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Metal to Ligand Charge-Transfer Photochemistry of Metal–Metal-Bonded Complexes. 6.[‡] Photochemistry of Ph$_3$SnM(CO)$_3$(α-diimine) (M = Mn, Re): Evidence for Different Primary Photoprocesses of the Mn and Re Complexes

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This article describes the photochemical reactions of the complexes Ph$_3$SnM(CO)$_3$L (M = Mn, Re; L = α-diimine) upon irradiation into their low-energy MLCT bands. The main reaction of the Mn complexes is loss of CO; the Re complexes only show homolysis of the metal–metal bond. Flash photolysis established that the CO-loss reaction is a primary photoprocess. Substitution reactions of the Mn complexes were performed with various Lewis bases and with CS$_2$. Irradiation of the complex Ph$_3$SnMn(CO)$_3$(tBu-DAB) in the absence of a nucleophile afforded, under specific conditions, a CO-loss product with, presumably, an agostic interaction between the tBu group and the Mn atom. The quantum yields of all reactions were high (0.2–0.8 mol/einstein) and hardly wavelength dependent throughout the visible region. The reactions are proposed to occur from the $^3\sigma\sigma^*$ state of the metal–metal bond after intramolecular energy transfer from the ^{3}MLCT state. The difference in primary photoprocesses between the Mn and Re complexes is attributed to differences in relative strengths of the metal–metal and metal–CO bonds in the $^3\sigma\sigma^*$ states of these complexes. The Mn compounds represent a unique group of complexes, since no such high quantum yields for breaking of a metal–CO bond have ever been observed upon irradiation with $\lambda \simeq 600$ nm.

Introduction

Although there is an extensive photochemistry of organometallic compounds, mechanistic studies are mainly confined to the transition-metal carbonyls. This also holds for the photochemistry of metal–metal bonds, for which detailed mechanistic information is only available for a few series of metal–metal-bonded carbonyls. Among the homodinuclear complexes, M$_2$(CO)$_{10}$ (M = Mn, Re), Cp$_2$Fe$_2$(CO)$_4$, Cp$_2$M$_2$(CO)$_6$ (M = Mo, W), and their derivatives have been studied in detail. The results of these studies have been reviewed by Geoffroy and Wrighton,[1] Meyer and Caspar,[2] and, recently, Stufkens.[3]

According to the results of flash-photolysis and matrix-isolation studies, both homolysis of the metal–metal bond and release of CO appeared to be primary photoprocesses for these carbonyl dimers. The homolysis reaction is assumed to occur from the repulsive $^3\sigma\sigma^*$ state, with release of CO from another excited state, presumably ^{3}LF in character.[2] Under normal conditions metal–metal bond scission is the dominating process and products of the CO-loss reaction are best observed by using low concentrations of the substituting ligand, by scavenging the radicals with e.g. CCl$_4$, or by photolysis of the parent compound in viscous or rigid media. In these latter media, the radicals formed by the homolysis reaction cannot escape from the solvent cage and will back-react to form the parent compound.

The same two primary photoprocesses have been observed for the substituted dimers and for all heterodinuclear complexes studied so far. Only in one case has a heterolytic splitting of the metal–metal bond been postulated.[4] Among the substituted dimers, those possessing a chelating ligand with a low-lying π^* orbital, such as bipyridine, are of special interest since their lowest energy transition has metal to ligand charge-transfer (MLCT) character instead of σ(M–M) $\rightarrow$ σ^*(M–M) or LF character. For several of these complexes with an α-diimine molecule (bipyridine, phenanthroline, etc.) as chelating ligand the photochemistry has been studied. Results have been or soon will be reported for the complexes (CO)$_5$MM'(CO)$_3$(L),[5-10] (CO)$_4$CoM(CO)$_3$(L),[11] (CO)$_2$CpFeRe(CO)$_3$(L),[12] and Ph$_3$SnRe(CO)$_3$(L)[13] (L = α-diimine; M = M' = Mn, Re). The most remarkable result of these studies is that these complexes undergo the same primary photoprocesses as the unsubstituted dimers. Again, homolysis of the metal–metal bond is the main reaction under normal conditions and loss of CO occurs in viscous and rigid media. Yet, there is one series of metal–metal-bonded complexes that show exceptional photochemical behavior at room temperature. These are the compounds Ph$_3$SnMn(CO)$_3$(α-diimine), which do not show evidence of a major homolysis reaction but instead lose CO upon irradiation. In this respect these complexes completely deviate from the corresponding Ph$_3$SnRe(CO)$_3$(α-diimine) complexes, which, according to Wrighton and co-workers, only show homolysis of the metal–metal bond.[13]

This article describes the photochemistry of these Ph$_3$SnM(CO)$_3$(α-diimine) (M = Mn, Re) complexes, in which the α-diimine ligands are 2,2'-bipyridine (bpy), pyridine-2-carbaldehyde imine (R-pyCa; C$_5$H$_4$N-2-CH=NR),[14] or 1,4-diaza-1,3-butadiene (R-DAB; RN=CHCH=NR).[14] A PLUTO drawing of one of these complexes, viz. Ph$_3$SnMn(CO)$_3$(tBu-DAB), is shown in Figure 1. The structural and spectroscopic properties of these complexes have been described previously.[15]

Experimental Section

Materials and Preparations. The ligands bpy and bpy' (4,4'-dimethyl-2,2'-bipyridine) were purchased (Merck) and used without fur-

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[‡] For part 5, see ref 32.

(1) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(2) Meyer, T. S.; Caspar, J. V. *Chem. Rev.* **1985**, *85*, 187.

(3) Stufkens, D. J. Steric and Electronic Effects on the Photochemical Reactions of Metal-Metal Bonded Carbonyls. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I. Ed.; Elsevier: Amsterdam, 1989; Vol. 3.

(4) Fletcher, S. C.; Poliakoff, M.; Turner, J. J. *J. Organomet. Chem.* **1984**, *268*, 259.

(5) Morse, D. L.; Wrighton, M. S. *J. Am. Chem. Soc.* **1976**, *98*, 3931.

(6) Kokkes, M. W.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A.; Christophersen, M.; Stam, C. H. *J. Mol. Struct.* **1985**, *131*, 11.

(7) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 2934.

(8) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4411.

(9) Kokkes, M. W.; de Lange, W. G. J.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1985**, *294*, 59.

(10) Stufkens, D. J.; Oskam, A.; Kokkes, M. W. In *Excited States and Reactive Intermediates*; Lever, A. B. P., Ed.; ACS Symposium Series 307; American Chemical Society: Washington, DC, 1986; p 66.

(11) Van Dijk, H. K.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.*, in press.

(12) Servaas, P. C.; Stor, G.; Stufkens, D. J. Unpublished results.

(13) Luong, J. C.; Faltynek, R. A.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 1597; **1980**, *102*, 7892.

(14) Most R-pyCa and R-DAB molecules have the general formula C$_5$H$_4$NCR'=NR and RN=CR'-CR''=NR, respectively. Normally, however, R' = R'' = H, and the abbrevations R-pyCa and R-DAB are used for this important subgroup. For the rarely encountered ligands C$_5$H$_4$NCR'=NR and RN=CR'CR''=NR (R' and R'' $\neq$ H) the abbreviations R-pyCa{R'} and R-DAB{R',R''} are used. See also: van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 151. Abbreviations used throughout the text are as follows: iPr = isopropyl, tBu = *tert*-butyl, iBu = isobutyl, cHex = cyclohexyl, pTol = *p*-tolyl, nBu = *n*-butyl.

(15) Andréa, R. R.; de Lange, W. G. J.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1988**, *149*, 77.

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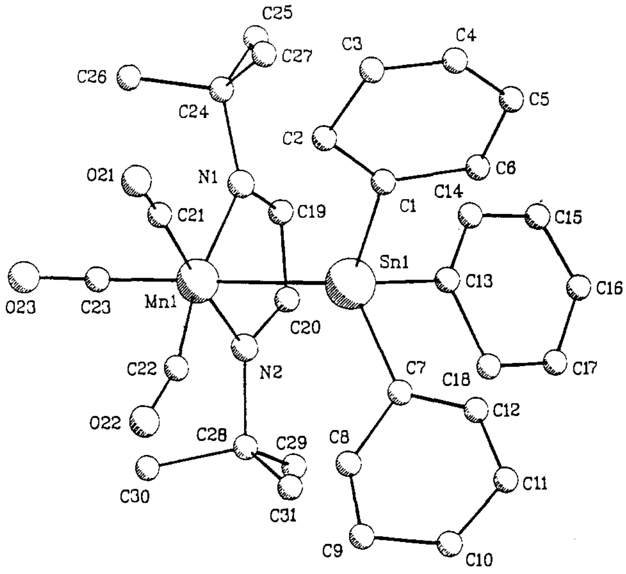

Figure 1. PLUTO drawing of $Ph_3SnMn(CO)_3(tBu\text{-}DAB)$.

ther purification. The syntheses of the R-DAB and R-pyCa ligands and of the complexes $Ph_3SnM(CO)_3L$ (M = Mn, Re; L = bpy′, iPr-pyCa, tBu-DAB, iPr-DAB) have been described elsewhere.[13-15] The complexes were identified by FTIR, ^1H NMR, and UV/vis spectroscopy and by elemental analysis. All phosphines, N-donor ligands, and solvents used were purified by distillation or sublimation and kept under a nitrogen atmosphere. Special care was taken to exclude oxygen from the reaction mixtures during the photochemical experiments.

The complex $Ph_3SnMn(CO)_2(tBu\text{-}DAB)(PPh_3)$ was synthesized by irradiation (λ_{irr} = 488 nm) of $Ph_3SnMn(CO)_3(tBu\text{-}DAB)$ with excess PPh_3 in THF.[15] The color of the solution then changed from orange-red to blue. After evaporation of the solution to dryness, the residue was washed several times with benzene/*n*-hexane (1:3). The yield was 98%.

Spectroscopic Measurements. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer equipped with a 3600 data station; resonance Raman spectra, on a Jobin-Yvon HG2S Ramanor spectrometer using a SP Model 171 argon ion laser as the excitation source. IR spectra were measured on a Nicolet 7199 B FTIR interferometer with a liquid-nitrogen-cooled Hg, Cd, Te detector (32 scans, resolution 0.5 cm^{-1}). ^1H and ^{31}P NMR spectra were recorded on Bruker WM 250 and Varian XL100-15 spectrometers, respectively, and ESR spectra, on a Bruker ER-200D-MR apparatus.

Photochemistry and Quantum Yields. For the photochemical reactions the complexes were irradiated by one of the lines of a Coherent CR 8 or Spectra Physics 2000 argon ion laser or of a Model CR 490 tunable dye laser with rhodamine 6G as a dye.

Photosubstitution quantum yields were determined by irradiating 2.4-mL stirred solutions ($\sim 10^{-4}$ M), which were carefully degassed, in quartz cells with a 0.5–2-mW laser beam. The photon flux was calculated from the laser power, which was measured by a Coherent Model 201 (1 mW-30 W) or Model 212 (1 μW-10 mW) power meter. The laser power was reduced by several neutral density filters (ϕ 1 in.; Oriel). Corrections were applied for reflections of the light within the cell, for transmission of the laser beam, and for adsorption of light by the photoproduct. The setup was tested with ferrioxalate actinometry and with quantum yield data from the literature.

The reactions, which only proceeded upon exposure to light, were followed with UV/vis absorption spectroscopy.

The experimental setup for the flash-photolysis experiment consisted of a Lambda Physik EMG-101 excimer laser as excitation source, filled with XeCl, thus providing 308-nm pulses of 10-ns duration. The output of the laser was typically 20 mJ/pulse. A monitoring beam from a Xenon flash lamp (EG&G, FX-42-C-3) was used (pulse duration 20 μs). The laser was fired when the Xe lamp output had reached its maximum. For detection a crossed-beam setup was applied and a Zeiss M4QIII single quartz prism monochromator with a RCA C-31025 C GaAs photomultiplier was used. 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 system time resolution was 10 ns.

Results

All complexes under study each possess an intensive ($\epsilon > 3000$ M^{-1} dm^3 cm^{-1}) absorption band in the visible region which, according to the resonance Raman spectra,[15] has all the characteristics of a MLCT band. The photochemical reactions were performed by irradiation into this band.

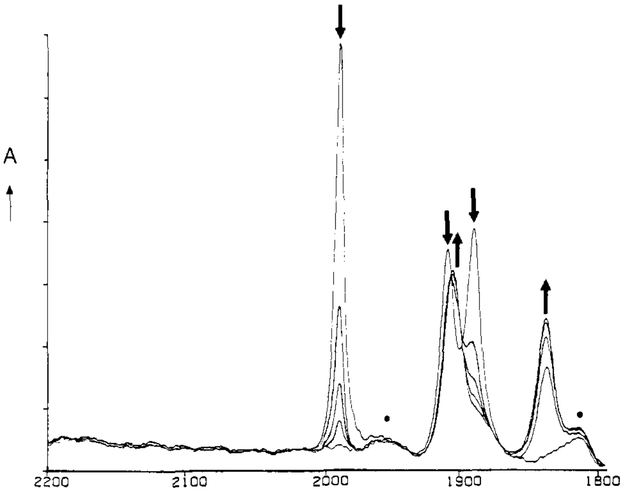

Figure 2. IR spectral changes in the CO stretching region during the photochemical reaction of $Ph_3SnMn(CO)_3(tBu\text{-}DAB)$ with PPh_3 in THF (T = 293 K) (● = PPh_3).

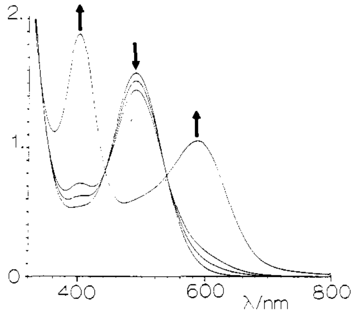

Figure 3. UV/vis spectral changes during the photochemical reaction of $Ph_3SnMn(CO)_3(tBu\text{-}DAB)$ with PPh_3 in THF (T = 293 K).

The complexes under study do not react thermally with the phosphines and other ligands used, not even under reflux (toluene) conditions. All reactions, discussed hereafter, are therefore photochemical in nature.

$Ph_3SnMn(CO)_3(\alpha\text{-diimine})$. Reactions with Lewis Bases. Irradiation of the complexes at room temperature in THF or 2-MeTHF, in the absence of a substituting ligand, did not lead to the formation of any photoproduct but only to decomposition of the parent compounds. Only at much lower temperatures were stable solvent-coordinated photoproducts formed. Raising the temperature caused a complete back-reaction of these photoproducts to the starting complexes. Although these photoproducts have structures similar to those obtained by reaction with P- and N-donor ligands, the latter complexes are more stable at room temperature and will therefore be discussed in more detail.

Figure 2 shows the IR spectral changes in the CO stretching region upon irradiation (λ = 488 nm, $P \simeq 1$ mW) at 293 K of a THF solution of $Ph_3SnMn(CO)_3(tBu\text{-}DAB)$ and PPh_3. The main consequence of the reaction for the IR spectra is the disappearance of the band at 1990 cm^{-1}, belonging to the stretching mode of the axial CO ligand.[15] This means that the axial CO ligand is photosubstituted. As a result of this photosubstitution, the two vibrations of the equatorial carbonyls shift to lower frequencies. As can be seen from Figure 3, the increase of electron density at Mn also causes a shift of the MLCT band to lower energy.

According to the isosbestic points in these spectra, the reactions take place without formation of side products or secondary photoproducts. Table I presents the CO stretching frequencies and MLCT band maxima of a series of photoproducts of $Ph_3SnMn(CO)_3(tBu\text{-}DAB)$. It is clear from these data that the frequency shifts caused by the photosubstitution reaction are

Table I. IR ν(CO) Frequencies and Electronic Absorption Spectral Data for the Complexes $Ph_3SnMn(CO)_2$(tBu-DAB)(L′) (L′ = CO, Lewis Base)

L′[a]	ν(CO), cm^{-1}			λ_{max}, nm		
CO[b]	1990	1912	1892			489
2-MeTHF (T = 183 K)[c]		1884	1811	442		680
THF (T = 213 K)[b]		1884	1810	450		644
THF (T = 243 K)[b,e]		1916	1878	446		570
(nPr)NH_2[b]		1889	1820	458		666
acetonitrile[d]		1896	1823	409		609
pyridine[b]		1890	1821	442		640
pyridazine[b]		1892	1822	430	535	620 (sh)
$P(OMe)_3$[b]		1917	1850	418		525
$P(nBu)_3$[b]		1906	1841	424		580
$P(iBu)_3$[b]		1905	1837	361		582
PPh_3[b]		1908	1840	401		586
$P(cHex)_3$		*f*		*f*		
CN-(cHex)[b]		1925	1867[g]	*h*		
CN-(pNO_2-Ph)[b]		1930	1878	*h*		

[a] [L′]/[complex] > 500. [b] In THF. [c] In 2-MeTHF. [d] In acetonitrile. [e] No coordination of L′. λ_{max} in *n*-pentane at 253 K: 445, 562 nm. [f] No reaction; $Ph_3SnMn(CO)_2$(iPr-pyCa)($P(cHex)_3$): ν(CO) 1891, 1828 cm^{-1}; λ_{max} 389, 634 nm. [g] A second rotamer is formed: ν(CO) 1918, 1851 cm^{-1}. [h] Polymerization of L′.

largest for O- and N-donor ligands.

Similar photoproducts were obtained from all types of nucleophiles, for sp^3 lone-pair ligands (PR_3, NR_3) as well as for sp^2 (pyridine, pyrazine) and sp (isocyanide, acetonitrile) lone-pair ligands. With pyridazine, photoproducts were obtained that possessed an extra absorption band between 520 and 550 nm, not present in the corresponding pyridine- and amine-substituted complexes. In agreement with the results for $Cr(CO)_5$(pyrazidine)[16] and $Cr(CO)_4(pyridazine)_2$,[17] this band is assigned to a Mn (d_π) → pyridazine (π^*) MLCT transition.

Apart from the low-energy MLCT band, all photoproducts show a second, intensive band between 350 and 450 nm, which is also shifted to longer wavelength with respect to the parent compound. This band is therefore assigned to one or more MLCT transitions, presumably directed to the second π^* orbital (π^*_2) of the α-diimine ligand. Such transitions are always observed for α-diimine complexes with low-lying MLCT transitions to π^*_1,[18-21] and, just as these latter transitions, they are intense and solvatochromic. There may be of course a LF band hidden under this second MLCT band. Prolonged irradiation (λ = 575 nm, P = 125 mW, t > 5 min) did not cause the photosubstitution of a second CO group. Finally, the photoproducts started to photodecompose.

At room temperature no photolysis products were obtained in THF or 2-MeTHF, due to the weak coordination of the solvent molecules at this temperature. Similar results were obtained for all other hard bases. Thus, the photoproducts of $Ph_3SnMn(CO)_3$(tBu-DAB) in neat pyridine and acetonitrile had to be identified rather rapidly in order to avoid the back-reaction or decomposition. Even in the case of PPh_3 a slow back-reaction to give the parent compound occurred and the weakness of the Mn–P bond in the photoproducts of this ligand is evident from the small change of ^{31}P chemical shift upon coordination (29.7 ppm).[15]

In the case of $Ph_3SnMn(CO)_3$(tBu-DAB) several reactions were inhibited by the bulky tBu groups. For instance, the sterically crowded ligand $P(cHex)_3$ (Tolman cone angle θ_p = 170°[22]) and also DPPE (θ_p = 125°) did not react with this complex although they did react with complexes of other α-diimine ligands.

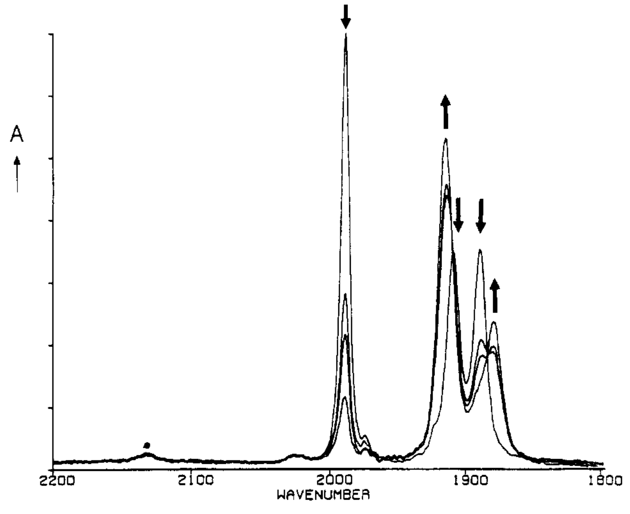

Figure 4. IR spectral changes in the CO stretching region during the photochemical reaction of $Ph_3SnMn(CO)_3$(tBu-DAB) in THF (T = 243 K) (● = free CO).

Remarkable Behavior of $Ph_3SnMn(CO)_3$(tBu-DAB). As mentioned above, all complexes undergo photosubstitution of CO by THF only at low temperatures (T < 223 K). At higher temperatures these photoproducts back-react to form the parent compound or photodecompose upon prolonged irradiation. In noncoordinating solvents such as toluene, the latter reactions are the only ones observed at all temperatures.

The complex $Ph_3SnMn(CO)_3$(tBu-DAB) shows, however, a different behavior in THF between 223 and 243 K and in toluene below 253 K. Figure 4 shows the IR spectral changes in the CO stretching region during the photochemical reaction of the tBu-DAB complex in THF at 243 K. It is evident from these spectra that the complex loses its axial CO ligand (ν_{CO} = 1990 cm^{-1}). The remaining two CO bands show smaller frequency shifts with respect to the parent compound bands than those for any of the photosubstitution products. Even the photoproduct of $P(OMe)_3$, the weakest base used, has its CO stretching modes at lower frequencies. Also, the MLCT band of this photoproduct is only slightly shifted (ca. 30 nm) to lower energy with respect to the starting complex.

There is no direct influence of the solvent since the same complex was obtained in toluene and THF. Besides, there is no question of a coordinately unsaturated species with an open site at Mn, since such a complex would back-react instantaneously with CO from the solution to form the parent compound. There is most probably a weak specific interaction between the Mn atom

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(16) (a) Balk, R. W.; Boxhoorn, G.; Snoeck, T. L.; Schoemaker, G. C.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1524. (b) Daamen, H.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1980**, *39*, 75.

(17) Timmers, F.; Brockhart, M. *Organometallics* **1985**, *4*, 1365.

(18) Van Dijk, H. K.; Stufkens, D. J.; Oskam, A. *J. Organomet. Chem.* **1988**, *340*, 227.

(19) Stufkens, D. J.; Snoeck, T. L.; Lever, A. B. P. *Inorg. Chem.* **1988**, *27*, 953.

(20) Balk, R. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chim. Acta* **1979**, *34*, 267.

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

(22) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

Table II. Photosubstitution Quantum Yields[a] of Product Formation (ϕ_p) for the Reaction of $Ph_3SnMn(CO)_3$(α-diimine) with Different Lewis Bases L′[b]

	L′[c]						
α-diimine	(nPr)NH_2	$P(OMe)_3$	DPPE	$P(nBu)_3$	$P(iBu)_3$	PPh_3	$P(cHex)_3$
tBu-DAB	0.77	0.68	*d*	0.80[e]	0.75	0.82[f]	*d*
iPr-DAB	0.69	0.65	0.62	0.77	0.74	0.72	0.70
bpy′	0.23	0.29	0.30	0.31	0.31	0.36	0.30

[a] Calculated at 600 nm (±10%); λ_{irr} = 488 nm, laser power 5 mW. [b] [L′]/[complex] > 750. [c] Tolman cone angles:[22] $P(OMe)_3$, 107°; DPPE, 125°; $P(nBu)_3$, 132°; $P(iBu)_3$, 143°; PPh_3, 145°; $P(cHex)_3$, 170°. [d] No reaction. [e] ϕ_p at different wavelengths of irradiation [mol/einstein (λ, nm)]: 0.73 (458), 0.73 (514.5), 0.82 (578), 0.63 (615). [f] ϕ_p for different ratios of [L′]/[complex] [mol/einstein (ratio)]: >0.6 (5), 0.83 (50), 0.82 (500).

and the tBu-DAB ligand. The weakness of this interaction is apparent from the observation that the parent compound is already re-formed quantitatively after standing in the dark for a few minutes.

More information about the kind of metal–ligand interaction was obtained from the ^1H NMR spectra, measured in THF-d_8 and in toluene-d_8. According to these spectra, the tBu-DAB ligand of the photoproduct contains two inequivalent imine protons and tBu groups in contrast to the parent compound and all of its other photosubstitution products.

Our preliminary conclusion from these results is that one of the tBu groups blocks the open axial site at Mn via an agostic[23] Mn---H–C interaction. Such agostic interactions have been found before for Mn and other complexes.[27-29] Unfortunately, no further evidence for such an agostic interaction could be obtained from the coupling constants, since the concentrations of the photoproducts were too low for such measurements.

Reactions with CS_2. Irradiation of $Ph_3SnMn(CO)_3$(iPr-pyCa) with λ = 488 nm in liquid CS_2 at 173 K afforded the photosubstitution product $Ph_3SnMn(CO)_2$(iPr-pyCa)(η^2-CS_2) with ν(CO) frequencies at 1961 and 1909 cm^{-1} and ν(C=S) at about 1160 cm^{-1}. This latter, weak band is characteristic for an η^2-bonded CS_2 ligand.[30] Raising the temperature to 223 K caused a thermal conversion of the photoproduct into two complexes, one having ν(CS) at 1255 cm^{-1}. This latter frequency is characteristic of a terminal C≡S group bound to a metal center; e.g., (η^5-C_5H_5)$Mn(CO)_2$(CS) has ν(C≡S) at 1254 cm^{-1}.[30] So, one of the products is proposed to be $Ph_3SnMn(CO)_2$(iPr-PyCa)(CS) and its formation out of the η^2-CS_2 photoproduct is accompanied with a shift of the CO stretching modes to still higher frequencies (2007 and 1953 cm^{-1}). These values are much higher than those of the other photoproducts (Table I) because of the strong π-acceptor capacity of the CS ligand. This complex is the only product formed upon irradiation at room temperature.

The second complex, formed out of the η^2-CS_2 photoproduct by raising the temperature to 223 K, has its CO stretching modes at much lower frequencies (1883 and 1821 cm^{-1}). This product, which is not formed at room temperature, is proposed to be $Ph_3SnMn(CO)_2$(iPr-pyCa)(SCS), in which the CS_2 ligand is σ-bonded to the metal via a sulfur lone pair. This coordination mode has e.g. been reported for $Fe(CO)_4$(SCS) by Baird et al.[31] and proposed to be the first product of the reaction of $Fe_2(CO)_9$ with CS_2.

Quantum Yields. The quantum yields of product formation (ϕ_p) are high (ϕ_p = 0.2–0.8 mol/einstein; see Table II) and, taking into account an estimated error of 10%, do not show a regular dependence on the substituting ligand. Similar values were obtained for N- and P-donor ligands and for PR_3 ligands with different basic properties or Tolman cone angles.[22] Also, variation of the phosphine concentration had no influence on ϕ_p.

As can be seen from Table II, there is a clear dependence of ϕ_p on the α-diimine ligand but no dependence on the wavelength of irradiation. These effects will be discussed in more detail in the Discussion.

Mechanistic Studies. All photochemical reactions discussed so far give rise to the formation of a photosubstitution product. From these results it may, however, not simply be concluded that the primary photoprocess of these reactions is loss of CO. On the contrary, there is evidence from ESR spectroscopy that irradiation of the complexes causes a homolytic splitting of the metal–metal bond and leads to the formation of $Mn(CO)_3$(α-diimine)$^\bullet$ radicals. This notation is used since the ESR spectrum of the persistent radical $Mn(CO)_3$(tBu-DAB)$^\bullet$ shows that the unpaired electron is mainly localized at the tBu-DAB ligand.[32]

In order to establish the relative importance of the homolytic splitting of the metal–metal bond with respect to loss of CO, a series of experiments have been performed.

First of all, the complexes were irradiated in CCl_4. This solvent is known to be an efficient radical scavenger and gives rise to the formation of $Mn(CO)_5Cl$ and $Mn(CO)_3$(α-diimine)Cl upon irradiation of the analogous $(CO)_5MnMn(CO)_3$(α-diimine) complexes.[3,5] No such chlorine complexes were, however, detected by IR spectroscopy when the complexes under study were irradiated with λ = 514.5 nm in CCl_4 at room temperature. The complexes merely photodecomposed, and free CO was observed at 2138 cm^{-1}. Only upon irradiation with light of shorter wavelength was a small amount of $Mn(CO)_3$(α-diimine)Cl detected, probably formed by reaction of photochemically produced Cl radicals with the parent compound.

The reaction with CCl_4 was also studied at lower temperatures in competition with PPh_3. In a typical experiment $Ph_3SnMn(CO)_3$(iPr-pyCa) was irradiated in 2-MeTHF at 223 K in the presence of a 10-fold excess of CCl_4 and PPh_3 (1:1). Both PPh_3 and the solvent-coordinated substitution product were then obtained, and again no presence of chloride product was observed in the IR spectrum. Raising the temperature to 233 K caused the substitution of the solvent molecules by PPh_3.

Finally, the reaction of $Ph_3SnMn(CO)_3$(iPr-pyCa) in THF was studied with flash photolysis in order to establish the primary photoprocess of the photosubstitution reaction. For this purpose the solution was irradiated by the 308-nm line of an excimer laser and the absorption spectral changes were studied in the time domain 20–820 ns after the flash. Excitation into the MLCT band was not possible since the output of the pulsed dye laser was too low (<4 mJ/pulse). This did, however, not influence the experiment, since the same reaction was observed at both wavelengths of irradiation. Already 20 ns after the flash the MLCT band of $Ph_3SnMn(CO)_2$(iPr-pyCa)(THF) appeared at 670 nm, and this observation supports release of CO as the primary photoprocess.

The above experiments show that homolysis of the metal–metal bond is not a major primary photoprocess. On the other hand, there is evidence for such a reaction not only from the above mentioned ESR experiments but also from the reaction of the

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(23) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

(24) Byrne, J. W.; Blaser, H. K.; Osborn, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 3871.

(25) Calvert, R. B; Shapley, J. R. *J. Am. Chem. Soc.* **1977**, *99*, 5225.

(26) Crocker, C.; Errington, R. J.; Mc Donald, W. S.; Odele, K. J.; Shaw, B. L.; Goodfellow, R. J. *J. Chem. Soc., Chem. Commun.* **1979**, 498.

(27) Brown, R. K.; Williams, J. M.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 981.

(28) Itoh, K.; Oshima, N. *Chem. Lett.* **1980**, *1219*.

(29) Howarth, O. W.; McAteer, C. H.; Moore, P.; Morris, G. E. *J. Chem. Soc., Chem. Commun.* **1981**, 506.

(30) Yaneff, P. V. *Coord. Chem. Rev.* **1977**, *23*, 183.

(31) Baird, M. C.; Hartwell, G., Jr.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 2037.

(32) Andréa, R. R.; de Lange, W. G. J.; van der Graaf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* **1988**, *7*, 1100.

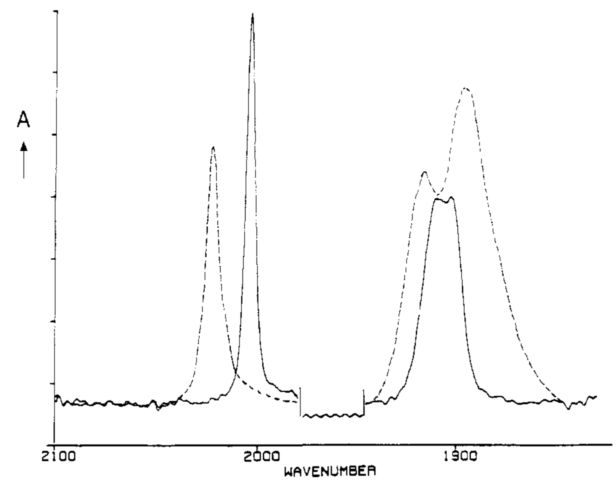

Figure 5. IR spectra in the CO stretching region of $Ph_3SnRe(CO)_3$(tBu-DAB) (—) and its photoproduct (---) in benzene (T = 293 K) (〰 indicates absorption by the solvent has been deleted).

$Ph_3SnMn(CO)_3(bpy')$ complex. Irradiation of this complex in benzene at 293 K produced, apart from decomposition products, a very small amount (less than 1%) of a side product with CO stretching modes at 1976, 1930, 1880, and 1860 cm^{-1}. These bands belong to the dimer $Mn_2(CO)_6(bpy')_2$, which has been characterized previously.[7,33] Just as in the case of $(CO)_5MnMn(CO)_3L$[7] and $(CO)_4CoMn(CO)_3L$[11] (L = bpy, phen), these photoproducts will be formed by dimerization of the $Mn(CO)_3L^•$ radicals.

$Ph_3SnRe(CO)_3$(α-diimine). Wrighton and co-workers[13] have already studied the photochemical reactions of several of these complexes in chlorocarbon solvents, and they observed the following reaction having a quantum yield of product formation of about 0.25 mol/einstein:

$$Ph_3SnRe(CO)_3L \xrightarrow[CH_2Cl_2 \\ CCl_4]{h\nu} Ph_3SnCl + ClRe(CO)_3L$$

L = bpy, phen, 2,2′-biquinoline

This reaction points to a homolytic splitting of the metal–metal bond, and a similar result was obtained by us upon irradiation of these complexes in nonchlorinated solvents. Contrary to the case of the Mn complexes, the Re compounds were much more photostable and they did not show photosubstitution of CO by nucleophiles. Instead, irradiation caused the formation of stable radicals $Re(CO)_3L^•$, which were characterized with ESR spectroscopy.[32]

From the characteristic ESR spectral properties, such as line widths (not larger than 0.5 G), lack of anisotropy in g, and the value of g itself (close to the free-electron value g_e = 2.0023), it was then concluded not that these radicals are metal centered but that the unpaired electron instead resides in the lower π* orbital of the ligand L. They are therefore best described as coordinatively unsaturated (16e) radical complexes $Re^+(CO)_3L^{•-}$, which will easily take up an extra ligand. Indeed, irradiation of $Ph_3SnRe(CO)_3$(tBu-DAB) in the presence of $P(OPh)_3$ caused the formation of a stable (18e) adduct $Re(CO)_3$(tBu-DAB)$^•$($P(OPh)_3$), which was also characterized with ESR spectroscopy.[32]

The photoproducts of these Re complexes were also characterized with IR spectroscopy, and Figure 5 shows the IR spectral changes during the photodecomposition of the $Ph_3SnRe(CO)_3$(tBu-DAB) complex in benzene at 293 K. Three new bands are then observed at 2023, 1917, and 1897 cm^{-1}, respectively, which might in principle belong to either a mononuclear or binuclear species.

A binuclear complex $Re_2(CO)_6$(tBu-DAB)$_2$ is, however, rather unlikely here, since the corresponding photoproduct $Mn_2(CO)_6(bpy')_2$ (vide supra) has four CO vibrations at lower frequencies than the three carbonyl stretching modes of the parent compound $Ph_3SnMn(CO)_3(bpy')$. Moreover, the photoproduct does not possess an intense low-energy MLCT band similar to those of the $Mn_2(CO)_6L_2$ complexes.[7,10]

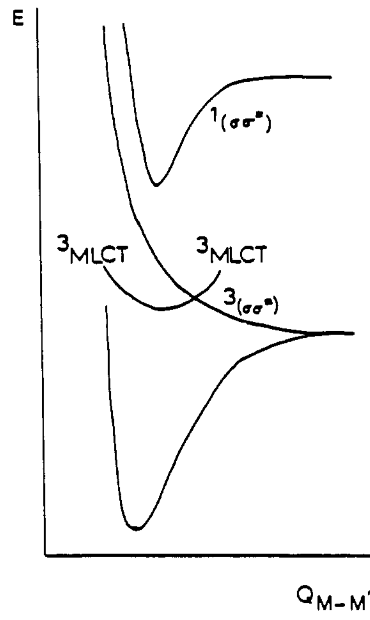

Figure 6. Schematic potential energy–coordinate diagram, showing the crossing between the ^{3}MLCT and $^3\sigma\sigma^*$ states.

The same photoproduct was obtained in perfluorobenzene, which means that no hydride is formed. On the basis of the above observations, the photoproduct is assumed to be the 16e radical complex $Re(CO)_3$(tBu-DAB)$^•$, which had already been detected with ESR spectroscopy in the reaction mixture (vide supra). This assumption is not remarkable since the corresponding 18e radical complex $Re(CO)_4$(tBu-DAB)$^•$ is a persistent radical, which could be detected practically unaltered after several days.[34] Quite recently the 16e radical complex $[Mn(CO)_3(DBCAT)]^-$ (DBCAT = di-*tert*-butylcatecholate) could even be isolated as a paramagnetic solid and structurally characterized by X-ray diffraction.[35] Just as these latter two radicals, the above photoproduct observed in the IR spectrum does not possess an intense MLCT band in the visible region. At this moment no further proof can be given for the proposed structure, since up to now attempts to isolate the photoproduct and to prepare single crystals for an X-ray determination have failed. Work is, however, in progress to accomplish such a structural characterization.

Discussion

The homolytic splitting of the metal–metal bond, observed by Wrighton and co-workers for $Ph_3SnRe(CO)_3L$ (L = bpy, phen, 2,2′-biquinoline), was proposed to occur from the lowest ^{3}MLCT state, having $^3\sigma\pi^*$ character.[13] Here, σ represents the σ(Sn–Re) bonding orbital, and π*, the lowest unoccupied orbital of the α-diimine ligand L. Population of this state by irradiation into the σ(Sn–Re) → π*(L) MLCT transition will then give rise to the observed homolytic splitting of the metal–metal bond.

This assignment of the lowest energy transition does, however, not agree with the resonance Raman (rR) spectral data, obtained by excitation into this absorption band.[15] These spectra do not show a rR effect for the metal–metal stretching mode of the Mn complexes and only show a very weak such effect for the corresponding vibration of the Re complexes. This means that the metal–metal bond is not or hardly affected by this electronic transition, in contrast to the conclusions of Wrighton and co-workers.[13]

Instead, just as for the mononuclear d^6 α-diimine complexes,[19-21,36-39] the low-energy absorption band of these complexes

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(33) Hieber, W.; Schropp, W. *Z. Naturforsch.* **1960**, *15B*, 271.

(34) Alberti, A.; Hudson, A. *J. Organomet. Chem.* **1983**, *248*, 199.

(35) Vlček, A., Jr. Personal communication.

(36) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1982**, 275.

has therefore been assigned to the electronic transitions from the different metal d_π orbitals, not involved in the metal–metal bond, to the lowest π^* orbital of the α-diimine ligand.[15] Normally, such $^3d_\pi\pi^*$(^{3}MLCT) states are not reactive[40] and population of these states will not give rise to the observed efficient photochemical reactions. Because of this, Meyer and Caspar[2] proposed an alternative energy diagram for such metal–metal-bonded carbonyls with a lowest ^{3}MLCT state (Figure 6).

Irradiation with visible light leads to population of the ^{1}MLCT state, followed by intersystem crossing to ^{3}MLCT and intramolecular energy transfer to the reactive $^3\sigma\sigma^*$ state of the metal–metal bond. Due to the repulsive character of this latter state, this surface crossing can even take place at very low energy. As a result, the complexes $M_2(CO)_8L$ (M = Mn, Re; L = phen, 2,2′-biquinoline) hardly showed a wavelength dependence of the quantum yield for the homolysis reaction.[5] A similar mechanism is postulated for the photochemical reactions of the complexes under study, which also show a wavelength independence of their quantum yields (see Table II).

The question remains as to how population of the $^3\sigma\sigma^*$ state can lead to loss of CO in the case of the Mn complexes and to cleavage of the metal–metal bond for the Re complexes. This may be the result of a weakening of both the metal–metal and metal–CO bonds in the $^3\sigma\sigma^*$ state. Although there are not theoretical data on the complexes under study and on the $Ph_3SnM(CO)_5$ compounds supporting this assumption, calculations on the analogous $M_2(CO)_{10}$ complexes show that such an effect is present there.[41] Population of the $^3\sigma\sigma^*$ state may then lead to breaking of the metal–metal or a metal–CO bond depending on the relative strengths of these bonds in this state. In the Mn complexes under study, the Sn–Mn bond will be relatively strong in the ground state, since the metal–metal bond of the corresponding complex $Ph_3SnMn(CO)_5$, from which they are derived, is chemically inert, even upon attack by chlorine.[42] Furthermore, the dissociation energy of $Ph_3SnMn(CO)_5$ is much higher than that of $Ph_3SnRe(CO)_5$,[43–46] whereas the Mn–CO bond is normally much weaker than the Re–CO bond.[47]

So, although the Sn–Mn bond will probably be more affected in the $^3\sigma\sigma^*$ state than the Mn–CO bonds, the latter bonds may still be the weaker ones and therefore be broken upon population of this state. The opposite situation apparently holds for the Re complexes.

Alternatively, the photochemical reactions of the Mn complexes might occur from the lowest ^{3}LF state, close in energy to the ^{3}MLCT state. Most mononuclear complexes, having a lowest ^{3}MLCT state, react photochemically by thermal occupation of such a close-lying ^{3}LF state.[40] There is not direct evidence for or against such a low-lying ^{3}LF state in the case of the Mn complexes under study. This information can, however, be obtained indirectly by comparing the absorption spectra of the closely analogous complexes $Ph_3SnMn(CO)_3$(TMED), $XMn(CO)_3$(TMED), and $XMn(CO)_3$(α-diimine) (X = Cl, Br; TMED = tetramethylethylenediamine). These complexes have their lowest LF transition at nearly the same wavelength (410 nm), which also means that the corresponding ^{3}LF states have similar energies for all three complexes. Irradiation with $\lambda > 500$ nm into the MLCT band of the $XMn(CO)_3$(α-diimine) complexes does not give rise to a photochemical reaction,[48] which means that there is no low-energy crossing from a ^{3}MLCT to a reactive ^{3}LF state for these complexes. In view of the close analogy between the LF transition of these complexes and those of the $Ph_3SnMn(CO)_3$(TMED) complexes and therefore also of the $Ph_3SnMn(CO)_3$(α-diimine) compounds under study, no low-energy ^{3}LF state is expected for these latter complexes either.

The photosubstitution quantum yields of the Mn complexes decrease upon going from the R-DAB and R-pyCa complexes to the bpy′ complex. This effect will not be due to a difference in relative strengths of the metal–metal and metal–CO bonds in the $^3\sigma\sigma^*$ state of these complexes, since this decrease of ϕ_p is not accompanied by a concomitant increase of the quantum yield for the metal–metal bond cleavage. Rather, the surface crossing between the ^{3}MLCT and $^3\sigma\sigma^*$ states is probably less effective for the bpy′ complex.

Conclusion

The complexes $Ph_3SnM(CO)_3$(α-diimine) represent a unique group of complexes, not only because of the difference in primary photoprocess between the Mn and Re complexes but also because of the high quantum yields for breaking of the Mn–CO bond even at a very low energy of excitation.

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(37) Balk, R. W.; Stufkens, D. J.; Crutchley, R. J.; Lever, A. B. P. *Inorg. Chim. Acta* **1982**, *64*, 49.

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

(39) Servaas, P. C.; Van Dijk, H. K.; Snoeck, T. L.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 4494.

(40) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.

(41) Heijser, W.; Baerends, E. J.; Ros, P. *Faraday Symp. Chem. Soc.* **1980**, *14*, 211.

(42) Chipperfield, J. R.; Ford, J.; Webster, D. E. *J. Organomet. Chem.* **1975**, *102*, 417.

(43) Terzis, A.; Strekas, T. C.; Spiro, T. G. *Inorg. Chem.* **1974**, *13*, 1346.

(44) Burnham, R. A.; Stobart, S. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1269.

(45) Onaka, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2444.

(46) Gager, H. M.; Lewis, J.; Ware, M. J. *J. Chem. Soc., Chem. Commun.* **1966**, 616.

(47) Connor, J. A. *Topics in Current Chemistry*; Springer-Verlag: Berlin, 1977; Vol. 71, p 71.

(48) Balk, R. W.; Stufkens, D. J.; Oskam, A. *J. Chem. Soc., Dalton Trans.* **1981**, 1124.