Inorg. Chem. **2004**, *43*, 4523–4530

Inorganic Chemistry

Article

Rhenium-to-Benzoylpyridine and Rhenium-to-Bipyridine MLCT Excited States of *fac*-[Re(Cl)(4-benzoylpyridine)$_2$(CO)$_3$] and *fac*-[Re(4-benzoylpyridine)(CO)$_3$(bpy)]$^+$: A Time-Resolved Spectroscopic and Spectroelectrochemical Study

Michael Busby,[†] Pavel Matousek,[‡] Michael Towrie,[‡] Ian P. Clark,[‡] Majid Motevalli,[†]
František Hartl,[§] and Antonín Vlček, Jr.*[,†]

Department of Chemistry and Centre for Materials Research, Queen Mary, University of London, Mile End Road, London E1 4NS, United Kingdom, Central Laser Facility, CCLRC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, United Kingdom, and Molecular Photonic Materials, van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, NL-1018 WV Amsterdam, The Netherlands

Received March 15, 2004

The lowest allowed electronic transition of *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$] (bopy = 4-benzoylpyridine) has a Re → bopy MLCT character, as revealed by UV–vis and stationary resonance Raman spectroscopy. Accordingly, the lowest-lying, long-lived, excited state is Re → bopy ^{3}MLCT. Electronic depopulation of the Re(CO)$_3$ unit and population of a bopy π^* orbital upon excitation are evident by the upward shift of ν(C≡O) vibrations and a downward shift of the ketone ν(C=O) vibration, respectively, seen in picosecond time-resolved IR spectra. Moreover, reduction of a single bopy ligand in the ^{3}MLCT excited state is indicated by time-resolved visible and resonance Raman (TR^3) spectra that show features typical of bopy$^{\bullet-}$. In contrast, the lowest allowed electronic transition and lowest-lying excited state of a new complex *fac*-[Re(bopy)(CO)$_3$(bpy)]$^+$ (bpy = 2,2′-bipyridine) have been identified as Re → bpy MLCT with no involvement of the bopy ligand, despite the fact that the first reduction of this complex is bopy-localized, as was proven spectroelectrochemically. This is a rare case in which the localizations of the lowest MLCT excitation and the first reduction are different. ^{3}MLCT excited states of both *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$] and *fac*-[Re(bopy)(CO)$_3$(bpy)]$^+$ are initially formed vibrationally hot. Their relaxation is manifested by picosecond dynamic shifts of ν(C≡O) IR bands. The X-ray structure of *fac*-[Re(bopy)(CO)$_3$(bpy)]PF$_6$·CH$_3$CN has been determined.

Introduction

Rhenium(I) carbonyl complexes of the type *fac*-[Re(Cl)(CO)$_3$(L)$_2$] or *fac*-[Re(L)(CO)$_3$(NN)]$^{n+}$ (NN = polypyridine or α-diimine, L = electron-accepting ligand) often exhibit very interesting properties, such as strong emission from long-lived excited states, inter- and intramolecular excited-state electron transfer, or ligand isomerization.[1−22] Complexes with specially designed L are used as sensors.[23−28] Re → L and Re → NN metal to ligand charge transfer (MLCT) excited states in these complexes often lie in a close energetic proximity to intraligand (IL) states localized either on NN

---

[*] Author to whom correspondence should be addressed. E-mail: a.vlcek@qmul.ac.uk.

[†] University of London.

[‡] CCLRC Rutherford Appleton Laboratory.

[§] University of Amsterdam.

(1) Stufkens, D. J. *Comments Inorg. Chem.* **1992**, *13*, 359−385.
(2) Stufkens, D. J.; Vlček, A., Jr. *Coord. Chem. Rev.* **1998**, *177*, 127−179.
(3) Chen, P.; Mecklenburg, S. L.; Meyer, T. J. *J. Phys. Chem.* **1993**, *97*, 13126−13131.
(4) Wang, Y.; Hauser, B. T.; Rooney, M. M.; Burton, R. D.; Schanze, K. S. *J. Am. Chem. Soc.* **1993**, *115*, 5675−5683.
(5) Chen, P.; Westmoreland, T. D.; Danielson, E.; Schanze, K. S.; Anthon, D.; Neveux, P. E., Jr.; Meyer, T. J. *Inorg. Chem.* **1987**, *26*, 1116−1126.
(6) Chen, P.; Duesing, R.; Graff, D. K.; Meyer, T. J. *J. Phys. Chem.* **1991**, *95*, 5850−5858.
(7) Trammell, S.; Goodson, P. A.; Sullivan, B. P. *Inorg. Chem.* **1996**, *35*, 1421−1422.
(8) Chen, P.; Danielson, E.; Meyer, T. J. *J. Phys. Chem.* **1988**, *92*, 3708−3711.
(9) Schoonover, J. R.; Chen, P.; Bates, W. D.; Dyer, R. B.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 793−797.
(10) Schoonover, J. R.; Strouse, G. F.; Chen, P.; Bates, W. D.; Meyer, T. J. *Inorg. Chem.* **1993**, *32*, 2618−2619.

10.1021/ic049659m CCC: $27.50

or L. Such a situation gives rise to a variety of photochemical and photophysical deactivation mechanisms that may be subtly tuned by structural variations of the NN and L ligands and the medium.[2]

The complex[29] *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$] contains the 4-benzoylpyridine (bopy) ligand, which is an electron acceptor. It possesses a relatively low-lying ${}^3n\pi^*$ IL state, in which the electron is excited from a nonbonding orbital on the ketone oxygen atom. Although an interplay between MLCT and IL states can be expected, this complex displays only a ^{3}MLCT emission both in a low-temperature glass and fluid solution.[29] The bopy ligand is actually very similar to benzophenone, whose long-lived ${}^3n\pi^*$ excited state shows a radical-like reactivity of the $C-O^{\bullet}$ group, abstracting hydrogen atoms from substrates such as 2-propanol. In inert media, benzophenone acts as a sensitizer by triplet energy transfer to suitable energy acceptors. Bopy, like benzophenone, can be reduced to the corresponding ketyl radical anion.[30] Electrochemical reduction of coordinated bopy ligands in [Re(Cl)(CO)$_3$(bopy)$_2$] occurs in two closely spaced one-electron steps at -1.53 and -1.64 V vs Fc/Fc$^+$.[30] The small potential difference demonstrates that the redox orbitals are almost entirely localized on single bopy ligands, with any bopy−bopy electronic interaction being very small. Reduction of one bopy ligand in *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$] has also been accomplished photochemically[31] by reductive quenching of the ^{3}MLCT excited state with NEt$_3$: the long-lived ^{3}MLCT excited state, which may be formally viewed as [Re^{II}(Cl)(CO)$_3$(bopy)(bopy$^{\bullet-}$)], is reduced in a bimolecular reaction with triethylamine to produce [Re^{I}(Cl)(CO)$_3$(bopy)(bopy$^{\bullet-}$)]$^-$ that subsequently reacts by a H-atom transfer forming an alcohol complex.[31] In [Re(bopy)(CO)$_3$(bpy)]$^+$, optical excitation may populate the Re → bopy or Re → bpy MLCT excited state, hereinafter called MLCT(bopy) and MLCT(bpy), respectively. Furthermore, population of a bopy ${}^1n\pi^*$ IL state is also a possibility. The nature of the lowest excited-state cannot thus be a priori predicted. The MLCT(bpy) exited state can either be stable and long-lived, as usual in this type of complexes, or undergo a bpy$^{\bullet-}$ → bopy interligand electron transfer, similar to that found[8,9,11,16,17,19] for *fac*-[Re(*N*-methyl-4,4′-bipyridinium)(CO)$_3$(bpy)]$^{2+}$.

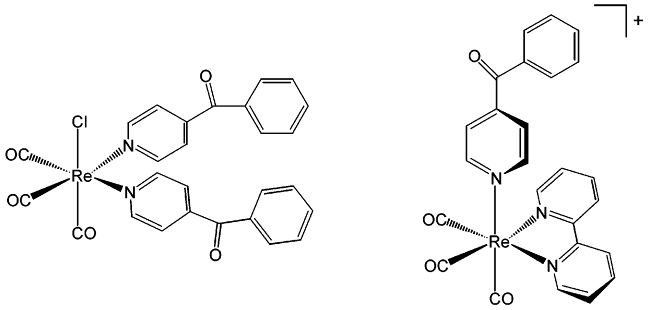

Figure 1. Schematic structures of *fac*-[Re(Cl)(bopy)$_2$(CO)$_3$] (left) and *fac*-[Re(bopy)(CO)$_3$(bpy)]$^+$ (right). These complexes are hereinafter denoted Re(bopy)$_2$ and Re(bopy)(bpy), respectively. The prefix *fac* will be omitted.

Aiming at detailed characterization of low-lying electronic transitions and excited states of Re−bopy complexes, we have investigated ground-state resonance Raman spectra and time-resolved visible and IR absorption spectra of *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$] and *fac*-[Re(bopy)(CO)$_3$(bpy)]$^+$, hereinafter called Re(bopy)$_2$ and Re(bopy)(bpy); see Figure 1. Through a combination of spectroscopic techniques, complemented with spectroelectrochemical measurements, it is shown that the lowest excited state of Re(bopy)$_2$ and Re(bopy)(bpy) have Re → bopy ^{3}MLCT and Re → bpy ^{3}MLCT character, respectively. The X-ray structure of the novel compound Re(bopy)(bpy) is also presented.

Experimental Section

Materials. *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$] was synthesized according to the literature method.[30] The novel complex *fac*-[Re(bopy)(CO)$_3$(bpy)]PF$_6$·CH$_3$CN was prepared using a modified standard procedure[20] for *fac*-[Re(L)(CO)$_3$(NN)]$^+$, in which the PF$_6^-$ counterion was used instead of ClO$_4^-$, through addition of an excess of NH$_4$PF$_6$ to *fac*-[Re(bopy)(CO)$_3$(bpy)]OTf dissolved in methanol.

Characterization of the Complexes. *fac*-[Re(Cl)(CO)$_3$(bopy)$_2$]: 89% yield;

FT-IR (acetonitrile) $\nu_{CO} = 2028$ (s), 1928 (s), 1893 (s), 1670 (m) cm^{-1};

^{1}H NMR [(CD$_3$)$_2$CO; 270 MHz] 7.59 (4H, dd, *J* 7.4, aromatic CH), 7.74 (2H, d, *J* 7.2, aromatic CH), 7.83 (4H, d, *J* 7.4, aromatic CH), 7.87 (4H, d, *J* 7.8, aromatic CH), 9.09 (4H, d, *J* 7.1, aromatic CH);

^{13}C NMR [(CD$_3$)$_2$CO; 67.9 MHz] 125.15, 128.95, 130.18, 134.07, 135.40, 146.87, 154.69, 193.47 (CO).

fac-[Re(bopy)(CO)$_3$(bpy)]PF$_6$·CH$_3$CN: 70% yield;

FT-IR (acetonitrile) $\nu_{CO} = 2036$ (s), 1933 (br), 1672 (s) cm^{-1};

^{1}H NMR [(CD$_3$)$_2$CO 270 MHz] 7.52 (2H, dd, *J* 8.1, aromatic CH), 7.70 (5H, m, aromatic CH), 8.01 (2H, dd, *J* 6.5, aromatic

---

(11) Liard, D. J.; Busby, M.; Farrell, I. R.; Matousek, P.; Towrie, M.; Vlček, A., Jr. *J. Phys. Chem. A* **2004**, *108*, 556−567.

(12) Cabana, L. A.; Schanze, K. S. *Adv. Chem. Ser.* **1990**, *No. 226*, 101−124.

(13) Lucia, L. A.; Wang, Y.; Nafisi, K.; Netzel, T. L.; Schanze, K. S. *J. Phys. Chem.* **1995**, *99*, 11801−11804.

(14) Wang, Y.; Lucia, L. A.; Schanze, K. S. *J. Phys. Chem.* **1995**, *99*, 1961−1968.

(15) Wang, Y.; Schanze, K. S. *J. Phys. Chem.* **1996**, *100*, 5408−5419.

(16) Westmoreland, T. D.; Le Bozec, H.; Murray, R. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5952−5954.

(17) Chen, P.; Curry, M.; Meyer, T. J. *Inorg. Chem.* **1989**, *28*, 2271−2280.

(18) Liard, D. J.; Kleverlaan, C. J.; Vlèek, A., Jr. *Inorg. Chem.* **2003**, *42*, 7995−8002.

(19) Liard, D. J.; Vlček, A., Jr. *Inorg. Chem.* **2000**, *39*, 485−490.

(20) Yam, V. W.-W.; Lau, V. C.-Y.; Wu, L.-X. *J. Chem. Soc., Dalton Trans.* **1998**, 1461−1468.

(21) Sun, S.-S.; Lees, A. J. *Organometallics* **2002**, *21*, 39−49.

(22) Lewis, J. D.; Perutz, R. N.; Moore, J. N. *Chem. Commun.* **2000**, 1865−1866.

(23) Sun, S.-S.; Lees, A. J.; Zavalij, P. Y. *Inorg. Chem.* **2003**, *42*, 3445−3453.

(24) Lo, K. K.-W.; Hui, W.-K.; Ng, D. C.-M.; Cheung, K.-K. *Inorg. Chem.* **2002**, *41*, 40−46.

(25) Yam, V. W.-W.; Lo, K. K.-W.; Cheung, K.-K.; Kong, R. Y.-C. *J. Chem. Soc., Chem. Commun.* **1995**, 1191−1193.

(26) Yam, V. W.-W.; Wong, K. M.-C.; Lee, V. W.-M.; Lo, K. K.-W.; Cheung, K.-K. *Organometallics* **1995**, *14*, 4034.

(27) Guo, X.-Q.; Castellano, F. N.; Li, L.; Lakowicz, J. R. *Anal. Chem.* **1998**, *70*, 632−637.

(28) Oriskovich, T. A.; White, P. S.; Thorp, H. H. *Inorg. Chem.* **1995**, *34*, 1629−1631.

(29) Giordano, P. J.; Fredericks, S. M.; Wrighton, M. S.; Morse, D. L. *J. Am. Chem. Soc.* **1978**, *100*, 2257−2259.

(30) Shu, C.-F.; Wrighton, M. S. *Inorg. Chem.* **1988**, *27*, 4326−4329.

(31) Fredericks, S. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1980**, *102*, 6166−6168.

CH), 8.47 (2H, dd, *J* 6.3, aromatic CH), 8.74 (2H, d, *J* 8.2, aromatic CH), 8.80 (2H, d, *J* 6.8, aromatic CH), 9.49 (2H, d, *J* 6.9, aromatic CH);

^{13}C NMR [$(CD_3)_2CO$; 67.9 MHz] 125.07, 125.82, 128.92, 129.29, 130.03, 134.18, 135.02, 141.62, 147.46, 153.14, 154.17, 156.11, 191.65 (CO), 192.87 (CO), 195.55 (CO);

ES-MS *m/z* 610.2, [M$^+$] − PF$_6$.

Instrumentation. X-ray data were recorded on a CAD4 diffractometer fitted with a low-temperature device operating in the $\omega/2\theta$ scan mode. The structures were solved by standard heavy atom techniques[32] and refined by least-squares fits[32] on F^2. The hydrogen atoms were calculated geometrically and refined with a riding model. The program[33] ORTEP-3 was used for drawing the molecules and WinGX[34] was used to prepare material for publication. Refinement details as well as a full list of atomic coordinates and bond lengths and angles are available in the Supporting Information. CIF data has been deposited at the CCDC, under deposition no. 230056.

Ground-state resonance Raman spectra were obtained using a Coherent Innova 90-5 UV argon-ion laser, with a power output of ca. 50 mW at 457.9 nm and 30 mW at 351.1 nm. The Raman spectra were recorded using 2 mm quartz flow tubes, and the scattered light was collected at 90° from the excitation beam passed through a Spex Triplemate 187 Series monochromator and dispersed across a Princeton Instruments LN/CCD-1024 CCD camera. Spectra were calibrated and solvent bands subtracted using CSMA CCD Spectrometric Multichannel Analysis Software, version 2.4a, Princeton Instruments Inc. program.

Time-resolved UV−vis absorption spectra were measured using the experimental setup at the Institute of Molecular Chemistry, University of Amsterdam.[35] A ∼130 fs and 390 nm pump pulse was generated by frequency doubling of the Ti:sapphire laser output. White-light continuum probe pulses were generated by focusing the 800 nm fundamental in a sapphire plate.

Time-resolved IR and Kerr-gate resonance Raman used the equipment and procedures described in detail previously.[11,36−41] In short, the sample solution was excited (pumped) at 400 nm, using frequency-doubled pulses from a Ti:sapphire laser of ∼200 fs duration (fwhm) in the case of time-resolved visible and IR absorption spectroscopy, while pulses of 1−2 ps duration were used for Raman and emission studies. TRIR spectra were probed with IR (∼200 fs) pulses obtained by difference-frequency generation. The IR probe pulses cover spectral range ca. 200 cm^{-1} wide and are tunable from 1000 to 5000 cm^{-1} (i.e., 2−10 μm). Kerr-gate TR^3 spectra were probed at 600 or 400 nm using an OPA or frequency-doubled Ti:sapphire laser pulses, respectively. Kerr gate was used to remove all long-lived emission from the Raman signal. TR^3 spectra were corrected for the Raman signal due to the solvent and the solute ground state by subtracting the spectra obtained at negative time delays (−50, −20 ps) and by subtracting any weak residual emission that passed through the Kerr gate. The sample solutions for picosecond TR^3 and TRIR experiments were flowed as a 0.5 mm open jet and through a 0.5 mm CaF$_2$ raster-scanned cell, respectively.

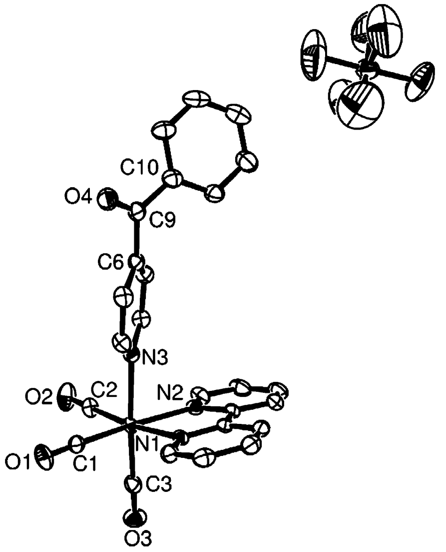

Figure 2. ORTEP diagram of [Re(bopy)(CO)$_3$(bpy)]PF$_6$•CH$_3$CN, showing 40% probability ellipsoids. The solvent molecule is omitted.

The spectral bands observed in TRIR spectra were fitted by Lorentzian functions to determine accurately their center positions, widths, and areas. All spectral fitting procedures were performed using Microcal Origin 7 software.

The cyclic voltammogram of Re(bopy)(bpy) was recorded on a model 270/250 potentiostat from EG&G Instruments Inc., Princeton Applied Research. A home-built electrochemical cell was used with a three-electrode system: working electrode (0.5 mm^2 Pt); auxiliary electrode (Pt coil); an Ag-coil pseudoreference electrode. All values were obtained at a scan rate of 100 mV/s with 0.1 M Bu$_4$NPF$_6$ supporting electrolyte and 1−2 mM concentration of the complex. Spectroelectrochemical experiments were performed in *n*-PrCN using OTTLE cells whose design was published previously.[42−44]

Results

X-ray Crystallography. Crystals of [Re(bopy)(CO)$_3$(bpy)]-PF$_6$•CH$_3$CN were grown from an acetonitrile solution by slow solvent evaporation. The structure was determined by X-ray diffraction. The ORTEP diagram is shown in Figure 2, and selected bond lengths and angles are summarized in Table 1, while all the structural data are collected in the Supporting Information. Bond distances and angles around the Re(1) metal center are typical for [Re(L)(CO)$_3$(NN)]$^+$ complexes,[45] with the N(1)−Re(1)−N(2) bite angle being

---

(32) Sheldrick, G. M. *SHELX97, Program for crystal structure determination and refinement*; University of Göttingen: Göttingen, Germany, 1998.

(33) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(34) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

(35) Vergeer, F. W.; Kleverlaan, C. J.; Stufkens, D. J. *Inorg. Chim. Acta* **2002**, *327*, 126−133.

(36) Vlček, A., Jr.; Farrell, I. R.; Liard, D. J.; Matousek, P.; Towrie, M.; Parker, A. W.; Grills, D. C.; George, M. W. *J. Chem. Soc., Dalton Trans.* **2002**, 701−712.

(37) Matousek, P.; Parker, A. W.; Taday, P. F.; Toner, W. T.; Towrie, M. *Opt. Comm.* **1996**, *127*, 307−312.

(38) Towrie, M.; Parker, A. W.; Shaikh, W.; Matousek, P. *Meas. Sci. Technol.* **1998**, *9*, 816−823.

(39) Matousek, P.; Towrie, M.; Stanley, A.; Parker, A. W. *Appl. Spectrosc.* **1999**, *53*, 1485−1489.

(40) Matousek, P.; Towrie, M.; Ma, C.; Kwok, W. M.; Phillips, D.; Toner, W. T.; Parker, A. W. *J. Raman Spectrosc.* **2001**, *32*, 983−988.

(41) Towrie, M.; Grills, D. C.; Dyer, J.; Weinstein, J. A.; Matousek, P.; Barton, R.; Bailey, P. D.; Subramaniam, N.; Kwok, W. M.; Ma, C. S.; Phillips, D.; Parker, A. W.; George, M. W. *Appl. Spectrosc.* **2003**, *57*, 367−380.

(42) Krejćik, M.; Danìk, M.; Hartl, F. *J. Electroanal. Chem., Interfacial Electrochem.* **1991**, *317*, 179−187.

(43) Hartl, F.; Luyten, H.; Nieuwenhuis, H. A.; Schoemaker, G. C. *Appl. Spectrosc.* **1994**, *48*, 1522−1528.

(44) Mahabiersing, T.; Luyten, H.; Nieuwendam, R. C.; Hartl, F. *Collect. Czech.. Chem. Commun.* **2003**, *68*, 1687−1709.

(45) Busby, M.; Liard, D. J.; Motevalli, M.; Toms, H.; Vlček, A., Jr. *Inorg. Chim. Acta* **2004**, *357*, 167−176.

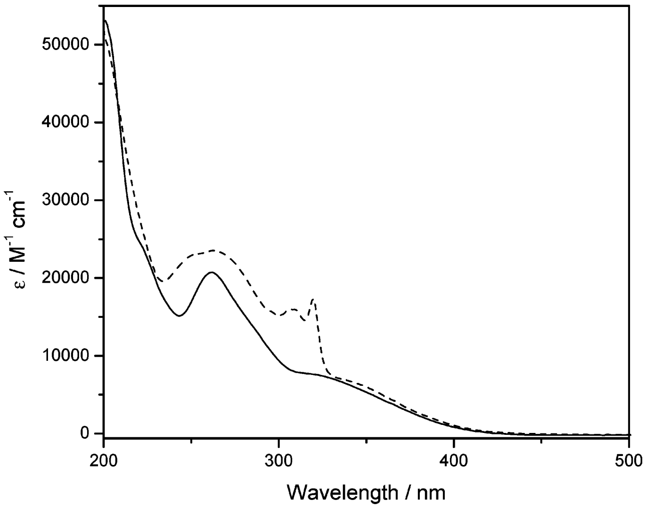

Figure 3. UV−vis absorption spectra of [Re(Cl)(bopy)$_2$(CO)$_3$] (solid line) and [Re(bopy)(CO)$_3$(bpy)]$^+$ (dashed line) measured in acetonitrile.

Table 1. Selected Bond Lengths and Angles of *fac*-[Re(bopy)(CO)$_3$(bpy)]PF$_6$

Lengths/Å			
Re(1)−C(1)	1.910(5)	O(1)−C(1)	1.158(7)
Re(1)−C(3)	1.923(6)	O(2)−C(2)	1.131(6)
Re(1)−C(2)	1.931(5)	O(3)−C(3)	1.152(7)
Re(1)−N(2)	2.159(4)	O(4)−C(9)	1.222(7)
Re(1)−N(1)	2.166(4)	C(6)−C(9)	1.516(7)
Re(1)−N(3)	2.218(4)	C(9)−C(10)	1.479(8)
Angles/deg			
C(1)−Re(1)−C(2)	86.9(2)	C(1)−Re(1)−N(3)	95.34(19)
C(1)−Re(1)−C(3)	89.4(2)	C(2)−Re(1)−N(3)	90.61(19)
C(3)−Re(1)−C(2)	88.1(2)	C(3)−Re(1)−N(3)	175.02(19)
C(1)−Re(1)−N(1)	96.84(18)	N(1)−Re(1)−N(2)	75.10(16)
C(3)−Re(1)−N(1)	97.61(18)	N(1)−Re(1)−N(3)	83.35(15)
C(2)−Re(1)−N(1)	173.18(18)	N(2)−Re(1)−N(3)	84.30(15)
C(1)−Re(1)−N(2)	171.93(18)	O(4)−C(9)−C(6)	118.2(5)
C(2)−Re(1)−N(2)	101.20(19)	O(4)−C(9)−C(10)	121.1(5)
C(3)−Re(1)−N(2)	91.21(19)	C(10)−C(9)−C(6)	120.6(5)

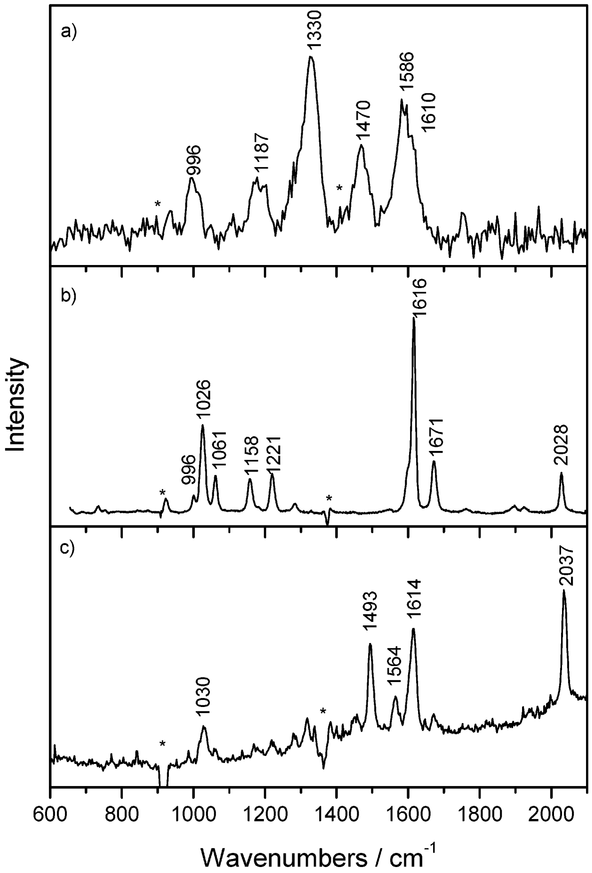

Figure 4. Ground and excited-state resonance Raman spectra: (a) Kerr-gate picosecond time-resolved resonance Raman spectrum (TR^3) of [Re(Cl)(bopy)$_2$(CO)$_3$], measured using 600 nm probe at 8 ps after 400 nm laser pulse excitation; (b) ground-state resonance Raman spectrum of [Re(Cl)(bopy)$_2$(CO)$_3$], measured using stationary 457.9 nm irradiation with emission background subtracted; (c) ground-state resonance Raman spectrum of [Re(bopy)(CO)$_3$(bpy)]$^+$, measured upon stationary irradiation at 351.1 nm. All spectra were measured in acetonitrile. Asterisks indicate regions of solvent subtraction.

characteristically small, 75.10°. The bopy C(9)−O(4) bond distance is 1.22 Å. This is a typical value for aromatic ketones such as benzophenone, for which an identical C═O bond length was determined.[46] The nonplanarity between the two rings of the bopy ligand indicates that there is no substantial π orbital overlap and conjugation that would overcome the steric repulsion between the rings, at least in the solid state. A similar twisted structure was found for benzophenone.[46]

UV−Vis Absorption and Resonance Raman Spectroscopy. UV−vis absorption spectra of both complexes (Figure 3) are very similar, exhibiting a broad absorption band between ca. 330 and 410 nm, which is characteristic of an MLCT transition, although IL(bopy) transitions may contribute as well. In addition to the bands seen for Re(bopy)$_2$, the spectrum of Re(bopy)(bpy) shows a typical structured absorption with sharp peaks at 320 and 307 nm due to bpy intraligand (IL) transitions. The band seen for both complexes at ca. 260 nm originates in an IL(bopy) $\pi\pi^*$ transition(s). To obtain more detailed information on the nature of low-lying electronic transitions of both complexes, their (pre)-resonance Raman spectra have been investigated.

The preresonance Raman spectrum of Re(bopy)$_2$ acquired upon CW excitation at 457.9 nm, Figure 4b, shows an enhanced band at 2028 cm^{-1} which is due to the A′(1) ν(C≡O) vibration of the Re(CO)$_3$ moiety and a group of bands corresponding to bopy-localized vibrations, including a band due to the bopy ν(C═O) vibration[29,30] at 1671 cm^{-1}. The most intense band at 1616 cm^{-1} seems to contain at least two unresolved vibrations, which correspond to ring C−C stretching modes.[47] Other bopy-localized vibrations are present between 1000 and 1250 cm^{-1} and are assigned to C−Ph/py stretching and C−H bending modes.[47] The resonance enhancement of Raman bands due to vibrations of both the Re(CO)$_3$ and the bopy ligand is indicative of the 457.9 nm excitation being in preresonance with the MLCT(bopy) transition, although a small contribution from a nearby IL-(bopy) transition cannot be entirely excluded.

Re(bopy)(bpy) shows a significantly different resonance Raman spectrum, Figure 4c. Excitation at 351.1 nm was used

---

(46) Kutzke, H.; Klapper, H.; Hammond, R. B.; Roberts, K. J. *Acta Crystallogr., Sect. B* **2000**, *56*, 486.

(47) Tahara, T.; Hamaguchi, H.; Tasumi, M. *J. Phys. Chem.* **1987**, *91*, 5875−5880.

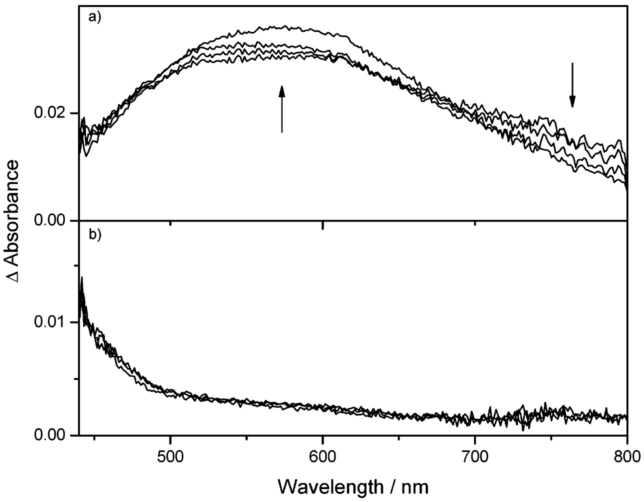

Figure 5. Time-resolved visible absorption spectra of (a) [Re(Cl)(bopy)$_2$(CO)$_3$], measured at 2, 3, 10, and 75 ps, and (b) [Re(bopy)(CO)$_3$(bpy)]$^+$, measured at 4, 40, and 1000 ps. Both were measured in acetonitrile, after excitation at 393 nm. The spectra evolve in the directions of the arrows.

to avoid interfering emission. The spectrum shows a strongly enhanced band pertaining to the A′(1) ν(C≡O) vibration at 2037 cm^{-1}. Its relative intensity is much stronger than in the case of Re(bopy)$_2$. The band due to the bopy C═O stretching vibration is extremely weak, probably not resonantly enhanced. Bands between 1000 and 1600 cm^{-1} can all be attributed[9,48,49] to vibrations of the bpy ligand. Overall, the resonance Raman spectrum of Re(bopy)(bpy) is similar to those[9,48] of [Re(Cl)(CO)$_3$(bpy)] and [Re(4-Etpy)(CO)$_3$(bpy)]$^+$, perhaps with the exception of the 1615 cm^{-1} band, whose much larger relative intensity could indicate a bopy contribution. It can be concluded that the lowest absorption band of Re(bopy)(bpy) originates predominantly in a MLCT(bpy) transition, with a possible IL(bopy) contribution.

Time-Resolved Visible Absorption (TA) and Resonance Raman Spectra (TR^3). TA spectra of the two complexes measured using 393 nm excitation show very different behavior; see Figure 5. For Re(bopy)$_2$, a very broad absorption is seen, with a maximum at ca. 575 nm, which closely resembles the UV−vis spectrum of the electrochemically generated [Re(Cl)(CO)$_3$(bopy)(bopy$^{\bullet-}$)]$^-$ radical anion.[30] This provides evidence that the 575 nm TA band originates in a $\pi\pi^*$ transition of a single reduced bopy$^{\bullet-}$ ligand which is formed upon MLCT(bopy) excitation. The TA spectrum is thus attributed to a ^{3}MLCT(bopy) excited state, formulated approximately as [Re^{II}(Cl)(CO)$_3$(bopy)(bopy$^{\bullet-}$)]. Interestingly, the TA band is seen to narrow and blue-shift during the first 10 ps, which is assigned to vibrational cooling of the excited molecule. Once the cooling is complete, the absorption decreases very slowly in intensity, indicating that the ^{3}MLCT(bopy) excited state lives into the nanoseconds time domain.

The assignment of the lowest excited state of Re(bopy)$_2$ as ^{3}MLCT is further supported by its time-resolved resonance Raman spectrum (TR^3); see Figure 4a. The spectrum was measured at 8 ps after 400 nm excitation using a probe wavelength of 600 nm that was tuned into the strong TA band. The TR^3 spectrum is consistent with the reduction of one bopy ligand upon excitation. The ground-state band at 1671 cm^{-1} due to the ketone ν(C═O) vibrations disappears. This vibration seems to be manifested in the excited-state TR^3 spectrum by a ~1610 cm^{-1} shoulder, as is indicated by comparison with TRIR spectra; vide infra. The new bands at 1586, 1470, 1330, 1187, and 996 cm^{-1} are attributed to the to C−Ph/py stretching and C−H bending modes of the bopy$^{\bullet-}$ radical-anionic ligand.[47]

For Re(bopy)(bpy), the TA signal is much weaker and comprises of a broad shoulder between 500 and 600 nm and an absorbance sharply rising into the UV region; see Figure 5b. The TA spectrum of Re(bopy)(bpy) is very similar to the spectra of typical ^{3}MLCT excited states[49,50] of [Re(Etpy)(CO)$_3$(dmb)]$^+$ (dmb = 4,4′-dimethyl-2,2′-bipyridine) and [Re(Cl)(CO)$_3$(bpy)], warranting the same assignment of the lowest excited state of Re(bopy)(bpy). The TA signal does not decay during the time interval investigated, in agreement with the expected long ^{3}MLCT(bpy) excited-state lifetime.

The assignment of the lowest excited state of Re(bopy)(bpy) as ^{3}MLCT(bpy) is further supported by its emission spectrum which shows a broad, unstructured MLCT-type band both in a glass and a fluid solution. The following emission maxima were determined (corrected for the instrument response): 515 nm (77 K, MeOH/EtOH (4/5 v/v) glass), 578 nm (RT (room temperature), CH$_3$CN), 580 nm (RT, MeOH/EtOH (4/ 5 v/v)). The Re(bopy)(bpy) emission in fluid CH$_3$CN occurs very close to the typical MLCT(bpy) emission of Re(4-Etpy)(CO)$_3$(bpy)]$^+$ (571 nm).[51] The observed rigidochromism is also characteristic of MLCT(bpy) states.

Time-Resolved Infrared Spectroscopy, TRIR. TRIR experiments were performed to investigate the behavior of the C≡O and C═O stretching modes of the Re(CO)$_3$ and bopy moieties, respectively, after 400 nm excitation.

For Re(bopy)$_2$, excitation essentially preserves the ground-state ν(C≡O) IR pattern with all the bands being shifted to higher wavenumbers, Figure 6. In particular, the A′(1) ν(C≡O) vibration shifts by +54 cm^{-1} upon excitation in both CH$_2$Cl$_2$ and acetonitrile, while the ketone ν(C═O) band[30] undergoes a downward shift[52] of −55 cm^{-1}, from 1670 to 1615 cm^{-1}, Figure 7. This behavior confirms the ^{3}MLCT(bopy) character of the lowest excited state: Decrease of the electron density at the Re atom upon MLCT excitation diminishes the Re → CO π back-donation, which is manifested by an upward shift of ν(C≡O) frequencies.[51,53−57]

---

(48) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067−1069.

(49) Liard, D. J.; Busby, M.; Matousek, P.; Towrie, M.; Vlček, A., Jr. *J. Phys. Chem. A* **2004**, *108*, 2363−2369.

(50) Kalyanasundaram, K. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 2401−2415.

(51) Dattelbaum, D. M.; Omberg, K. M.; Schoonover, J. R.; Martin, R. L.; Meyer, T. J. *Inorg. Chem.* **2002**, *41*, 6071−6079.

(52) The assignment of the 1615 cm^{-1} band as ν(C═O) is based on its high intensity and comparison with IR spectra[62] of radical anions of benzophenone derivatives bearing an electron-accepting substituent on the phenyl rings, whose spectra were assigned by isotopic substitution.

(53) Glyn, P.; George, M. W.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1655−1657.

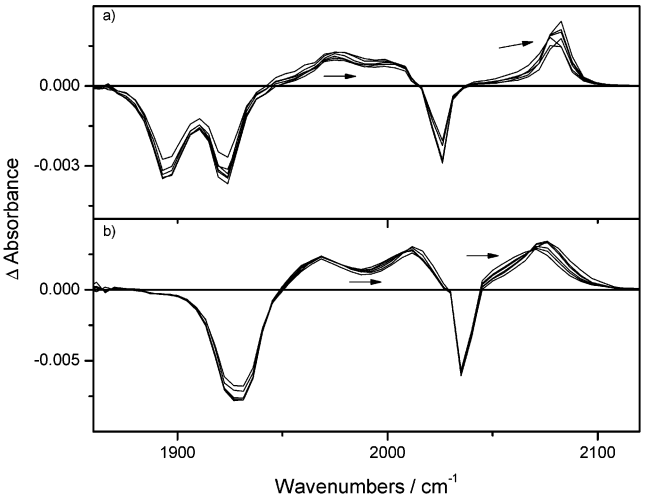

Figure 6. Time-resolved infrared spectra in the region of Re(CO)$_3$ $\nu(\mathrm{C\equiv O})$ vibrations measured in acetonitrile after 400 nm excitation: (a) [Re(Cl)(bopy)$_2$(CO)$_3$], spectra measured at 2, 4, 8, 10, 100, and 1000 ps; (b) [Re(bopy)(CO)$_3$(bpy)]$^+$, spectra measured at 2, 3, 4, 10, 15, and 1000 ps. The IR features undergo small dynamical shifts in the directions of the arrows. Experimental points are separated by 4−5 cm^{-1}.

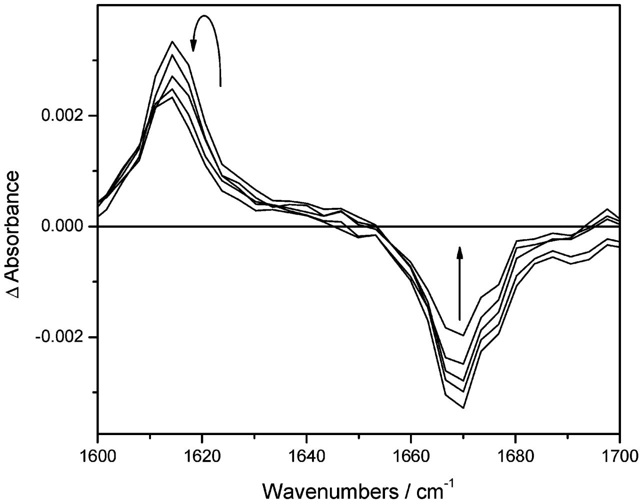

Figure 7. Time-resolved infrared spectra [Re(Cl)(bopy)$_2$(CO)$_3$] in the region of the ketone $\nu(\mathrm{C=O})$ measured in acetonitrile at 2, 4, 40, 100, and 1000 ps after 400 nm excitation. The spectra evolve in the directions of the arrows. Experimental points are separated by 4−5 cm^{-1}.

At the same time, the excited electron density populates a π^* orbital of a bopy ligand, weakening the ketone C=O bond. This results in a decrease of the C=O stretching frequency. The observed $\nu(\mathrm{C\equiv O})$ shift is higher than that measured for [Re(Cl)(CO)$_3$(4,4′-bpy)$_2$] (+30 cm^{-1}),[54,55] though less than that found for [Re(Cl)(CO)$_3$(XQ$^+$)$_2$]$^{2+}$, where XQ$^+$ is *N*-methyl-4,4′-bipyridinium (MQ$^+$) and *N*-phenyl-4,4′-bipyridinium (PQ$^+$), (+67 and +65 cm^{-1}, respectively.[58] (Note that the magnitude of the shift is related to the charge separation upon MLCT excitation.) Downward shifts of organic $\nu(\mathrm{C=O})$ vibrations were seen previously upon MLCT excitation of complexes with carboxylated 2,2′-bipyridine ligands [Ru(bpy)$_2$(4-CO$_2$Et)-4′-CH$_3$-2,2′-bpy)]$^{2+}$ [59] and [Re(4-Etpy)(CO)$_3$(4,4′-CO$_2$Et)-2,2′-bpy)]$^+$ [60] and in [Pt(Cl)$_2$(4,4′-CO$_2$Et)-2,2′-bpy)].[61] The $\nu(\mathrm{C=O})$ shifts in these complexes fall between −26 and −46 cm^{-1}. The −55 cm^{-1} $\nu(\mathrm{C=O})$ shift, found herein, is less than that accompanying benzophenone reduction, −262 cm^{-1}, but close to values found for the reduction of benzophenone derivatives bearing electron-accepting substituents.[62] This can be rationalized by the excited electron density being largely delocalized over the bopy$^{\bullet-}$ ligand, polarized toward the pyridine ring. The N-coordinated Re$^{\mathrm{II}}$(CO)$_3$ unit acts as an electron acceptor toward the bopy$^{\bullet-}$ ligand. It follows that the charge separation in the excited state is not complete and the C=O group acquires only partial ketyl, C$^\bullet$−O$^-$, character. This conclusion agrees with the relatively small upward shift of the $\nu(\mathrm{C\equiv O})$ vibrations of Re(CO)$_3$.

The upward shift of $\nu(\mathrm{C\equiv O})$ IR bands consists of two components: one instantaneous that occurs within the instrument time resolution; a dynamic one that follows on a picosecond time scale and originates in vibrational relaxation and solvation.[63] In particular, the +54 cm^{-1} shift of the A′$_1$ band consists of a ca. +45.6 cm^{-1} "instantaneous" shift and a +8.4 ± 0.9 cm^{-1} dynamic shift that is biexponential with time constants of 1.8 ± 0.2 ps (88%) and 17.1 ± 4.3 ps (12%). The width of this band narrows by ca. 30% with a time constant of 5.6 ± 0.9 ps. The bopy $\nu(\mathrm{C=O})$ band shows a small dynamic blue-shift of about +1.5 cm^{-1} with a time constant estimated as 14.5 ± 2.5 ps.

For Re(bopy)(bpy) in acetonitrile, the TRIR spectrum displays an upward shift of the Re(CO)$_3$ $\nu(\mathrm{C\equiv O})$ bands on excitation, while the lower ground-state broad band, which corresponds to merged A″ + A′(2) vibrations, splits into two bands, Figure 6b and Table 2. As observed also in TA, the TRIR bands do not undergo any decay, in accordance with the very long excited-state lifetime. The change of the excited-state $\nu(\mathrm{C\equiv O})$ IR spectral pattern and the +42 cm^{-1} upward shift of the high-energy 2034 cm^{-1} A′(1) $\nu(\mathrm{C\equiv O})$ band upon excitation are similar to those observed for [Re(Etpy)(CO)$_3$(dmb)]$^+$ (34 cm^{-1}),[11,49] providing good evidence that the excited electron density is localized on the bpy ligand, instead of bopy. This conclusion is further supported by the lack of any changes in the region of ketone $\nu(\mathrm{C=O})$ vibrations, between 1600 and 1700 cm^{-1}. It can thus be concluded that the lowest excited state of Re(bopy)(bpy) has a ^{3}MLCT(bpy) character.

---

(54) George, M. W.; Johnson, F. P. A.; Westwell, J. R.; Hodges, P. M.; Turner, J. J. *J. Chem. Soc., Dalton Trans.* **1993**, 2977−2979.

(55) Gamelin, D. R.; George, M. W.; Glyn, P.; Grevels, F.-W.; Johnson, F. P. A.; Klotzbucher, W.; Morrison, S. L.; Russell, G.; Schaffner, K.; Turner, J. J. *Inorg. Chem.* **1994**, *33*, 3246−3250.

(56) Dattelbaum, D. M.; Meyer, T. J. *J. Phys. Chem. A* **2002**, *106*, 4519−4524.

(57) Záliš, S.; Farrell, I. R.; Vlček, A., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 4580−4592.

(58) Busby, M.; Matousek, P.; Towrie, M.; Vlček, A., Jr. Manuscript in preparation.

(59) Chen, P.; Omberg, K. M.; Kavaliunas, D. A.; Treadway, J. A.; Palmer, R. A.; Meyer, T. J. *Inorg. Chem.* **1997**, *36*, 954−955.

(60) Chen, P.; Palmer, R. A.; Meyer, T. J. *J. Phys. Phem. A* **1998**, *102*, 3042−3047.

(61) Weinstein, J. A.; Grills, D. C.; Towrie, M.; Matousek, P.; Parker, A. W.; George, M. W. *Chem. Commun.* **2002**, 382−383.

(62) Juchnovski, I. N.; Kolev, T. M. *Spectrosc. Lett.* **1985**, *18*, 481−490.

(63) Asbury, J. B.; Wang, Y.; Lian, T. *Bull. Chem. Soc. Jpn.* **2002**, *75*, 973−983.

Table 2. Ground- and Excited-State ν(CO) Wavenumbers of [Re(Cl)(bopy)$_2$(CO)$_3$], [Re(Cl)(4,4′-bpy)$_2$(CO)$_3$], [Re(bopy)(CO)$_3$(bpy)]$^+$, and [Re(Etpy)(CO)$_3$(dmb)]$^+$, Measured in Acetonitrile, at 500 ps, Once Vibrational Relaxation Is Completed

	ground state				excited state				$\Delta\nu$			
compd	C=O	A″	A′(2)	A′(1)	C=O	A″	A′(2)	A′(1)	C=O	A″	A′(2)	A′(1)
Re(bopy)$_2$	1670	1895	1923	2026	1615	1976	1999	2080	−55	+81	+76	+54
Re(4,4-bpy)$_2$^{a} [55]		1891	1927	2025		1957	1992	2055		+66	+65	+30
Re(bopy)(bpy)	1670	1929^{b}	1929	2035		1968	2012	2076		+39	+83	+41
Re(Etpy)(dmb)[11,49]		1930^{b}	1930	2034		1970	2013	2068		+40	+83	+34

^{a} Measured in CH$_2$Cl$_2$. ^{b} Merged doublet.

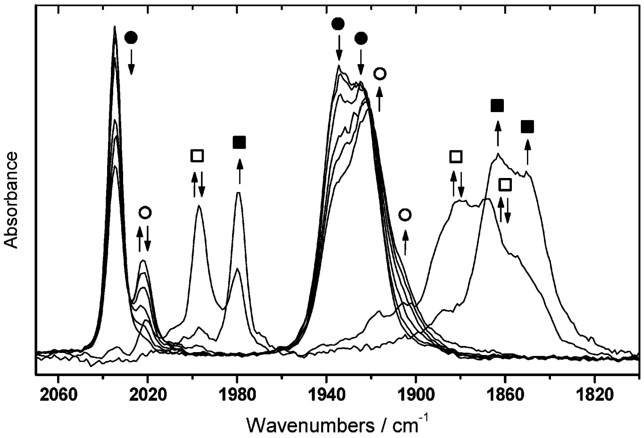

Figure 8. Low-temperature IR spectroelectrochemical reduction of Re(bopy)(bpy) measured in butyronitrile in the presence of 10^{-1} M Bu$_4$NPF$_6$ at 223 K: ●, Re(bopy)(bpy); ○, Re(bopy$^{\bullet-}$)(bpy); □, Re(bopy$^{\bullet-}$)(bpy$^{\bullet-}$); ■, [Re(PrCN)(CO)$_3$(bpy^{2-})]$^-$.

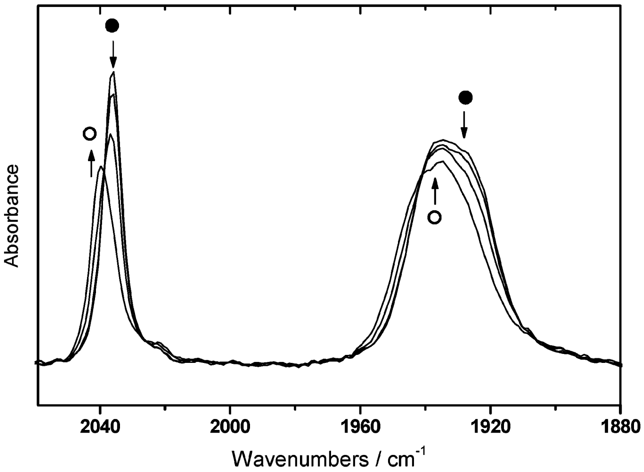

Figure 9. Room-temperature IR spectroelectromical reduction of Re(bopy)(bpy) measured in butyronitrile in the presence of 10^{-1} M Bu$_4$NPF$_6$ at 293 K: ●, Re(bopy)(bpy); ○, [Re(PrCN)(CO)$_3$(bpy)]$^+$.

The A′(1) ν(C≡O) band shift has an instantaneous component of $+21.7 \pm 2$ cm^{-1} followed by a biexponential dynamic shift of $+21.3 \pm 2$ cm^{-1}, which occurs with 1.6 ± 0.2 ps (85%) and 26.6 ± 3.6 ps (15%) time constants. The band narrows by 30% with a 3.0 ± 0.2 ps time constant. The middle excited-state ν(C≡O) band at 2012 cm^{-1} also shows an upward shift and narrowing. These vibrational dynamics are very similar to those found for [Re(Etpy)(CO)$_3$(dmb)]$^+$ in acetonitrile[11,49] and [Re(Cl)(CO)$_3$(bpy)] in dimethylformamide.[63]

Electrochemistry and Spectroelectrochemistry of Re(bopy)(bpy). Re(bopy)(bpy) in a CH$_3$CN solution is reduced in two electrochemically and chemically reversible one-electron steps at $E_{1/2} = -1.44$ and -1.66 V (vs Fc/Fc$^+$). These values are close to the first reduction potentials of Re(bopy)$_2$ (-1.53 V)[30] and [Re(4-Et-pyridine)(CO)$_3$(bpy)]$^+$ (-1.56 V),[51] respectively. This makes it hard to decide whether the first reduction is localized on the bopy or the bpy ligand. Nevertheless, the bopy localization of the first reduction step was confirmed by IR spectroelectrochemistry measured at low temperature, 223 K; see Figure 8. In situ reduction initially produces a species characterized by IR bands at 2022, 1919, 1905, and 1624 cm^{-1}. The disappearance of the parent ketone ν(C═O) band at 1670 cm^{-1} and its shift to 1624 cm^{-1} demonstrate[52,62] that the first reduction is indeed bopy-localized, producing Re(bopy$^{\bullet-}$)(bpy). This conclusion is further supported by the ν(CO) wavenumbers, which are very close to those measured for [Re(L)(CO)$_3$(bpy)] complexes where L is an anionic ligand (e.g.: L = HCOO$^-$, 2019, 1916, 1894 cm^{-1}; L = Cl$^-$, 2020, 1914, 1897 cm^{-1}).[64] A much larger downward shift of ν(CO) wavenumbers would be expected for a bpy-localized reduction.[64,65] UV−vis spectroelectrochemistry studied at 223 K in *n*-PrCN shows that reduction of Re(bopy)(bpy) is accompanied by growth of a band at ca. 360 nm and of a broad band with maxima at 500 and ~570 nm, which tails toward ca. 700 nm. These features resemble the visible spectrum[30] of Re(bopy$^{\bullet-}$)(bopy), again supporting the formulation of the first reduction product as Re(bopy$^{\bullet-}$)(bpy). Accordingly, the typical[66] bpy$^{\bullet-}$ $\pi\pi^*$ bands at 800 nm and longer wavelengths are missing. The IR features of Re(bopy$^{\bullet-}$)(bpy) decrease during continuing reduction, being replaced by IR bands at 1997 and 1884 cm^{-1}, which are attributed to the second reduction product Re(bopy$^{\bullet-}$)(bpy$^{\bullet-}$). This assignment is based on comparison with the spectra[64] of the complexes [Re(Cl)(CO)$_3$(bpy$^{\bullet-}$)]$^-$ (1998, 1885, 1868 cm^{-1}) and [Re(HCOO)(CO)$_3$(bpy$^{\bullet-}$)]$^-$ (1997, 1879 cm^{-1}) which contain bpy$^{\bullet-}$ *and* an anionic axial ligand. Further reduction is accompanied by bopy$^{\bullet-}$ substitution, producing [Re(PrCN)(CO)$_3$(bpy^{2-})]$^-$, which is characterized by ν(CO) bands at 1980, 1863, and 1851 cm^{-1}.[64]

IR spectroelectrochemistry at room temperature (Figure 9) shows completely different behavior, whereby the bopy ligand undergoes an electrode-catalyzed substitution[67,68] by the solvent forming [Re(PrCN)(CO)$_3$(bpy)]$^+$ (2040, 1935 (br)

---

(64) Johnson, F. P. A.; George, M. W.; Hartl, F.; Turner, J. J. *Organometallics* **1996**, *15*, 3374−3387.

(65) van Outersterp, J. W. M.; Hartl, F.; Stufkens, D. J. *Organometallics* **1995**, *14*, 3303−3310.

(66) Krejčík, M.; Vlček, A. A. *J. Electroanal. Chem.* **1991**, *313*, 243−257.

(67) Miholová, D.; Vlček, A. A. *J. Organomet. Chem.* **1982**, *240*, 413−419.

cm^{-1}).[65] Free bopy, characterized by an undiminished 1670 cm^{-1} band, is also present in the solution.

Discussion

By a combination of steady-state and time-resolved spectroscopic techniques, it has been demonstrated that the lowest allowed electronic transition of $Re(bopy)_2$ is Re → bopy MLCT, which is closely followed in energy by a $\pi\pi^*$ bopy IL transition. Accordingly, the lowest-lying electronic excited state is ^{3}MLCT(bopy), in which the excited electron density is predominantly localized on a single bopy ligand, which acquires $bopy^{\bullet-}$ character. This excited state is long-lived, and a radical-like photochemical reactivity can thus be expected from $Re(bopy)_2$.

Re(bopy)(bpy) is an interesting case of a complex that contains two electron-accepting ligands which have similar reduction potentials. The lowest excited state of Re(bopy)(bpy) can be either of a MLCT(bopy) or MLCT(bpy) character. As was demonstrated electrochemically and spectroelectrochemically, the bopy ligand is reduced first, 0.22 V less negatively than bpy. On the basis of electrochemical data, MLCT(bopy) is expected to be the lowest excited state. Nevertheless, resonance Raman, emission and time-resolved visible, and IR absorption spectra clearly show that Re(bopy)(bpy) has a Re → bpy lowest-allowed electronic transition and a ^{3}MLCT(bpy) lowest-lying excited state, which can be formulated as $[Re^{II}(bopy)(CO)_3(bpy^{\bullet-})]^+$. The complex Re(bopy)(bpy) thus represents a very unusual case where the lowest unoccupied redox orbital, i.e., π^*-bopy, is different from the lowest unoccupied optical orbital, i.e., π^*-bpy. To understand the different localizations of the first electrochemical reduction and the lowest MLCT excitation, it has to be considered that the electrochemical potentials and excited-state energies are pertinent to species with different Re formal oxidation states, that is, I and II, respectively. A π delocalization of the excited electron over the $Re^{II}(bpy^{\bullet-})$ chelate ring will stabilize the MLCT(bpy) excited state relative to the MLCT(bopy) state where the excited electron is delocalized over the ketone group, farther away from the Re^{II} center. Moreover, the monodentate pyridine unit of the bpy ligand provides weaker π interaction with Re than chelating bpy. In an alternative, but conceptually equivalent, view, we can express the extra stabilization of a MLCT by the term $-e^2/r_{eh}$, where e is the electron charge and r_{eh} is the effective distance between the excited electron and hole. This effective distance is much shorter when the electron is excited to bpy than to bopy, stabilizing the MLCT(bpy) state over MLCT(bopy). Obviously, these effects are not included in the reduction potentials since neither stabilizing π interaction nor the electron−hole interaction occurs in the reduced state. The Re(bopy)(bpy) complex behaves differently from a similar complex with two electron-accepting ligands, $[Re(MQ^+)(CO)_3(dmb)]^+$ (MQ^+ = *N*-methyl-4,4′-bipyridine, dmb = 4,4′-dimethyl-2,2′-bipyridine), whose MLCT(MQ) lies below the MLCT(dmb) state. Nevertheless, optical excitation of $[Re(MQ^+)(CO)_3(dmb)]^+$ populates first MLCT(dmb) and the MLCT(MQ) state is formed subsequently by a $dmb^{\bullet-} \rightarrow MQ^+$ interligand electron transfer (ILET).[8,11,16,17] Neither $bopy^{\bullet-}$ → bpy nor $bpy^{\bullet-}$ → bopy ILET occurs upon excitation of Re(bopy)(bpy) since the optically populated MLCT(bpy) state is the lowest excited state. Finally, it should be noted that no evidence was found for any delocalization of the excited electron density from $bpy^{\bullet-}$ to bopy, i.e., for mixing between MLCT(bpy) and MLCT(bopy) excited states.

The observation of dynamic shifts of $\nu(C\equiv O)$ IR bands upon MLCT excitation shows that ^{3}MLCT excited states of both complexes are formed initially vibrationally hot. Since no $v = 1 \rightarrow 2$ $\nu(C\equiv O)$ bands are seen in the TRIR spectra, we can conclude that the energy released during intersystem crossing from the optically populated ^{1}MLCT excited states (ca. 6400 cm^{-1})[49] is rapidly (<1 ps) redistributed into low-frequency skeletal, solvent−solute, and first solvation shell vibrations, whose relaxation occurs on a picosecond time scale by energy dissipation into the bulk solvent. This vibrational dynamics are typical for MLCT excited states of $[Re(L)(CO)_3(diimine)]^{n+}$ complexes.[11,49,63]

In conclusion, the ^{3}MLCT(bopy) and ^{3}MLCT(bpy) were found to be the lowest excited states of $[Re(Cl)(CO)_3(bopy)_2]$ and $[Re(bopy)(CO)_3(bpy)]^+$, respectively. It follows that the bpy ligand introduces a MLCT(bpy) state at rather low energies even if another, more strongly, electron-accepting ligand (i.e. bopy) is present in the coordination sphere. The different localizations of the lowest MLCT excitation and the first reduction are caused by an extra stabilization of the $Re^{II}(bpy^{\bullet-})$ chelate ring in the MLCT(bpy) excited state. Both excited states are long-lived, but rather different photochemical behavior can be expected for these complexes. This study also demonstrates the great power of TRIR spectroscopy in revealing the nature and dynamics of low-lying excited states of organometallics, by following the spectral and temporal changes of vibrations of *both* the metal−carbonyl unit and functional groups of an organic ligand.

Acknowledgment. Mr. Michiel M. Groeneveld of the Molecular Photonic Materials, van 't Hoff Institute for Molecular Sciences, University of Amsterdam, is thanked for his help with measuring the time-resolved UV−vis, and Dr. Anders Gabrielsson (QMUL) is thanked for measuring the emission spectra. EPSRC and COST Action D14 are acknowledged for funding this research.

Supporting Information Available: Additional tables. This material is available free of charge via the Internet at http://pubs.acs.org.

IC049659M

---

(68) Hershberger, J. W.; Klingler, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1983**, *105*, 61−73.