.

At the same time the change-transfer band in the visible region disappeared. In agreement with the assignment of Ozin[24] and Turner[25] the complex band at 1900–1960 cm^{-1} is tentatively assigned to $M'(CO)_x$ (x = 1–5) fragments.

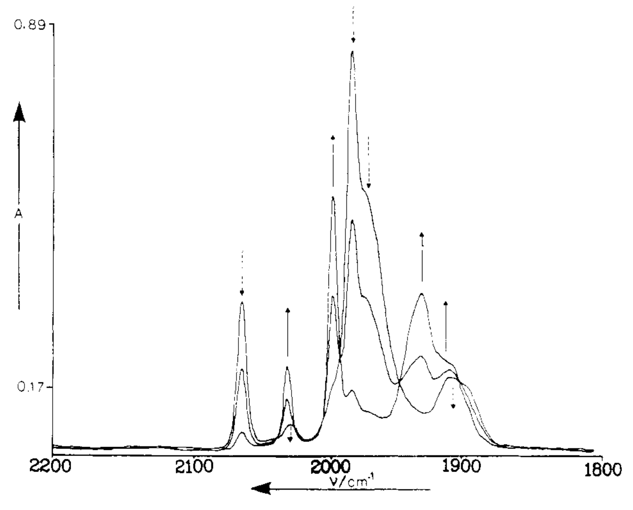

Figure 6. IR spectral changes in the CO stretching region upon photolysis of $(CO)_5MnMn(CO)_3$(*i*-Pr-DAB) with λ = 514.5 nm (30 mW) in a PVC film, cast from THF, at 293 K.

Irradiation of $(CO)_5ReRe(CO)_3$(*i*-Pr-DAB) in a CH_4 matrix at 10 K with visible light did not result in a chemical reaction. Only upon irradiation with UV light did the complex decompose with formation of $Re_2(CO)_{10}$ and other products.

Photolysis in PVC Films. Photolysis reactions of these complexes have also been studied in PVC films, cast from THF, at different temperatures.

Contrary to the reactions in matrices, not only one but three of the four $(CO)_5MM'(CO)_3$(*i*-Pr-DAB) complexes (M, M′ = Mn, Re except M = M′ = Re) were converted into $(CO)_3M$(*i*-Pr-DAB)$M'(CO)_3$ by irradiation in PVC. Moreover, the same reaction was also found for complexes containing other R-DAB ligands. Thus, photolysis of $(CO)_5MnMn(CO)_3$(R-DAB) (R = *i*-Pr, *p*-Tol) in a PVC film with the 514.5-nm line of an argon ion laser at 293 K, resulted in the formation of $(CO)_3Mn$(R-DAB)$Mn(CO)_3$ with similar CO frequencies as those of $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$ produced in a CH_4 matrix (see Table I). Figure 6 shows the IR spectral changes accompanying this reaction in PVC. In this medium, IR bands are much broader than in an inert-gas matrix. Because of this, one broad band shows up between 1910 and 1950 cm^{-1} for $(CO)_3Mn$(*i*-Pr-DAB)$Mn(CO)_3$ in PVC instead of the three bands at 1940, 1925, and 1908 cm^{-1} for $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$ in a CH_4 matrix. The CO frequencies of several $(CO)_3M$(R-DAB)$M'(CO)_3$ complexes are collected in Table I. Just as during the formation of $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$ in a CH_4 matrix, the charge-transfer band at about 500 nm disappears in PVC. No free CO is observed upon photolysis in PVC at 293 K because of the broadness of its IR band at this temperature. However, upon photolysis at 193 K free CO is observed with ν = 2135 cm^{-1}. At this temperature not only are the CO frequencies of $(CO)_3Mn$(*i*-Pr-DAB)$Mn(CO)_3$ observed but also IR bands at 2112 (w), 2040 (m), 2005 (m), 1908 (m), and 1869 (m).[26] These extra bands slowly disappear upon raising the temperature of the film in the dark to 293 K with formation of the parent compound. These bands are tentatively assigned to $(THF)(CO)_4MnMn(CO)_3$(*i*-Pr-DAB). In order to produce $(CO)_3Mn$(*i*-Pr-DAB)$Mn(CO)_3$ by photolysis of $(CO)_5MnMn(CO)_3$(*i*-Pr-DAB), CO must be released from the $Mn(CO)_5$ moiety of the complex. Substitution by THF may then compete with attack by the *i*-Pr-DAB ligand, thus giving rise to the formation of (THF)-

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[26] Relative intesities used in the text are as follows: w = weak, m = medium, s = strong, vs = very strong, sh = shoulder, and br = broad.

$(CO)_4MnMn(CO)_3$(*i*-Pr-DAB). This latter complex is thermodynamically less table than the parent compound, and raising the temperature will lead to back-substitution of THF by CO still present in the PVC film. Substitution of CO by THF in a PVC film has also been observed by Hooker and Rest upon photolysis of $M(CO)_6$ (M = Cr, Mo, W).[27] The resulting complex $M(CO)_5THF$ reacted back with CO to the parent compound when the photoproduct was left in the dark.

Contrary to the Mn–Mn complex, $(CO)_5MnRe(CO)_3$(R-DAB) (*R* = *i*-Pr, *p*-Tol) only reacted in a PVC film to $(CO)_3Mn$(R-DAB)$Re(CO)_3$ upon irradiation with UV light (unfiltered medium-pressure Hg lamp). Apart from the CO frequencies of this photoproduct, IR bands were observed at 2099 (w), 2019 (m), 2010 (s), 1908 (s), and 1901 (sh) cm^{-1}, which are comparable to those of (THF)$(CO)_4MnMn(CO)_3$(*i*-Pr-DAB) and are therefore assigned to (THF)$(CO)_4MnRe(CO)_3$(*i*-Pr-DAB). Photolysis of $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB) into the charge-transfer band with λ = 514.5 nm resulted in the formation of different photoproducts, depending on the temperature. These reactions are much slower than those discussed before. Upon photolysis at 193 K, no CO is released, while the charge-transfer band disappears from the absorption spectrum. Similar effects have been observed by us upon irradiation of $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB) in 2-Me-THF at 133 K.[12] Moveover, the CO frequencies of the photoproduct obtained in 2-Me-THF (2032 (m), 2003 (m), 1917 (vs), 1883 (s), and 1871 (sh) cm^{-1}) closely resemble those of the product of this reaction in PVC (2036 (m), 2021 (w), 1995 (m), 1923 (vs), $\simeq$ 1880 (sh), and 1860 (sh) cm^{-1}). The band at 2021 cm^{-1} observed in PVC probably belongs to a sideproduct since its intensity varies from one experiment to another. The photoproduct in 2-Me-THF has been identified as $(CO)_5MnRe(CO)_3$(σ-*i*-Pr-DAB)(2-Me-THF), a complex in which the *i*-Pr-DAB ligand is monodentately σ-bonded to Re via one of its N atoms. The open site at Re is occupied by 2-Me-THF, which is a weakly coordinating solvent at 133 K (for a detailed discussion see ref. 12). In accordance with this reaction in 2-Me-THF the photoproduct in PVC is characterized as $(CO)_5MnRe(CO)_3$(σ-*i*-Pr-DAB)(THF). This assignment is further supported by the analogous behavior of both complexes upon raising the temperature. Both complexes $(CO)_5MnRe(CO)_3$(σ-*i*-Pr-DAB)(2-Me-THF) and $(CO)_5MnRe(CO)_3$(σ-i-Pr-DAB)(THF) then lose their coordinating solvent molecule with back-formation of the parent compound. It has to be mentioned here that, in contrast to the formation of (THF)$(CO)_4MnMn(CO)_3$(*i*-Pr-DAB) (vide supra), no CO is released during this photolysis reaction in PVC and 2-Me-THF.

Such monodentately σ-bonded α-diimine ligands have been shown to be present in $Cr(CO)_5$(R-DAB),[5a] $M(CO)_5$(4,4′-dialkyl-2,2′-bipyridine) (M = Cr, Mo, W),[28] $W(CO)_5$(α-diimine),[8] $MCl_2(PPh_3)$(*t*-Bu-DAB) (M = Pd, Pt),[29] and $[Ir(bpy)_2(OH)(bpy)]^{2+}$.[30] They have also been postulated as intermediates in several thermal[31] and photochemical[6,9,10,12] reactions of α-diimine complexes. Thus, irradiation of $Fe(CO)_3$(R-DAB) complexes in solution at room temperature in the presence of a nucleophile results in photosubstitution of one or two carbonyls via an intermediate in which the R-DAB ligand is monodentately σ-bonded.[6]

Upon photolysis of $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB) in PVC at 293 K with λ = 514.5 nm, neither $(CO)_5MnRe(CO)_3$(σ-*i*-Pr-DAB)(THF) nor $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$ is formed. Instead new CO bands show up at 2053 (m), 2021 (m), 1996 (s), 1965 (m), 1935 (vs, br), and 1898 (s) cm^{-1} as the result of a rather slow reaction. Total conversion of the parent compound only occurred after 5 h of irradiation with a laser beam of 50 mW. Up to now this photoproduct could not be characterized. Breaking of a metal-nitrogen bond is again assumed to be the primary photoprocess. At 293 K the $(CO)_5MnRe(CO)_3$(σ-*i*-Pr-DAB) fragment formed can however not be stabilized by THF anymore, and it will react further to give this up to now unidentified product.

The complexes $(CO)_5ReMn(CO)_3$(R-DAB) (R = *i*-Pr, *p*-Tol) hardly react photochemically upon irradiation with λ = 514.5 nm at 193 K. At 293 K $(CO)_3Re$(R-DAB)$Mn(CO)_3$ is formed (see Table I for the observed CO frequencies), mainly upon irradiation with UV light. Irradiation with λ = 514.5 nm results in the formation of a similar uncharactized complex as in the case of $(CO)_5MnRe(CO)_3$(R-DAB). No photoproduct with a σ-monodentate R-DAB ligand could be observed for these complexes.

Photochemical Mechanism. It has been shown in the previous sections that irradiation of $(CO)_5MM'(CO)_3$(R-DAB) (M, M′ = Mn, Re) can lead to the formation of different photoproducts depending on M and M′ and on the circumstances of irradiation (matrix or PVC film, thermal or light energy). How can these reactions be explained within the scheme of the energy vs. distortion diagram of Figure 2? Formation of both $(CO)_3Mn$(R-DAB)$M'(CO)_3$ and (THF)$(CO)_4MnM'(CO)_3$(R-DAB) (M′ = Mn, Re) will be the result of substitution of CO at the $Mn(CO)_5$ moiety of the $(CO)_5MnM'(CO)_3$(R-DAB) complex by THF (in PVC) or the R-DAB ligand (both in the matrix and in PVC). Both photoproducts will therefore by the result of the same primary photoprocess.

Photochemical loss of CO has been observed by us before from the $^3d_\pi\pi^*$ states of d^6-$M(CO)_4$(α-diimine) (M = Cr, Mo, W) and d^8-$M'(CO)_3$(R-DAB) (M′ = Fe, Ru) complexes. In the case of the d^6-complexes, photosubstitution of CO was explained by delocalization of the $^3d_\pi\pi^*$ state over the carbonyls in the cis position with respect to the α-diimine ligand.[7] As the result of this delocalization, a metal–carbonyl bond is weakened in the excited state, causing the release of CO. In the case of the d^8-complexes $M'(CO)_3$(R-DAB) (M′ = Fe, Ru) on the other hand, photosubstitution of CO by PPh_3 has been explained with a strong coupling model,[6] according to which fast conversion of excited-state energy into vibrational motions of the molecule leads to breaking of a metal–nitrogen bond.[6a] The open site at the metal is then occupied by PR_3, and CO is released with simultaneous re-formation of the metal–ligand chelate bond.

Both mechanisms can not account for loss of CO from the $Mn(CO)_5$ moiety upon irradiation of $(CO)_5MnM'(CO)_3$(R-DAB) into the charge-transfer band of its $M'(CO)_3$(R-DAB) moiety. First of all, delocalization of the excited state over the carbonyls of the $Mn(CO)_5$ moiety is highly improbable since these carbonyls are in a staggered position with respect to the R-DAB ligand as can be seen from the crystal structure of $(CO)_5ReMn(CO)_3$(*i*-Pr-DAB).[5b] Secondly, the strong coupling model of the d^8-$M'(CO)_3$(R-DAB) (M′ = Fe, Ru) complexes is not valid here. This model has been shown to explain the breaking of a metal–nitrogen bond in $(CO)_5MnRe(CO)_3$(α-diimine) upon irradiation in 2-Me-THF at 133 K.[12] Substitution of CO at the $Mn(CO)_5$ moiety will therefore not occur from the $^3d_\pi\pi^*$ state of the complex but from the $^3\sigma_b\pi^*$ state (Figure 2). A reaction from this state leads to breaking of the metal–metal bond.[12] In the matrix and in PVC most of the radicals formed will react back to the parent compound since they can not diffuse from the matrix site. However, some of these radicals appear to lose CO with formation of $(CO)_3Mn$(R-DAB)$M'(CO)_3$ or (THF)$(CO)_4MnM'(CO)_3$(R-DAB) (M′ = Mn, Re). This substitution of CO may occur via a dissociative or an associative mechanism. In the past, dissociative CO substitution has been proposed for the $Mn(CO)_5$ radical.[32] This CO loss may then be followed by an attack of the C=N group of the R-DAB ligand (in a matrix and in PVC) or by THF (in PVC). However, such a dissociative mechanism is unlikely here. $Mn(CO)_5$ radicals have been shown to be quite stable in

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a matrix,[25] and since they absorb at about 800 nm,[25,33] photodecomposition of the $Mn(CO)_5$ radicals by the laser can be excluded. Futhermore, recent studies have shown that CO substitution of the $Mn(CO)_5$ radical may proceed via an associative mechanism.[34,35] Therefore, we propose an associative mechanism for the formation of $(CO)_3Mn(R\text{-}DAB)M'(CO)_3$ and $(THF)(CO_4)MnM'(CO)_3(R\text{-}DAB)$ (M′ = Mn, Re), the nucleophile being the C=N group of the R-DAB ligand (both in the matrix and in PVC) or THF (in PVC).

The complex $(CO)_5ReRe(CO)_3$(*i*-Pr-DAB) does not photolyze in the matrix upon irradiation with visible light. It is not yet clear whether this photostability against visible light is due to a stronger metal–metal bond or to a greater stability of the radicals formed.

In PVC several reactions are different because of the higher flexibility of this medium especially at higher temperatures and because of the presence of THF in the film. The higher thermal energy is probably responsible for the formation of $(CO)_5Mn(R\text{-}DAB)Mn(CO)_3$, which is not formed in the matrix. In the PVC film the $Mn(CO)_3(R\text{-}DAB)$ radicals have apparently enough activation energy for the changeover from σ,σ- to $\sigma,\sigma,\eta'^2,\eta'^2$-coordination of the R-DAB ligand within their lifetimes. Furthermore, because of the presence of THF in the film, the $Mn(CO)_5$ radicals formed will not only react with the $M'(CO)_3(R\text{-}DAB)$ radicals but also with THF under formation of $(THF)(CO)_4MnM'(CO)_3(R\text{-}DAB)$. A further difference is that a reaction in PVC can take place from the $^3d_\pi\pi^*$ state, which is prevented in the matrix. Just as for the $d^8\text{-}M'(CO)_3(R\text{-}DAB)$ (M′ = Fe, Ru) complexes in solution,[6a] a reaction from this $^3d_\pi\pi^*$ state leads to breaking of a metal–nitrogen bond of $(CO)_5MnRe(CO)_3(R\text{-}DAB)$ dissolved in PVC. Contrary to the situation in the matrix, the R-DAB ligand can now rotate more freely and the open site at Re will be occupied by THF, thus preventing the back-reaction to the parent compound. This reaction appears to be the only reaction for $(CO)_5MnRe(CO)_3(R\text{-}DAB)$ in PVC upon irradiation into the low-energy charge-transfer band. This means that in PVC only the reaction from the $^3d_\pi\pi^*$ state is observed and in the matrix only the reaction from the $^3\sigma_b\pi^*$ tate. Upon photolysis with UV light, reactions may occur from higher excited states belonging to $\sigma_b \rightarrow \sigma^*$ and $d_\pi(M,M') \rightarrow \pi^*(CO)$ transitions. This may account for the formation of $(CO)_3Mn(R\text{-}DAB)Re(CO)_3$ and $(CO)_3Re(R\text{-}DAB)Mn(CO)_3$ in PVC films, which are not formed in this medium upon photolysis with visible light.

Conclusion

The results reported here clearly show that intramolecular photochemical reactions of metal–metal-bonded carbonyls can be favored by photolysis in inert-gas matrices and PVC films. The PVC film is less rigid than the matrix, and photolysis can take place in this medium at higher temperatures, thus providing the necessary activation energy for secondary thermal reactions of the primary photoproducts.

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Registry No. Corvic D60/11, 9002-86-2; THF, 109-99-9; $(CO)_5MnMn(CO)_3$(*i*-Pr-DAB), 71603-98-0; $(CO)_5MnRe(CO)_3$(*i*-Pr-DAB), 71604-02-9; $(CO)_5ReMn(CO)_3$(*i*-Pr-DAB), 97747-73-4; $(CO)_5ReRe(CO)_3$(*i*-Pr-DAB), 97698-45-8; $(THF)(CO)_4MnMn(CO)_3$(*i*-Pr-DAB), 98874-72-7; $(THF)(CO)_4MnRe(CO)_3$(*i*-Pr-DAB), 98858-64-1; $(CO)_3Mn$(*i*-Pr-DAB)$Mn(CO)_3$, 98858-62-9; $(CO)_3Mn$(*i*-Pr-DAB)$Re(CO)_3$, 98858-60-7; $(CO)_3Re$(*i*-Pr-DAB)$Mn(CO)_3$, 98858-65-2; $(CO)_5MnMn(CO)_3$(*p*-Tol-DAB), 71604-00-7; $(CO)_5MnRe(CO)_3$(*p*-Tol-DAB), 71604-03-0; $(CO)_5ReMn(CO)_3$(*p*-Tol-DAB), 97570-66-6; $(CO)_3Mn$(*p*-Tol-DAB)$Mn(CO)_3$, 98858-61-8; $(CO)_3Mn$(*p*-Tol-DAB)$Re(CO)_3$, 98858-63-0; $(CO)_3Re$(*p*-Tol-DAB)$Mn(CO)_3$, 98858-66-3; $(CO)_3Mn$(*t*-Bu-DAB)$Mn(CO)_3$, 98858-67-4; $Re_2(CO)_{10}$, 14285-68-8; CH_4, 74-82-8.

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Contribution from the Department of Chemistry,
University of Arizona, Tucson, Arizona 85721

^{95}Mo NMR Study of Mononuclear Oxomolybdenum(IV) Complexes

CHARLES G. YOUNG and JOHN H. ENEMARK*

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A total of 38 representative oxo–Mo(IV) compounds have been studied by ^{95}Mo NMR spectroscopy. The compounds include the following: $MoO(S\text{-}S)_2$ and $MoO(S\text{-}S)_2(PR'_3)$ ($S\text{-}S = S_2CNR_2^-$, R = Et, *n*-Pr, *n*-Bu, R′ = Me, Et, *n*-Bu; $S\text{-}S = S_2P(OEt)_2^-$, R′ = Me), $(PPh_4)_2[MoO(mnt)_2]$ (mnt = *cis*-1,2-dicyanoethenedithiolate), $K_2[MoO(SCH_2CH_2S)_2]\cdot 2EtOH$, $K_4[MoO_2(CN)_4]\cdot 6H_2O$, $K_3[MoO(OH)(CN)_4]$, $MoOX_2P_3$ ($P = PMe_3$, $X = Cl^-, NCO^-, NCS^-$; $P = PMe_2Ph$, $X = Cl^-, Br^-, I^-, NCO^-, NCS^-$; $P = PPh_2Me$, $X = Cl^-$; $P = PEt_2Ph$, $X = Cl^-$), $MoOCl_2(N\text{-}N)(PPh_2Me)$ (N-N = 2,2′-bipyridine, 1,10-phenanthroline), $MoO(ox)_2(PPh_2Me)$ (ox = 8-hydroxyquinolinate), *trans*-$[MoOX(CNMe)_4]BPh_4$ ($X = Cl^-, Br^-$), *trans*-$[MoOCl(dppe)_2]BPh_4$ (dppe = 1,2-bis(diphenylphosphino)ethane), and LMoO(S-S) (L = hydrotris(3,5-dimethylpyrazolyl)borate, $S\text{-}S = S_2CNR_2^-$, R = Me, Et, *n*-Pr; $S\text{-}S = S_2P(OEt)_2^-$). The compounds display a large ^{95}Mo chemical shift range (δ 1035–3180) and highly variable line widths ($W_{1/2} = 240$ to >5000 Hz). The five-coordinate S-donor ligand complexes exhibit resonances over the range δ 1400–2450; the ligand shielding order is $S_2CNR_2^- < S_2P(OEt)_2^- < SCH_2CH_2S^{2-} < mnt^{2-}$. Coordination of phosphines to the $MoO(S\text{-}S)_2$ complexes shields the molybdenum nuclei in the order $P(n\text{-}Bu)_3 < PEt_3 < PMe_3$. Six-coordinate $MoOX_2P_3$ complexes exhibit resonances between δ 1590 and 2200 and display an inverse halogen dependence of the chemical shift. The most deshielded resonances (ca. δ 3180) occur for $MoOCl_2(N\text{-}N)(PPh_2Me)$ complexes whereas the $[MoOX(CNMe)_4]^+$ complexes possess the most shielded resonances (δ 1035–1050). The latter also display an inverse halogen dependence of the chemical shift. An experimental methodology for the observation of these broad ^{95}Mo NMR resonances is described.

Introduction

In recent years the characterization of coordination and organometallic complexes of molybdenum by ^{95}Mo NMR spectroscopy has developed rapidly. In general, the measurement of the spectra of Mo(VI), Mo(II), and Mo(0) complexes has become routine and the chemical shift ranges and halogen dependencies of such complexes are well-defined.[1] For these oxidation states,

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