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Syntheses, spectroscopic properties and photochemistry of $[Re(R)(CO)_3(4,4'-Me_2-bpy)]$ (R = alkyl) complexes

Cornelis J. Kleverlaan, Derk J. Stufkens^{*}

Anorganisch Chemisch Laboratorium, Institute of Molecular Chemistry, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands

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Abstract

The complexes $[Re(R)(CO)_3(dmb)]$ (dmb = 4,4'-dimethyl-2,2'-bipyridine; R = CH₃, CD₃, Et, Bz, or iPr) were synthesized and their spectroscopic (¹H, and ¹³C NMR, IR, UV–Vis, resonance Raman) properties were studied. According to the resonance Raman spectra the lowest-energy electronic transition has mainly MLCT character. It is therefore concluded that the ³ σ (Re–R) π *(dmb) state from which these complexes undergo homolysis of the Re–alkyl bond, is occupied by surface crossing from the nonreactive MLCT states. The [Re(CO)₃(dmb)]⁺ radicals, formed by the homolysis reaction, were trapped by nitrosodurene and PPh₃, and their adducts were identified with EPR spectroscopy. The thermal reactions of the radicals in different media were followed with IR spectroscopy. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

The complexes $[\operatorname{Re}(L')(\operatorname{CO})_3(\alpha\text{-diimine})]^{n+}$ $(n = 0,1; \alpha$ diimine = 2,2'-bipyridine, etc.; L' = halide, O- or N-donor ligand) [1-5] have the special property that variation of L' may not only influence the energy of the lowest-excited state but also change its character and reactivity. Thus, replacing Cl⁻ by I⁻ changes this character from MLCT into L'LCT (halide to α -diimine charge transfer) [6]. If L' is instead an organic donor molecule such as 4-(dimethylamino)benzonitrile (DMABN) [4], the L'LCT (DMABN to a-diimine charge transfer) transition is overlap forbidden. However, even then the L'LCT state becomes occupied if MLCT excitation is followed by intramolecular electron transfer from DMABN to the Re centre [4]. A special situation occurs when L' represents a metal fragment (ML_n) or alkyl (R) group. For, the complexes $[Re(ML_n)(CO)_3(\alpha-diimine)]$ and $[Re(R)(CO)_3(\alpha \text{-diimine})]$ have a high-lying $\sigma(Re-ML_n/2)$ R) orbital. MLCT ($d_{\pi}(Re)$ to α -diimine) excitation is then followed by electron transfer from that $\sigma(\text{Re-ML}_n/\text{R})$ orbital to $d_{\pi}(\text{Re})$, by which the excited state obtains $\sigma(\text{Re}-\text{ML}_n/\text{Re})$ R) $\pi^*(\alpha$ -diimine) character. Occupation of this state normally leads to homolysis of the $\sigma(\text{Re-ML}_n/\text{R})$ bond with formation of radicals. In the case of the metal-metal bonded complexes $[\text{Re}(\text{ML}_n)(\text{CO})_3(\alpha\text{-diimine})]$ the ${}^3\sigma\pi^*$ state is always lower in energy than the MLCT states and very reactive if ML_n = Mn(CO)₅, Re(CO)₅, Co(CO)₄, or FeCp(CO)₂ [1,7–20]. Only the complexes [Re(SnPh₃)-(CO)₃(α -diimine)] are stable in their lowest ${}^3\sigma\pi^*$ state due to the strength of their Re–Sn bond [21]. Similar homolysis reactions occur for the metal–alkyl complexes [M(R)(CO)₃(α -diimine)] (M = Mn, Re) [22–27], [Ru(X)-(R)(CO)₂(α -diimine)] (X = halide) [26,28], [Ir(R)(CO)-(PAr₃)₂(mnt)] [29], [Pt(CH₃)₄(α -diimine)] [30], and [Zn-(R)₂(α -diimine)] [31], but their photoreactivity often varies with R. Several of these ${}^3\sigma\pi^*$ states have recently been detected and characterized with time-resolved absorption, emission and IR spectroscopy [22,32].

Preliminary experiments on the [Re(R)(CO)₃(α -diimine)] (R = CH₃, CD₃, Et, Bz and iPr) complexes showed that the photochemical behaviour not only depends on R, but also on the α -diimine ligand. Thus, the quantum yield of the photoreaction is only 0.15 for the complexes [Re(CH₃)(CO)₃(iPr-PyCa)] and [Re(CH₃)(CO)₃(R-DAB)] (iPr-PyCa = pyridine-2-carbaldehyde-*N*-isopropyl and R-DAB = *N*,*N'*-diorgano-1,4-diaza-butadiene) [22], whereas the reaction proceeds with nearly unit efficiency for [Re(CH₃)(CO)₃(dmb)] [27]. In order to determine the factors that influence the excited-state properties of these complexes, we have started an investigation of their spectroscopic and photochemical

^{*}Corresponding author. Tel.: +31-20-525-6451; fax: +31-20-525-6456.

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Fig. 1. Schematic structure of the complexes $[{\rm Re}(R)({\rm CO})_3({\rm dmb})]$ and of the dmb ligand used.

properties. In this paper we present the syntheses and spectroscopic data, as well as the photoreactions of the complexes $[Re(R)(CO)_3(dmb)]$ (R = CH₃, CD₃, Et, Bz and iPr) (see Fig. 1).

2. Experimental

2.1. Materials and preparations

 $[\text{Re}_2(\text{CO})_{10}]$ (Strem), Br₂, CH₃I, CD₃I, EtI, BzBr (Aldrich) and 4,4'-dimethyl-2,2'-bipyridine (dmb) (Fluka) were used without further purification. Silicagel for column chromatography (Kieselgel 60, 70–230 mesh, Merck) was activated by heating overnight in vacuo at 160°C.

Solvents for synthetic purposes were of reagent grade and carefully dried over sodium wire (THF, n-hexane, diethyl ether), $CaCl_2$ (CH_2Cl_2) or CaH_2 (CH_3CN) and freshly distilled under nitrogen prior to use. Solvents for spectroscopy were of analytical grade, dried over sodium and distilled under N₂ before use. CH_3MgI , CD_3MgI , EtMgI, BzMgBr and iPrMgI were synthesized by published procedures.

The complexes $[Re(X)(CO)_3(dmb)]$ (X = Cl, Br) were synthesized according to previously reported procedures [33]. The complexes $[Re(R)(CO)_3(dmb)]$ (R = CH₃, CD₃, Et, Bz, iPr) were prepared by a modified literature procedure [22]. Excess (\sim 1.2 mmol) of the relevant Grignard reagent was added to a solution of 1.0 mmol [Re(Br)(CO)₃(dmb)] in 50 ml THF at room temperature. In case of the Et, Bz and iPr Grignard the $[Re(R)(CO)_3(dmb)]$ complex was formed immediately. [Re(CH₃/CD₃)(CO)₃(dmb)] was formed after 1 h of stirring at room temperature. The excess Grignard was quenched by adding 2 ml CH₂Cl₂ to the solution. The magnesium salts were removed from the mixture by flash column chromatography of the reaction mixture on a short silica column. After evaporation of the solvent, the complex was purified by column chromatography on silica using gradient elution with n-hexane/THF. Yield: 50-90%.

[Re(CH₃)(CO)₃(dmb)]: ¹H NMR (CDCl₃, 293 K) δ : 8.90 (2H, d, 5.7 Hz, py-H₆), 7.95 (2H, s, py-H₃), 7.20 (2H, d, 5.7 Hz, py-H₅), 2.56 (6H, s, py-CH₃), -0.95 (3H, s, CH₃) ppm; ¹³C NMR ATP (CDCl₃, 293 K) δ : 204.0 (Re–CO), 192.6 (Re–CO), 154.2 (py-C₂), 151.8 (py-C₆), 148.5 (py-C₄), 126.8 (py-C₃), 123.1 (py-C₅), 21.2 (py-CH₃), -0.6 (CH₃) ppm; IR ν (CO) (THF, 293 K): 1998 (s) 1880 (s, br)

cm⁻¹; UV–Vis λ_{max} (ε in M⁻¹ cm⁻¹) (CH₂Cl₂): 415 nm (2.5 × 10³). MS(FAB⁺): *M*(calc) 469.51, *M*(exp) 470.52⁻¹. [Re(CD₃)(CO)₃(dmb)]: ¹H NMR (CDCl₃, 293 K) δ : 8.90 (2H, d, 5.7 Hz, py-H₆), 7.95 (2H, s, py-H₃), 7.20 (2H, d, 5.7 Hz, py-H₅), 2.56 (6H, s, py-CH₃); ²D NMR (CDCl₃, 293 K) δ : –0.95 (3D, s, CH₃) ppm; IR ν (CO) (THF, 293 K): 1998 (s) 1880 (s, br) cm⁻¹; UV–Vis λ_{max} (CH₂Cl₂): 415 nm. MS(FAB⁺): *M*(calc) 472.51, *M*(exp) 473.08⁻¹.

[Re(Et)(CO)₃(dmb)]: ¹H NMR (CDCl₃, 293 K) δ : 8.90 (2H, d, 5.7 Hz, py-H₆), 7.95 (2H, s, py-H₃), 7.20 (2H, d, 5.7 Hz, py-H₅), 2.56 (6H, s, py-CH₃), 1.32 (3H, t, 7.8 Hz, CH₂CH₃), -0.28 (2H, q, 7.8 Hz, CH₂CH₃) ppm; ¹³C NMR ATP (CDCl₃, 293 K) δ : 204.6 (Re–CO), 192.8 (Re–CO), 154.1 (py-C₂), 151.7 (py-C₆), 148.3 (py-C₄), 126.7 (py-C₃), 123.1 (py-C₅), 21.3 (py-CH₃), 18.6 (CH₃), 17.4 (CH₂) ppm; IR ν (CO) (THF, 293 K): 1987 (s) 1877 (s, br) cm⁻¹; UV–Vis λ_{max} (ε in M⁻¹ cm⁻¹)(CH₂Cl₂): 425 nm (3.0 × 10³). MS(FAB⁺): *M*(calc) 483.54, *M*(exp) 484.55⁻¹.

[Re(iPr)(CO)₃(dmb)]: ¹H NMR (CDCl₃, 293 K) δ : 8.90 (2H, d, 5.7 Hz, py-H₆), 7.97 (2H, s, py-H₃), 7.22 (2H, d, 5.7 Hz, py-H₅), 2.56 (6H, s, py-CH₃), 1.25 (6H, d, 7.0 Hz, CH(*CH*₃)₂), -1.02 (1H, sept, 7.0 Hz, *CH*(CH₃)₂) ppm; ¹³C NMR ATP (CDCl₃, 293 K) δ : 204.6 (Re–CO), 192.5 (Re–CO), 154.2 (py-C₂), 151.7 (py-C₆), 148.3 (py-C₄), 126.7 (py-C₃), 123.1 (py-C₅), 30.2 (*C*H(CH₃)₂), 29.0 (CH(*C*H₃)₂), 21.3 (py-CH₃) ppm; IR ν (CO) (THF, 293 K): 1987 (s); 1878 (s, br) cm⁻¹; UV–Vis λ_{max} (ε in M⁻¹ cm⁻¹)(CH₂Cl₂): 434 nm (2.6 × 10³).

[Re(Bz)(CO)₃(dmb)]: ¹H NMR (CDCl₃, 293 K) δ : 8.63 (2H, d, 5.7 Hz, py-H₆), 7.73 (2H, s, py-H₃), 7.08 (2H, d, 5.7 Hz, py-H₅), 6.58 (2H, pst, arom-H), 6.43 (1H, t, 7.1 Hz, arom-H) 5.97 (2H, d, 7.4 Hz, arom-H), 2.56 (6H, s, py-CH₃), 1.73 (2H, s, CH₂-Ph) ppm; ¹³C NMR ATP (CDCl₃, 293 K) δ : 202.9 (Re–CO), 192.2 (Re–CO), 154.0 (py-C₂), 152.6 (Ph-C), 151.5 (py-C₆), 148.4 (py-C₄), 126.9 (Ph-C), 126.5 (py-C₃), 125.0 (Ph-C), 122.8 (py-C₅), 118.7 (Ph-C), 24.3 (CH₂), 21.2 (py-CH₃) ppm; IR ν (CO) (THF, 293 K): 1993 (s); 1882 (br, s) cm⁻¹; UV–Vis λ (ε in M⁻¹ cm⁻¹)(CH₂Cl₂): 400 nm (2.5 × 10³). MS(FAB⁺): *M*(calc) 545.61, *M*(exp) 546.62⁻¹.

[Re(Cl)(CO)₃(dmb)]: ¹H NMR (CDCl₃, 293 K) δ : 8.89 (2H, d, 6.0 Hz, py-H₆), 7.99 (2H, s, py-H₃), 7.34 (2H, d, 6.0 Hz, py-H₅), 2.58 (6H, s, py-CH₃) ppm; IR ν (CO) (CH₂Cl₂, 293 K): 2021 (s) 1916 (m) 1894 (m) cm⁻¹; UV–Vis λ_{max} (CH₂Cl₂): 375 nm.

2.2. Spectroscopic measurements

Samples for spectroscopic studies were prepared under purified N_2 by use of Schlenk techniques. The solutions were carefully handled in the dark before the experiments were performed.

¹ Mass of M-H⁺, due to abstraction of the matrix solvent in the mass spectrometer.

Electronic absorption spectra were measured on a Varian Carv 4E spectrophotometer, infrared spectra on a Bio-Rad FTS-60A FT-IR spectrometer equipped with a liquid-nitrogen-cooled MCT detector. The photoreactions of the complexes were monitored with Rapid-Scan-FTIR, the experimental set-up has been described elsewhere [34]. The ¹H, ²D and ¹³C NMR spectra were recorded on a Bruker AMX 300 spectrometer. Resonance Raman spectra were recorded on a Dilor XY spectrometer, using an SP Model 2016 Ar⁺ laser as the excitation source. The 425 nm excitation wavelength was obtained using stilbene as a dye. Spectra were recorded at 80 K for the complexes dispersed in a KNO₃ pellet (\sim 15 mg complex in 150 mg KNO₃). The EPR spectra were measured on a Varian E-104A spectrometer. The fast atom bombardment (FAB) mass spectrometry measurements were carried out at the Institute of Mass Spectrometry of the University of Amsterdam.

3. Results and discussion

3.1. ¹H and ¹³C NMR spectra

The ¹H NMR spectra of the $[Re(R)(CO)_3(dmb)]$ compounds show resonances for the dmb ligand at approximately 2.6 ppm and in the region 8.9-7.0 ppm. These shifts indicate that this ligand is coordinated to the metal as a chelate [35]. The resonances of the alkyl groups have a low value of δ , which means that the Re atom has a strong shielding effect. The alkyl proton resonances show a normal coupling pattern. The ¹H spectrum of [Re(CD₃)(CO)₃-(dmb)] reveals the resonances of the dmb ligand, the ²D spectrum that of the CD₃ ligand at -0.95. The ¹³C NMR spectra of the complexes show resonances in the region 155-120 ppm (py-C) and at approximately 21 ppm (py-CH₃) for the dmb ligand. Resonances of the alkyl ligands are observed at relatively low ppm values: -0.6 (CH₃), 17.4 (CH₂CH₃), 24.3 (CH₂Ph) and 30.2 (CH(CH₃)₂). For the complexes [Ru(I)(CH₃)(CO)₂(iPr-DAB)] and [Ru(Cl)(Bz)-(CO)₂(iPr-DAB)] similar resonances have been observed; -5.5 ppm (Ru-CH₃) and 14.0 ppm (Ru-CH₂Ph), respectively [36,37].

3.2. IR spectra

The infrared spectra of all $[\text{Re}(\text{R})(\text{CO})_3(\text{dmb})]$ compounds show two bands in the $\nu(\text{CO})$ frequency region, the one at lower frequency being broad and consisting of two, nearly coinciding, vibrations. These bands are assigned to the three IR-active CO stretching modes (2a' + a'') of this type of complexes having C_s symmetry [33,38,39]. The wavenumbers of these vibrations decrease slightly in the order Bz > CH₃ > Et > iPr due to an increase of electron donation by the alkyl group. A similar effect was observed for other [Re(R)(CO)₃(α -diimine)] complexes [22].

Table 1

Maxima^a and solvatochromism $(\Delta)^{b}$ of the lowest-energy absorption bands of [Re(R)(CO)₃(dmb)] complexes (R = Me, Et, iPr and Bz)

CH ₃ CN	THF	Toluene	$\Delta^{\rm b}$
400	417	435	2011
406	425	444	2108
416	435	454	2012
486	512	525	1528
	CH ₃ CN 400 406 416 486	CH ₃ CN THF 400 417 406 425 416 435 486 512	CH ₃ CN THF Toluene 400 417 435 406 425 444 416 435 454 486 512 525

^a λ_{\max} in nm.

^b Difference in energy (cm⁻¹) between the absorption maxima in toluene and acetonitrile.

3.3. Electronic absorption spectra

The complexes are yellow to red–brown due to the presence of an absorption band in the region 300–500 nm which has a maximum extinction coefficient in CH₂Cl₂ of $2.5-3.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$. The bands show negative solvatochromism (see Table 1), which indicates that they belong to metal-to-ligand charge-transfer (MLCT) transitions [13,22,24,40].

Changing the alkyl group from CH₃ to Et and iPr causes the MLCT band to shift to lower energy (see Fig. 2). This is due to an increase in energy of the $d_{\pi}(\text{Re})$ -orbitals as the alkyl group becomes more electron donating. The spectrum of the Bz complex shows a structured absorption band, not observed for the other complexes. An analogous effect was observed for the [Re(Bz)(CO)₃(α -diimine)] (α -diimine = iPr-DAB; tBu-DAB) complexes and was then ascribed to a splitting of the $d_{\pi}(\text{Re})$ -orbitals due to an interaction of the d_{xy} - and/or d_{yz} -orbitals with the π orbitals of the phenyl group of the benzyl ligand [22].

3.4. Resonance Raman spectra

Resonance Raman (rR) spectroscopy is a valuable technique for the assignment of allowed electronic transitions,



Fig. 2. Absorption spectra of $[Re(R)(CO)_3(dmb)]$ (R = CH₃, Et, iPr and Bz) in toluene at 293 K.

Table 2			
Resonantly enhanced Raman bands of [Re	$(R)(CO)_3(dmb)]$ (R = CD ₃ , CH ₂	(3) at 80 K, together with relevan	nt literature data

Compound	Ref.	Raman shift (cm ⁻¹) (2000–200 cm ⁻¹)	
[Re(CD ₃)(CO) ₃ (dmb)]		1974, 1535, 1472, 1312, 1270, 1255, 1166, 750, 733, 530, 499, 482, 451, 212	
$[\operatorname{Re}(\operatorname{CD}_3)(\operatorname{CO})_3(\operatorname{dmb})]$		1974, 1535, 1472, 898, 621, 570, 518, 502, 491, 468, 212	
		(M–CO and M–C only)	
$[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dmb})]$		499, 482, 451	
$[\text{Re}(\text{CD}_3)(\text{CO})_3(\text{dmb})]$		502, 491, 468	
[Re(CH ₃)(CO) ₃ (iPr-DAB)]	[24]	503, 488, 451	
[Re(CH ₃)(CO) ₃ (tBu-DAB)]	[24]	492, 484, 452	
[Re(CH ₃)(CO) ₃ (pAn-DAB)]	[24]	513, 470, 450	
$[\text{Re}(\text{CH}_3)(\text{CO})_5]$	[45]	531, 471, 450 and 473 (M–CH ₃)	
$[\operatorname{Re}(\operatorname{CD}_3)(\operatorname{CO})_5]$	[45]	531, 463, 448 and 426 (M–CD ₃)	
[Re(SnPh ₃)(CO) ₃ (tBu-DAB)]	[39]	570, 490, 460	
[Re(Cl)(CO) ₃ (Mes-DAB)]	[41]	525, 490, 450	
[Re(Cl)(CO) ₃ (pTol-DAB)]	[41]	500, 470, 430	
[Re(Cl)(CO) ₃ (iPr-DAB)]	[6]	502, 485, 438	
[Re(Br)(CO) ₃ (iPr-DAB)]	[6]	514, 500, 442	
[Re(I)(CO) ₃ (iPr-DAB)]	[6]	504, 487, 440	
$[Re\{(Mn(CO)_5\}(CO)_3(pTol-PyCa)]$	[41]	516, 480, 426	

since only those vibrations are normally observed in such spectra, which are coupled to these transitions [41–44]. For the complexes [$Re(R)(CO)_3(dmb)$] such rR data might therefore be useful for the identification of their lowest electronic transitions which eventually lead to their photo-induced homolysis reactions.

Attempts to measure the rR spectra of $[Re(R)(CO)_3$ -(dmb)] (R = Et, iPr and Bz) failed due to the photodecomposition of these complexes by the exciting laser beam. Only the complexes $[Re(R)(CO)_3(dmb)]$ (R = CH₃, CD₃) are photostable, albeit only at low temperatures. Their rR spectra were measured at 80 K in a KNO₃ pellet with exciting argon ion laser lines that were varied throughout the absorption band (425–514.5 nm). Table 2 presents the most important Raman bands of the complexes. Fig. 3



Fig. 3. Resonance Raman spectra of $[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dmb})]$ dispersed in KNO₃ (λ_{exc} (top to bottom) = 514.5, 488.0, 457.9 and 425.0 nm; T = 80 K; $* = \text{NO}_3^{-1}$)

shows the Raman spectra of $[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dmb})]$ recorded at four wavelengths of excitation, while the spectra of CH₃ and CD₃ complexes in the 800–200 cm⁻¹ region are depicted in Fig. 4.

The assignment of the Raman bands is based on a comparison with data for the related complexes [Re(L)-(CO)₃(α -diimine)] (L = halide, alkyl) [6,24,39,41], and [M(R)(CO)₅] (M = Mn, Re; R = CH₃, CD₃) [45] (see Table 2). In agreement with the Raman spectra recorded previously for several [Re(L)(CO)₃(α -diimine)] (L = halide, alkyl) complexes [6,24], only one CO vibration, viz. the highest-frequency symmetric stretching mode, appears as a resonantly enhanced Raman band in the spectra. A detailed vibrational study of the closely related complex [Re(Cl)-(CO)₃(4,4'-bpy)₂] has shown that this band belongs to the



Fig. 4. Part of the resonance Raman spectra of $[\text{Re}(\text{CD}_3)(\text{CO})_3(\text{dmb})]$ (top) and $[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dmb})]$ (bottom) dispersed in KNO₃ ($\lambda_{\text{exc}} = 488.0 \text{ nm}; T = 80 \text{ K}; * = \text{NO}_3^-$)

symmetric ν (CO) vibration, in which the axial and equatorial carbonyl ligands move in phase [46]. Such a movement will be the result of MLCT excitation. In the lower-frequency symmetric CO vibration (~1880 cm⁻¹), the axial and equatorial carbonyls move out-of-phase. As a result, the total distortion along this latter normal coordinate is small and the resonance Raman effect will be too weak for this vibration to be observed. In the frequency region of the α diimine stretching modes (1600–1200 cm⁻¹), strong Raman bands are observed at 1535 and 1472 cm⁻¹, which belong to coupled CN- and CC-vibrations of dmb.

In the lower frequency region $(1200-200 \text{ cm}^{-1})$, many bands are found, some of them showing a resonance effect. The assignment of these bands is not straightforward but some of them can be assigned by comparison of the spectra of the CH₃ and CD₃ complexes. The band observed for the CH₃ complex at 1166 cm⁻¹ shifts to 898 cm⁻¹ on deuteration. It is assigned to $\delta_s(CH_3/CD_3)$ in agreement with the data obtained by McQuillan et al. for [Re(R)(CO)₅] (R = CH₃, CD₃) [45]. For these complexes $\delta_s(CH_3)$ was observed at 1193 cm⁻¹, $\delta_s(CD_3)$ at 910 cm⁻¹. Similar bands were observed for the related complexes [Re(CH₃)(CO)₃-(R-DAB)] [24] ($\delta_s = 1160 \text{ cm}^{-1}$), [Ru(CH₃)(SnPh₃)(CO)₂-(iPr-DAB)] ($\delta_s = 1148 \text{ cm}^{-1}$) [47], [Ru(X)(CH₃/CD₃)-(CO)₂(iPr-DAB)] (X = Cl⁻, I⁻) ($\delta_s(CH_3) = 1148 \text{ cm}^{-1}$, $\delta_s(CD_3) = 908 \text{ cm}^{-1}$) [37].

The rR spectra of [Re(CH₃)(CO)₃(dmb)] show two other bands, at 750 and 733 cm⁻¹, which shift to 621 and 570 cm⁻¹, respectively, on replacing the CH₃ group by CD₃. The corresponding [Re(R)(CO)₅] complexes showed only a single band in solution, at 777 cm⁻¹ (R = CH₃) and at 577 cm⁻¹ (R = CD₃) [45], which was, however, split into two bands for [Re(CH₃)(CO)₅] in the gas phase (802 and 758 cm⁻¹) [45]. These bands were assigned to a rocking mode (ρ) of the CH₃/CD₃ ligand. Similar bands were found for the related complexes [Re(CH₃)(CO)₃(R-DAB)] (ρ (CH₃) = 730 cm⁻¹) [24] and [Ru(X)(R)(CO)₂(iPr-DAB)] (X = Cl⁻, I⁻) (ρ (CH₃) \cong 800 cm⁻¹, ρ (CD₃) = 614 and 600 cm⁻¹) [37]. The splitting of the ρ (CH₃) band of [Re(R)(CO)₃(dmb)] (750–733 = 17 cm⁻¹) is rather small compared with that of ρ (CD₃) (621–570 = 51 cm⁻¹).

Raman bands belonging to ν (Re–CH₃) and ν (Re–CD₃) have been observed for [Re(CH₃/CD₃)(CO)₅] at 473 and 426 cm^{-1} , respectively [45]. For the complexes under study they are expected at similar frequencies in the rR spectra, provided that they are resonance enhanced by excitation into the visible absorption band. However, the assignment of Raman bands in this frequency region is not straightforward since it contains also bands due to ν_s (Re–CO) and δ (Re–C– O) vibrations, which could couple to ν (Re–CH₃/CD₃). In $400-550 \text{ cm}^{-1}$ the region the rR spectra of [Re(CH₃)(CO)₃(dmb)] show four bands at 451, 482, 499, and 530 cm^{-1} , which shift to 468, 491, 502, and 518 cm⁻¹, respectively, on deuteration (Table 2, Fig. 4). The first three bands are found in the rR spectra of most $[Re(L)(CO)_3(\alpha$ diimine)] complexes as demonstrated by the literature data

presented in Table 2. They belong to metal-CO stretching and metal-C-O deformation modes of the Re(CO)₃-mojety. In some cases only two bands are observed, but this is probably due to the coincidence of the two higher frequency bands. In view of this close correspondence between the spectra of the various $Re(L)(CO)_3(\alpha$ -diimine) complexes, none of these bands can be assigned to ν (Re–CH₃/CD₃), especially since deuteration has only a minor effect on their frequencies. The fourth band observed at 530 cm^{-1} for the CH_3 -complex shifts to 518 cm⁻¹ on deuteration. Although this band might belong to ν (Re–CH₃/CD₃), its frequency is much higher than that observed for Re(CH₃/CD₃)(CO)₅ $(473/426 \text{ cm}^{-1})$. Besides, the effect of deuteration is far too small (12 versus 47 cm^{-1}). This band most likely belongs to a δ (Re–C–O) vibration. The shift on deuteration may be caused by two effects. First of all, the δ (Re–C–O) vibration may mix with ν (Re–CH₃/CD₃). Deuteration will then also affect the frequency of this Raman band but the effect will be smaller than expected for a pure ν (Re–CH₃/ CD₃) vibration. It is also possible that the δ (Re–C–O) vibration mixes with the rocking modes of the methyl group. On deuteration these latter vibrations approach the δ (Re–C– O) mode, shifting it to lower frequency. Anyhow, this band does not belong to ν (Re–CH₃/CD₃). On the other hand, even if this were the case, its resonance Raman effect would be too small for the Re-CH₃/CD₃ bond to be affected appreciably by the lowest-energy electronic transition.

The lowest-frequency band in this region shifts from 451 to 468 cm⁻¹ on deuteration. Such a shift to higher frequency is exceptional, and deviates from the behaviour of ν (Re–CH₃/CD₃) in the parent complexes [Re(CH₃/CD₃)(CO)₅]. In these latter complexes the frequency of ν (Re–CH₃) shifts from 473 to 426 cm⁻¹ on deuteration. The 451 cm⁻¹ Raman band of [Re(CH₃)(CO)₃(dmb)] can therefore not be assigned to ν (Re–CH₃). It may instead belong to a mixed vibration which changes its composition appreciably on deuteration, thus causing a shift to higher frequency. The Raman band at 212 cm⁻¹ does not shift on deuteration. In agreement with literature data it is assigned to ν_s (Re–N) [39,41].

Thus, according to these rR data, the lowest-energy transition of these complexes affects the dmb and carbonyl ligands, the metal–dmb and metal–CO bonds, but not the Re–CH₃/CD₃ bond. This means that it is not a σ (Re–CH₃/CD₃) $\rightarrow \pi^*$ (dmb) transition, but has instead d_{π}(Re) $\rightarrow \pi^*$ (dmb) (MLCT) character. It is noteworthy that deformation and rocking modes of the CH₃/CD₃ ligand are coupled to this electronic transition. This effect of MLCT excitation on the angles of the CH₃/CD₃ ligand may be due to a change of hybridization as a result of the oxidation of the metal or to the repulsive interaction between the CH₃/CD₃ ligand and the radical anion of dmb in the MLCT state.

3.5. Photochemistry

All complexes $[Re(R)(CO)_3(dmb)]$ under study are photolabile and their reactions were followed in situ by

IR, UV–Vis, ¹H NMR and EPR spectroscopy in different solvents and at various temperatures. The complexes reacted thermally in neat CCl₄ and in CCl₄:THF (1:10, vol./vol.) to give [Re(Cl)(CO)₃(dmb)]. They are, however, thermally stable in CHCl₃, CH₂Cl₂ and CCl₄:CH₂Cl₂ (1:10, vol./vol.). Irradiation of the complexes in these latter solvents into their MLCT band ($\lambda_{irr} > 420 \text{ nm}$) resulted in the formation of [Re(Cl)(CO)₃(dmb)]. The quantum yield of this photoreaction varies from 0.4 for $R = CH_3$ and CD_3 to \sim 1 for R = Et, iPr, and Bz. In a typical ¹H NMR experiment a solution of [Re(Et)(CO)₃(dmb)] in CDCl₃ was irradiated in a CIDNP probe through a fiber. The ¹H NMR spectra showed the disappearance of the proton signals of the complex while new signals were observed at 8.89 (d, 2H, 6.0 Hz, py-C₆), 7.99 (s, 2H, py-C₃), 7.34 (d, 2H, 6.0 Hz, py-C₅) and 2.58(s, 6H, py-Me) ppm, belonging to [Re(Cl)(CO)₃(dmb)] [35]. The same product was formed on irradiation of the other complexes and its identity was further established by comparing its IR and UV-Vis spectra with those of a separately prepared sample of $[Re(Cl)(CO)_3(dmb)]$ (see Section 2).

The product formation is consistent with the reaction sequence of Eq. (1). Irradiation causes the homolytic cleavage of the Re–alkyl bond with formation of $[\text{Re}(\text{CO})_3(\text{dmb})]$ and alkyl radicals. The former radicals react with the chlorinated solvent to give $[\text{Re}(\text{Cl})_3(\text{dmb})]$, the secondary reactions of the alkyl radicals were not further investigated during this study.

$$[\operatorname{Re}(\operatorname{R})(\operatorname{CO})_{3}(\operatorname{dmb})] \xrightarrow{h\nu} [\operatorname{Re}(\operatorname{CO})_{3}(\operatorname{dmb})]^{\bullet} + \operatorname{R}^{\bullet}$$
$$[\operatorname{Re}(\operatorname{CO})_{3}(\operatorname{dmb})]^{\bullet} + \operatorname{R}'\operatorname{Cl} \to [\operatorname{Re}(\operatorname{Cl})(\operatorname{CO})_{3}(\operatorname{dmb})] + \operatorname{R}'^{\bullet}$$
(1)

The formation and properties of the [Re(CO)₃(dmb)] radicals were studied in more detail by performing the photoreactions in nonchlorinated solvents at various temperatures, in the presence and absence of other reactants. First of all, the $[Re(R)(CO)_3(dmb)]$ complexes were irradiated in toluene, in the presence of a small excess of the spin trap nitrosodurene. The photolysis was carried out in situ within the EPR spectrometer, using a high-pressure Xelamp and an optical fiber ($\lambda_{irr} > 420$ nm). The EPR data (coupling constants and g-values) of the radical adducts are collected in Table 3, while Fig. 5 presents the measured and simulated EPR spectra of the trapped radicals [ArN(O')-R] $(R = CH_3, Et, Bz and iPr)$. In all cases, only a very low concentration of the [ArN(O')-Re(CO)₃(dmb)] radicals is observed. The measured coupling constants and g-values agree well with those previously reported for these trapped radicals [22,28,48]. Thus, the hyperfine constant $a_{\text{Re}} = 36.0 \text{ G of } [\text{ArN}(\text{O'}) - \text{Re}(\text{CO})_3(\text{dmb})]$ is similar to that of the related radical complex [ArN(O')-Re(CO)3(iPr- $PyCa)](a_{Re} = 36.1 \text{ G})$ [22].

The $[Re(CO)_3(dmb)]$ radicals are coordinatively unsaturated species and will therefore easily take up a Lewis

Table 3

EPR Parameters ^a of the radical adducts [ArN(O')–Re(CO)₃(dmb)], ArN(O')–R and [Re(PPh₃)(CO)₃(dmb)]' formed on irradiation ($\lambda_{exc} > 420$ nm) of [Re(R)(CO)₃(dmb)] in the presence of nitrosodurene (ArNO) ^b and PPh₃ ^c in toluene (293 K)

Complex	Coupling constants	g-value
$R = Me$ $R = Et$ $R = Bz$ $R = iPr$ $[Re(PPh_3)(CO)_3(dmb)]'$	$a_{\rm N} = 13.7; a_{\rm H} = 12.2$ $a_{\rm N} = 13.7; a_{\rm H} = 11.1$ $a_{\rm N} = 13.8; a_{\rm H} = 8.0$ $a_{\rm N} = 13.8; a_{\rm H} = 6.7$ $a_{\rm P} = 26.1; a_{\rm Re} = 19.2$ $a_{\rm H} = 13.4; a_{\rm H} = 36.0$	2.0062 2.0071 2.0071 2.0066 2.0033 2.0047
$[AI-NO-Ke(CO)_3(dIIID)]$	$u_{\rm N} = 13.4, \ u_{\rm Re} = 50.0$	2.0047

^a Coupling constants in Gauss (±0.1G).

^b Spin-adduct formed with 10-fold excess of nitrosodurene (ArNO).

^c Radical formed with 100-fold excess of PPh₃.

^d Low concentration.

base. In order to confirm this adduct formation, the $[Re(R)(CO)_3(dmb)]$ complexes were irradiated in toluene (T = 293 K) in the presence of excess PPh₃. The EPR spectrum of the photoproduct is shown in Fig. 6. The spectrum is simulated with the parameters $a_{\rm P} = 26.1 \, {\rm G}$, $a_{\text{Re}} = 19.2 \text{ G}$ and g = 2.0033. These values are in good agreement with those derived by Klein et al. from the EPR spectrum of the electrochemically prepared radical $[\text{Re}(\text{PPh}_3)(\text{CO})_3(\text{dmb})]$ $(a_{\text{P}} = 20 \text{ G}; a_{\text{Re}} = 20 \text{ G}$ and g = 2.0018 in THF/10⁻¹ M BuNClO₄) [49]. Fig. 6 also presents the EPR spectrum of the radical formed by irradiation in toluene in the absence of PPh₃. When excess PPh₃ is added to this solution after irradiation, the EPR signal changes into that of the [Re(PPh₃)(CO)₃(dmb)] radical. Irradiation of [Re(R)(CO)₃(dmb)] in 2-MeTHF or 2-propanol at T = 123 K gives rise to the formation of similar radical products [26].

The products formed after irradiation of [Re(R)-(CO)₃(dmb)] at different temperatures were characterized with IR spectroscopy; their CO wavenumbers and their assignments are collected in Table 4. Irradiation of the complexes in a 2-MeTHF glass at 123 K results in the formation of a species having CO-stretching vibrations at 2007, 1892 and 1878 cm⁻¹. Similar frequencies have been observed for [Re(EtCN/PrCN)(CO)₃(dmb)] obtained by the one-electron reduction of [Re(Br)(CO)₃(dmb)] in a mixture of EtCN and PrCN [50]. The product IR bands are therefore assigned to the radical species [Re(2-MeTHF)(CO)3-(dmb)]. When this reaction is, however, performed in EtCN/PrCN (4:5, vol./vol.) at room temperature, the [Re-(EtCN/PrCN)(CO)₃(dmb)] radical is not the only product anymore. Extra $\nu(CO)$ bands show up at 2037 and 1933 cm⁻¹, which belong to the cation [Re(EtCN/PrCN)- $(CO)_{3}(dmb)]^{+}$ [50].

Even more, irradiation of the complexes dissolved in THF (RT) causes the formation of three instead of two photoproducts (see Fig. 7). The major product, which is obtained in ~50% yield and which has ν (CO) frequencies of 2018, 1914 and 1893 cm⁻¹, is assigned to the cation [Re(THF)(CO)₃(dmb)]⁺ [51]. Each of the other two pro-



Fig. 5. EPR spectra obtained after irradiation ($\lambda_{irr} > 420$ nm) of [Re(R)(CO)₃(dmb)] in toluene in the presence of nitrosodurene (1:10) at room temperature; (A) R = CH₃; (B) R = Et; (C) R = Bz; (D) = iPr (top) experimental (bottom) simulation.



Fig. 6. EPR spectra obtained after irradiation (λ_{irr} > 420 nm) of [Re(Bz)(CO)₃(dmb)] at room temperature; (left) in toluene, (right) in toluene in the presence of PPh₃ (1:100) (top) experimental (bottom) simulation.

ducts has a yield of \sim 25%, and ν (CO) frequencies of 2004, 1875 cm^{-1} and 1997, 1875 cm^{-1} , respectively. These bands are tentatively assigned to the solvated and naked radicals [Re(THF)(CO)₃(dmb)] and [Re(CO)₃(dmb)], respectively. The formation of radical products agrees with the EPR spectra. We did not observe the formation of the dimer $[\text{Re}_2(\text{CO})_6(\text{dmb})_2]$ from the $[\text{Re}(\text{CO})_3(\text{dmb})]$ radicals produced by irradiation in neat THF. This contrasts with the result reported by Lucia et al. [27] and the observation that such a dimer is formed by the electrochemical reduction of the complexes $[\text{Re}(X)(\text{CO})_3(\text{dmb})]$ $(X = \text{Cl}^-, \text{Br}^-, \text{I}^-,$ Otf^{-} [51]. When, however, the [Re(R)(CO)₃(dmb)] complex is dissolved in a THF/0.1 M Bu₄NBr solution used for the electrochemical experiments, irradiation causes also the formation of $[\text{Re}_2(\text{CO})_6(\text{dmb})_2]$. This is evidenced by the appearance of its ν (CO) bands at 1988, 1951, 1887 and 1859 cm⁻¹ and of the characteristic long-wavelength

absorption band at 800 nm [11,12,51]. The major product is again [Re(THF)(CO)₃(dmb)]⁺, just as observed on irradiation of the complex in neat THF. The remaining ν (CO) frequencies at 2000 and ~1875 cm⁻¹, are tentatively assigned to the solvated radical species.

3.6. Electronic transitions versus photochemistry

The photochemical reactions of these complexes were studied by irradiation into the visible absorption band which, according to the absorption and rR spectra, belongs to MLCT transitions. MLCT states are normally not reactive, but occupation of such a state may still lead to a reaction by surface crossing to a close-lying reactive state. Best known are the ligand-field or metal-centered states, whose population normally gives rise to a heterolytic splitting of a metal-ligand bond. Exceptional are those Table 4

Solvent	<i>T</i> (K)	ν (CO) cm ⁻¹	Yield (%)	(Photo)products	Ref.
2-MeTHF	123	2007 (s) 1892 (s) 1878 (s)	100	[Re(2-MeTHF)(CO) ₃ (dmb)]	
THF/PPh3	293	2018 (s) 1924 (s) 1895 (s)	100	$[\text{Re}(\text{PPh}_3) (\text{CO})_3(\text{dmb})]$	
EtCN/PrCN	293	2011 (s) 1899 (s, br)	35	[Re(EtCN/PrCN)(CO) ₃ (dmb)]	
		2037 (s) 1933 (s, br)	65	[Re(EtCN/PrCN) (CO) ₃ (dmb)] ⁺	
THF/Bu ₄ NBr	293	1988 (s) 1950 (s) 1887 (s) 1845 (s)	25	$[\operatorname{Re}_2(\operatorname{CO})_6(\operatorname{dmb})_2]$	
		2000~1875	25	[Re(THF)(CO) ₃ (dmb)]	
		2017 (s) 1914 (s) 1887 (s)	50	[Re(THF)(CO) ₃ (dmb)] ⁺	
THF	293	1997~1875	25	[Re(THF)(CO) ₃ (dmb)]	
		$2004 \sim 1875$	25	$Re(CO)_3(dmb)]$	
		2018 (s) 1914 (s) 1893 (s)	50	[Re(THF)(CO) ₃ (dmb)] ⁺	
PrCN/Bu ₄ NBr	293	2010 (s) 1905 (s) 1885 (s)		[Re(PrCN)(CO) ₃ (bpy)]	[50]
PrCN/Bu ₄ NBr	293	2039 (s) 1963 (s)		$[Re(PrCN)(CO)_3(bpy)]^+$	[50]
THF/Bu ₄ NBr	293	2015 (s) 1919 (s) 1892 (s)		[Re(PPh ₃)(CO) ₃ (bpy)]	[51]
THF/Bu ₄ NBr	293	2019 (s) 1917 (s) 1894 (s)		[Re(THF)(CO) ₃ (bpy)] ⁺	[51]
THF/Bu ₄ NBr	293	1988 (s) 1951 (s) 1887 (s) 1859 (s)		$[\text{Re}_2(\text{CO})_6(\text{bpy})_2]$	[51]

IR ν (CO) frequencies of the photoproducts of [Re(R)(CO)₃(dmb)] in different solvents and at various temperatures, together with relevant literature data



Fig. 7. IR spectral changes in the carbonyl-stretching region obtained on irradiation at 293 K with 457.9 nm of $[\text{Re}(\text{CH}_3)(\text{CO})_3(\text{dmb})](\times)$ in (left) THF/10⁻¹ M Bu₄NBr and (right) neat THF; (*) = $[\text{Re}(\text{Sv})(\text{CO})_3(\text{dmb})]^+$, (+) = $[\text{Re}(\text{CO})_3(\text{dmb})]^-$, (Δ) = $[\text{Re}(\text{Sv})(\text{CO})_3(\text{dmb})]^-$, (\Box) = $[\text{Re}_2(\text{CO})_6(\text{dmb})_2]$.

complexes in which MLCT excitation leads to homolysis of a metal–ligand bond with formation of radicals. We have observed this phenomenon for quite a few complexes, which all possess a ligand with a high-lying σ orbital (metal fragment [1,7–21], alkyl group [22–26], or halide [6]) and a second ligand (α -diimine, sulfurdiimine, etc.) with a low-lying empty e.g. π^* orbital (see also Section 1). We have explained the occurrence of such a homolyis reaction by the presence of a reactive ${}^3\sigma\pi^*$ state and, quite recently, we have established its triplet character by measuring the nanosecond time-resolved EPR spectra of several of the alkyl radicals formed [26].

According to the MO calculations [52] the HOMO of the model complex [Ru(SnH₃)₂(CO)₂(H-DAB)] is a combination of $p_z(Ru)$ and the antisymmetric combination of the lone pairs of the axial SnH₃-ligands; it mixes strongly with the lowest π^* orbital of H-DAB which has the same

symmetry. As a result the $\sigma \rightarrow \pi^*$ transition of this complex and of related complexes $[Ru(L_1)(L_2)(CO)_2(\alpha-diimine)]$ $(L_1, L_2 = metal fragment, alkyl)$ [32] is strongly allowed, and the MLCT transition can only be weak. In the case of the complexes $[Zn(R)_2(\alpha-diimine)]$ [31] and $[Pt(CH_3)_4(\alpha-di-di)_4)$ imine)] [30], there are even no competing metal– d_{π} orbitals, which might give rise to low-lying MLCT transitions. For most other metal-metal and metal-alkyl bonded complexes there is a strong mixing between the metal-d_{π} and α diimine- π^* orbitals, which makes the MLCT transitions strongly allowed and the $\sigma \rightarrow \pi^*$ transition overlap forbidden [1, and Refs. therein]. The lowest-energy absorption band of these complexes therefore belongs to one or more MLCT transitions, and this MLCT character is indeed evident from the intensity and solvent dependence of the band and from the rR spectra of these complexes. However, even then surface crossing from the MLCT states to the reactive

 ${}^{3}\sigma\pi^{*}$ state and radical formation may occur provided that these states are close in energy. This is evidenced by the observation that variation of the relative energies of the metal- d_{π} orbitals, responsible for the MLCT transitions, and the metal-ligand σ orbital, directly influences the photoreactivity of these complexes [22,28,37]. In some cases the rR spectra more or less agreed with the proposed absence of a $\sigma \rightarrow \pi^*$ transition. Much stronger evidence is, however, provided by the present rR spectra of [Re(CH₃/ $(CD_3)(CO)_3(dmb)$ which show that the effect of deuteration on the resonance Raman active vibrations is only small. Thus, the rR spectra do not provide any evidence for a $\sigma \rightarrow \pi^*$ transition. Because of this, such a transition can only be very weak and at most a minor contributor to the visible absorption band. On the basis of these rR spectra we conclude that the lowest-energy electronic transition of these Re-alkyl complexes has predominant MLCT character. Surface crossing from this state to the reactive ${}^{3}\sigma\pi^{*}$ state will then be followed by homolysis of the Re-R bond.

4. Conclusion

Although the spectroscopic data show that the lowestenergy transitions of these [Re(R)(CO)₃(dmb)] complexes have MLCT character, and that homolysis of the Re–alkyl bond must occur by surface crossing to the reactive ${}^{3}\sigma\pi^{*}$ state, the mechanism of this excited state process can only be established with the use of photochemical quantum yields and time-resolved absorption and emission spectral data. Such investigations are in progress.

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