

Geometrical and electronic structures of the acetyl complex $\text{Re}(\text{bpy})(\text{CO})_3(\text{COCH}_3)$ and of $[\text{M}(\text{bpy})(\text{CO})_4](\text{OTf})$, $\text{M} = \text{Mn}, \text{Re}$

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Abstract

The compound *fac*- $\text{Re}(\text{bpy})(\text{CO})_3(\text{COCH}_3)$ (**1**) (bpy = 2,2'-bipyridine) with three different kinds of π -acceptor ligands coordinated to rhenium(I) has been investigated by infrared spectroelectrochemistry to reveal the occupation of the $\pi^*(\text{bpy})$ MO on one-electron reduction to $\mathbf{1}^{\bullet-}$ with negligible participation of the π -accepting acetyl group. The results are discussed in relation to the spectroscopy (NMR, IR) and the crystal structure analysis of the neutral complex **1**, which reveals a short C–O(acetyl) (1.157(12) Å) and a long Re–C(acetyl) bond (2.245(12) Å) and an orientation of the Re–C(O)CH₃ plane parallel to the C_2 axis of the coordinated bpy. The result is an orthogonal arrangement of $d_{xz}/\pi^*(\text{bpy})$ and $d_{xy}/\pi^*(\text{acetyl})$ orbitals. This situation stands in distinct contrast to the structure reported for the complex salt $[\text{Re}(\text{L})(\text{CO})_3(\text{COCH}_3)](\text{PPN})$ (PPN⁺ = bis(triphenylphosphoranylidene)ammonium) with a cyclometallated 2-phenylpyridine ligand L. The crystal structures of the related complexes $[\text{M}(\text{bpy})(\text{CO})_4](\text{OTf})$, $\text{M} = \text{Re}$ and Mn, were determined for comparison. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Acetyl ligand; Carbonyl complexes; Crystal structure; Manganese compounds; Rhenium compounds

1. Introduction

A wide variety of tricarbonylrhenium(I) complexes have been synthesized and studied due to their stability and special electrochemical, photochemical or spectroscopic properties [1–7]. Of particular interest are those systems where an α -diimine ligand $\text{N}^{\wedge}\text{N}$ binds to *fac*- $(\text{OC})_3\text{Re}^+$, leaving the sixth position free for a ‘substrate’ L such as halides, CO_2 or other π acceptors such as substituted pyridines [5–11]. In the latter situation the electron transfer to and between the different acceptors L and $\text{N}^{\wedge}\text{N}$ has been studied [8,9]. It was also recently demonstrated that complex ions $[\text{fac}\text{-Re}(\text{N}^{\wedge}\text{N})(\text{CO})_3(\text{L})]^{2+}$ with L = *N*-methyl-4,4'-bipyridinium exhibit different patterns on reduction, viz. electron uptake by L or by the varied $\text{N}^{\wedge}\text{N}$ chelate ligands [10].

In this work we describe the crystal structure and additional spectroelectrochemical properties of the acetyl complex *fac*- $\text{Re}(\text{bpy})(\text{CO})_3(\text{COCH}_3)$ (**1**) whose synthesis, cyclic voltammetry and EPR spectroscopy was recently reported [11]. Although formally anionic, the acetyl group is π accepting through the C=O π^* orbital. A closely related acetyl complex salt $[\text{Re}(2\text{-}(\text{phenyl-}\kappa\text{C}^2)\text{pyridine-}\kappa\text{N})(\text{CO})_3(\text{COCH}_3)](\text{PPN})$ (**2**) (PPN⁺ = bis(triphenylphosphoranylidene)ammonium) was recently structurally characterized [12] with a cyclometallated 2-phenylpyridine instead of an α -diimine as chelate ligand. For structural comparison we also report the crystal structures of the complexes $[\text{M}(\text{bpy})(\text{CO})_4](\text{OTf})$, OTf = SO_3CF_3 , $\text{M} = \text{Re}$ (**3**) and Mn (**4**). Both complex cations were described [13,14], however, only the structure of the rhenium homologue is available with PF_6^- as counter ion [13]. Carbonyl complexes of positively charged metal centers have drawn attention recently because of the innovative work by Willner and Aubke [15]; formally, systems **1** and **3** differ by a CH_3^- anion at one carbonyl carbon.

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Table 1
Crystallographic data and refinement parameters for compounds **1**, **3** and **4**^a

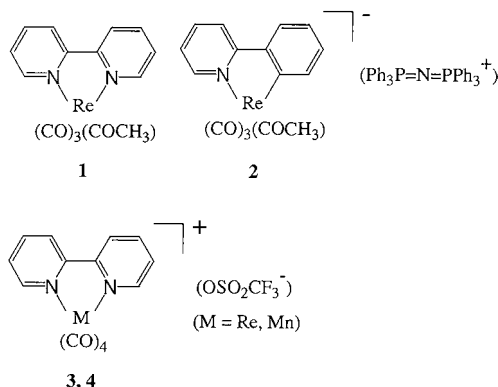
	Re(bpy)(CO) ₃ (COCH ₃) (1)	[Re(bpy)(CO) ₄](OTf)·0.5CH ₂ Cl ₂ (3)	[Mn(bpy)(CO) ₄](OTf)·0.5CH ₂ Cl ₂ (4)
Empirical formula	C ₁₅ H ₁₁ N ₂ O ₄ Re	C _{15.5} H ₉ ClF ₃ N ₂ O ₇ ReS	C _{15.5} H ₉ ClF ₃ MnN ₂ O ₇ S
Formula weight	469.46	645.96	513.69
Crystal size (mm)	0.3 × 0.2 × 0.2	0.4 × 0.3 × 0.3	0.3 × 0.2 × 0.2
Temperature (K)	173(2)	173(2)	173(2)
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>
Unit cell dimensions			
<i>a</i> (Å)	10.621(3)	9.6100(10)	23.368(3)
<i>b</i> (Å)	10.623(3)	13.976(2)	11.6691(9)
<i>c</i> (Å)	13.658(3)	15.639(2)	14.7642(10)
α (°)	90.00	87.560(11)	90.00
β (°)	110.46(2)	73.110(9)	94.149(11)
γ (°)	90.00	89.600(11)	90.00
<i>V</i> (Å ³)	1443.7(7)	2008.0(4)	4015.4(6)
<i>Z</i>	4	4	8
<i>D</i> _{calc} (g cm ⁻³)	2.160	2.137	1.699
Absorption coefficient (cm ⁻¹)	0.8436	0.6358	0.963
2 θ Range (°)	4.1–60.02	3.9–56.0	3.5–55.0
Index ranges	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 14, −19 ≤ <i>l</i> ≤ 18	0 ≤ <i>h</i> ≤ 12, −18 ≤ <i>k</i> ≤ 18, −19 ≤ <i>l</i> ≤ 20	−30 ≤ <i>h</i> ≤ 30, −14 ≤ <i>k</i> ≤ 0, −19 ≤ <i>l</i> ≤ 19
Reflections collected	4405	10 275	9130
Number of unique reflections	4203	9703	4583
GOF(<i>F</i> ²) ^b	1.157	1.132	1.019
Data/restraints/parameters	4203/0/199	9464/24/547	4421/1/318
<i>R</i> indices (all data) ^{c,d}	<i>R</i> ₁ = 0.0602, <i>wR</i> ₂ = 0.1435	<i>R</i> ₁ = 0.0601, <i>wR</i> ₂ = 0.1337	<i>R</i> ₁ = 0.0695, <i>wR</i> ₂ = 0.1113
Largest residual density (e Å ⁻³)	0.366	0.451	0.291

^a All structures were obtained on a Siemens four-circle diffractometer P4, graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å).

^b GOF = $\{\sum w(|F_o|^2 - |F_c|^2)^2 / (n - m)\}^{1/2}$; *n* = number of data; *m* = number of variables.

^c *R* = $(\sum ||F_o| - |F_c||) / \sum |F_o|$.

^d *R*_w = $\{\sum [w(|F_o|^2 - |F_c|^2)^2] / \sum [w(F_o^4)]\}^{1/2}$.



2. Experimental

2.1. Synthesis

Compounds **1** and **3** were synthesized as described before [11,13]. Ruby-red single crystals of **1** for X-ray structure analysis were obtained from a saturated solution in dichloromethane overlaid with diethyl ether. Pale yellow crystals of **3** were obtained from a saturated solution in dichloromethane at -20°C .

Compound **4** was prepared by treating Mn(CO)₅Cl with 1.1 equivalents of AgOTf in dichloromethane at

room temperature. After 18 h stirring in the dark and filtration of AgCl, the filtrate was combined with an equimolar amount of bpy in dichloromethane. After 8 h stirring and addition of *n*-hexane a yellow precipitate

Table 2
Selected bond lengths (Å) and angles (°) of [Re(bpy)(CO)₃(COCH₃)] (**1**)

Bond lengths			
Re–C(13)	1.912(8)	C(11)–O(11)	1.157(12)
Re–C(12)	1.916(9)	C(11)–C(15)	1.494(13)
Re–C(14)	1.971(9)	C(12)–O(12)	1.152(11)
Re–N(2)	2.156(6)	C(13)–O(13)	1.159(10)
Re–N(1)	2.163(7)	C(14)–O(14)	1.158(12)
Re–C(11)	2.245(12)	N(1)–C(1)	1.343(10)
		C(5)–C(6)	1.472(11)
Bond angles			
C(13)–Re–C(12)	90.3(4)	C(13)–Re–C(11)	89.8(4)
C(13)–Re–C(14)	91.7(4)	C(12)–Re–C(11)	91.1(4)
C(12)–Re–C(14)	90.7(4)	C(14)–Re–C(11)	177.6(3)
C(13)–Re–N(2)	96.6(3)	N(2)–Re–C(11)	83.2(3)
C(12)–Re–N(2)	171.0(4)	N(1)–Re–C(11)	84.0(3)
C(14)–Re–N(2)	94.8(3)	O(11)–C(11)–Re	121.0(8)
C(13)–Re–N(1)	170.5(3)	O(12)–C(12)–Re	178.6(9)
C(12)–Re–N(1)	97.1(3)	O(13)–C(13)–Re	175.7(8)
C(14)–Re–N(1)	94.2(3)	O(14)–C(14)–Re	174.9(8)
N(2)–Re–N(1)	75.5(2)		

Table 3
Selected bond lengths (Å) and angles (°) of [Re(bpy)(CO)₄](OTf)_{0.5} CH₂Cl₂ (3)

Bond lengths			
Re(1)–C(112)	1.921(7)	Re(2)–C(212)	1.922(8)
Re(1)–C(113)	1.938(7)	Re(2)–C(213)	1.931(8)
Re(1)–C(114)	2.005(7)	Re(2)–C(211)	2.024(7)
Re(1)–C(111)	2.022(8)	Re(2)–C(214)	2.030(7)
Re(1)–N(11)	2.171(6)	Re(2)–N(21)	2.158(6)
Re(1)–N(12)	2.172(6)	Re(2)–N(22)	2.169(6)
C(15)–C(16)	1.484(9)	C(25)–C(26)	1.466(10)
C(111)–O(11)	1.139(10)	C(211)–O(21)	1.109(9)
C(112)–O(12)	1.145(9)	C(212)–O(22)	1.137(10)
C(113)–O(13)	1.145(9)	C(213)–O(23)	1.146(10)
C(114)–O(14)	1.127(9)	C(214)–O(24)	1.102(10)
Bond angles			
C(112)–Re(1)–C(113)	88.9(3)	C(212)–Re(2)–C(213)	88.2(3)
C(112)–Re(1)–C(114)	86.6(3)	C(212)–Re(2)–C(211)	85.9(3)
C(113)–Re(1)–C(114)	89.0(3)	C(213)–Re(2)–C(211)	88.4(3)
C(112)–Re(1)–C(111)	89.3(3)	C(212)–Re(2)–C(214)	90.9(3)
C(113)–Re(1)–C(111)	90.9(3)	C(213)–Re(2)–C(214)	91.5(3)
C(114)–Re(1)–C(111)	175.9(3)	C(211)–Re(2)–C(214)	176.9(3)
C(112)–Re(1)–N(11)	173.0(3)	C(212)–Re(2)–N(21)	173.8(3)
C(113)–Re(1)–N(11)	98.0(3)	C(213)–Re(2)–N(21)	97.9(3)
C(114)–Re(1)–N(11)	92.7(3)	C(211)–Re(2)–N(21)	92.9(3)
C(111)–Re(1)–N(11)	91.4(3)	C(214)–Re(2)–N(21)	90.2(3)
C(112)–Re(1)–N(12)	97.9(3)	C(212)–Re(2)–N(22)	98.8(3)
C(113)–Re(1)–N(12)	173.1(3)	C(213)–Re(2)–N(22)	173.0(3)
C(114)–Re(1)–N(12)	90.8(3)	C(211)–Re(2)–N(22)	92.0(3)
C(111)–Re(1)–N(12)	89.8(2)	C(214)–Re(2)–N(22)	88.5(3)
N(11)–Re(1)–N(12)	75.1(2)	N(21)–Re(2)–N(22)	75.1(2)
O(11)–C(111)–Re(1)	174.8(7)	O(21)–C(211)–Re(2)	172.7(6)
O(12)–C(112)–Re(1)	178.3(7)	O(22)–C(212)–Re(2)	178.8(8)
O(13)–C(113)–Re(1)	179.2(7)	O(23)–C(213)–Re(2)	179.1(7)
O(14)–C(114)–Re(1)	173.2(7)	O(24)–C(214)–Re(2)	176.0(8)

formed on cooling the solution to -18°C . After filtration the product was obtained in 73% yield as a yellow powder. Anal. Calc. for C₁₅H₈F₃MnN₂O₇S: C, 38.15; H, 1.71; N 5.93. Found C, 38.13; H 1.68; N 6.03%. IR (CH₂Cl₂): $\nu_{\text{CO}} = 2118, 2044, 2023, 1982 \text{ cm}^{-1}$. ¹H-NMR (CD₂Cl₂): $\delta = 7.71$ (t, 2H), 8.23 (t, 2H), 8.41 (d, 2H), 9.15 (d, 2H). Yellow crystals of **4** were obtained from a saturated solution in dichlormethane at -20°C .

2.2. Instrumentation

¹H-NMR spectra were taken on a Bruker AC 250 spectrometer, infrared spectra were obtained using Perkin–Elmer 684 and 283 instruments. UV–vis/NIR absorption spectra were recorded on Shimadzu UV160 and Bruins Instruments Omega 10 spectrophotometers. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OT-TLE) cell [16].

2.3. Crystallography

The structure of **1** was solved by direct methods. The structures of **3** (two crystallographically independent complex ions in the unit cell) and **4** were solved by the Patterson method, the refinement was carried out employing full-matrix least-squares methods [17]. Absorption correction (ψ -scan) did not improve *R* values or standard deviations. All non-hydrogen atoms were refined anisotropically except for the oxygen and fluorine atoms of one of the OTf[−] ions in **3**, which exhibit rotational disorder around the C4–S41 axes of 60° . The result are relatively high standard deviations for the bond parameters in **3** as similarly observed for the other Re compounds **1** and **2**. The hydrogen atoms were introduced at proper geometric positions and treated according to the riding model with isotropic thermal parameters fixed at 20% greater than that of the bonded atom. Anisotropic thermal parameters were refined for all non-hydrogen atoms. Crystal,

Table 4
Selected bond lengths (Å) and angles (°) of [Mn(bpy)(CO)₄](OTf)_{0.5} CH₂Cl₂ (4)

Bond lengths			
Mn–C(12)	1.820(3)	C(6)–C(5)	1.467(4)
Mn–C(13)	1.828(3)	O(14)–C(14)	1.125(3)
Mn–C(11)	1.870(3)	O(13)–C(13)	1.133(3)
Mn–C(14)	1.892(3)	O(12)–C(12)	1.139(4)
Mn–N(2)	2.045(2)	C(11)–O(11)	1.129(3)
Mn–N(1)	2.049(2)		
Bond angles			
C(12)–Mn–N(2)	173.53(12)	C(12)–Mn–C(11)	92.23(13)
C(13)–Mn–N(2)	96.08(11)	C(13)–Mn–C(11)	88.70(12)
C(11)–Mn–N(2)	90.91(10)	C(12)–Mn–C(14)	89.27(12)
C(14)–Mn–N(2)	87.75(9)	C(13)–Mn–C(14)	89.74(11)
C(12)–Mn–N(1)	95.39(12)	C(11)–Mn–C(14)	177.83(11)
C(13)–Mn–N(1)	174.93(10)	O(13)–C(13)–Mn	177.7(3)
C(11)–Mn–N(1)	90.52(10)	O(14)–C(14)–Mn	176.9(2)
C(12)–Mn–C(13)	89.65(13)	O(12)–C(12)–Mn	177.6(3)
		O(11)–C(11)–Mn	178.2(2)

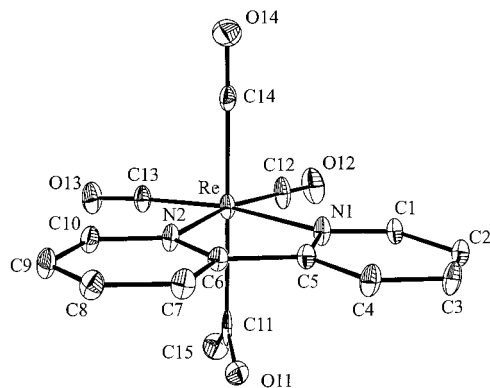


Fig. 1. Molecular structure of compound **1** in the crystal.

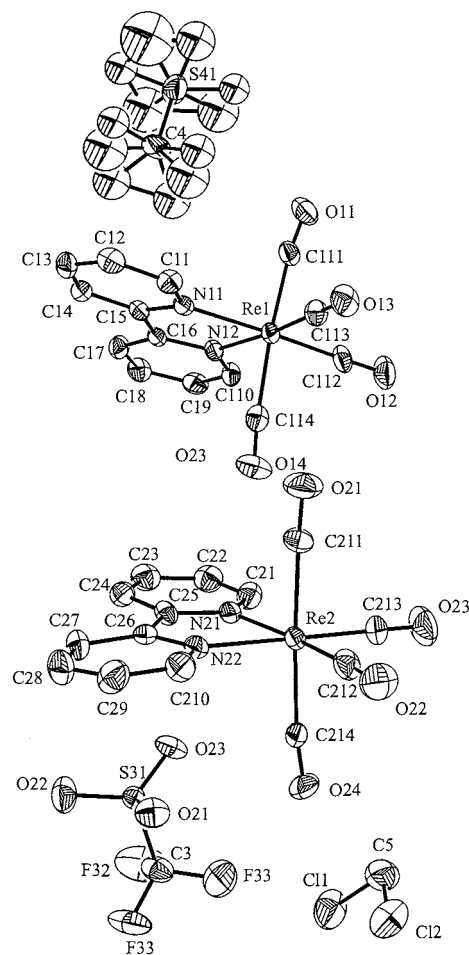


Fig. 2. Molecular structures of the crystallographically independent components of compound **3** in the crystal.

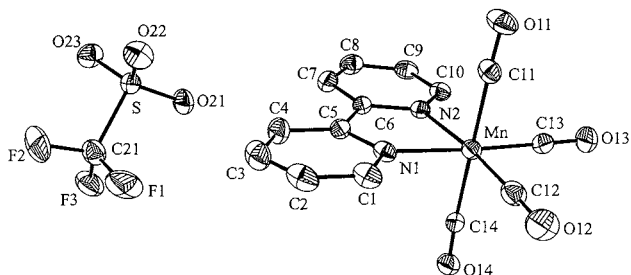


Fig. 3. Molecular structure of compound **4** in the crystal (solvent molecule not shown).

data collection and refinement parameters are summarized in Table 1. Selected bond data are given in Tables 2–4

3. Results and discussion

The molecular structures of the acetyl compound **1** and of the tetracarbonylmetal complex triflates **3** and **4** are depicted in Figs. 1–3. There are no special inter-

molecular interactions in the crystals. Table 1 contains essential crystallographic information for the three complexes, Tables 2–5 summarize selected bond parameters.

As evident from the carbonyl vibrational splitting pattern and as expected for this kind of complexes [1–9], the acetyl compound **1** exists in the *fac* configuration. The most conspicuous feature of the acetyl group is its orientation strictly parallel to the C_2 axis of the chelating bipyridine ligand. The CO(acetyl) bond points directly towards the five membered Re/bpy chelate ring (Fig. 1). In the coordinate system of Fig. 4 [7], the d_{xz} orbital thus interacts conventionally with the π^* orbital (b_1 or ψ) [18] of the bpy system whereas the occupied metal d_{xy} orbital can interact with the π^* (acetyl) MO in this configuration.

There is a stark difference between the arrangement found for **1** (Fig. 1) and the orientation reported for **2**. In this less symmetrical case **2**, the angle between the Re–C(O)CH₃ plane and the xz axis is about 65° whereas it is close to 0° for **1**. Presumably, the negative charge introduced by the phenyl anion donor dominates in **2** and determines the conformation, causing a twist of the acetyl substituent away from the carbanionic center.

The bond parameters support this view: With 1.157(12) Å, the acetyl C–O bond length is rather short in **1**, it lies in the same region as the carbonyl C–O bond lengths in compounds **1**–**4** (Table 5) or in carbonylmetal complexes in general [15]. In **2** the acetyl C–O bond is distinctly longer at 1.232(9) Å [12].

Conversely, the Re–C(acetyl) distance of **1** is that of a typical single bond (2.245(12) Å) whereas **2** exhibits a significant shortening to 2.149(7) Å according to increased contributions from resonance structure **B** (Scheme 1) [12]. Structural data from a large number of acetylrhodium complexes with β -diketonate ligands [19] support this view of rather short C–O(acetyl) and long Re–C(acetyl) bonds in compound **1**.

This description is further substantiated by the CO(acetyl) vibrational stretching frequency in the infrared spectrum which shows a high energy shift on going from **2** to **1**; a similar shift is experienced by the metal-carbonyl bands (Table 5). The axial carbonyl groups in **1** and **2** also show some structural differences (*trans* influence), the Re–C distance being comparatively short for compound **1** (Table 5).

Both tetracarbonylmetal complexes **3** and **4** exhibit the effects of positive charge [15], e.g. high-energy carbonyl stretching bands, the main difference being the generally 0.1 Å longer M–C bonds for the rhenium derivative. Interestingly, the interannular distance between the six-membered rings of the chelate ligands shows no significant variation for compounds **1**–**4**; the π back donation from the d^6 metal centers seems to be

Table 5
Comparison of structural and spectroscopic data

	1	2	3	4
<i>Bond lengths (Å)</i>				
M–CO _{ax}	1.971(9)	2.014(7)	2.022(8) 2.005(7)	1.870(3) 1.892(3)
M–CO _{eq}	1.916(9) 1.912(8)	1.884(7) 1.909(8)	1.921(7) 1.938(7)	1.820(3) 1.828(3)
M–COR	2.245(12)	2.149(7)	–	–
C _{py} –C _{py}	1.472(11)	1.470(1)	1.484(9)	1.467(4)
C–O in M–CO _{ax}	1.158(12)	1.158(9)	1.139(10) 1.127(9)	1.129(3) 1.125(3)
C–O in M–CO _{eq}	1.152(11) 1.159(10)	1.162(9) 1.16(1)	1.145(9) 1.145(9)	1.139(4) 1.133(3)
C–O in M–COR	1.157(12)	1.232(9)	–	–
<i>δ (13C-NMR) (ppm)</i>				
	(In acetone- <i>d</i> ₆) 266.68 (CH ₃ –CO–Re), 205.78 (CO), 195.48 (CO), 50.99 (CH ₃ –CO–Re)	(In CD ₂ Cl ₂) 278.9 (CH ₃ –CO–Re), 210.4 (CO), 207.9 (CO), 202.9 (CO), 53.0 (CH ₃ –CO–Re)	–	–
<i>ν</i> (CO) (cm ⁻¹) (in CH ₂ Cl ₂)	1999, 1899, 1889	1964, 1853, 1841	2124, 2028, 2011, 1969	2118, 2044, 2023, 1982
<i>λ</i> _{max} (nm) (in CH ₂ Cl ₂)	1591 (COR) 348, 438	1561 (COR) n.r.	– 317	– 368

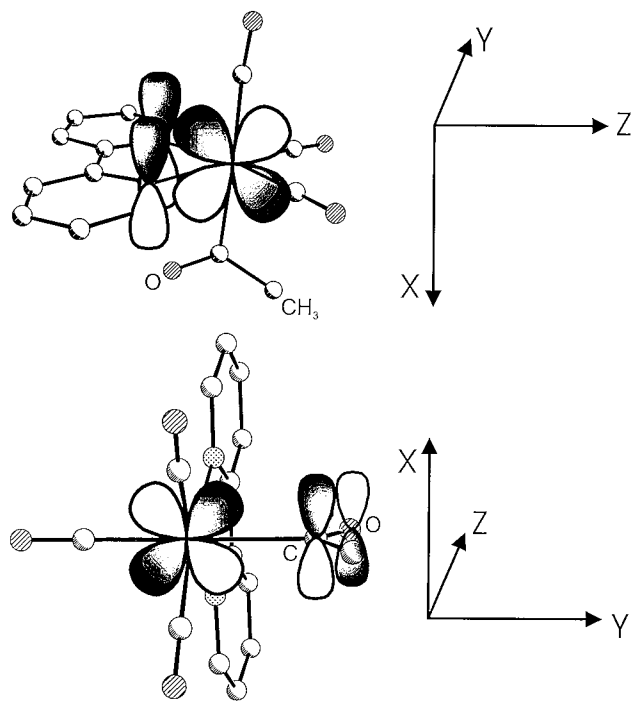
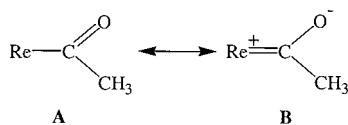


Fig. 4. Orbital overlap $d_{xz}/\pi^*(bpy)$ (top) and $d_{xy}/\pi^*(acetyl)$ (bottom) in compound **1**.



Scheme 1.

rather moderate in all instances. On the other hand, the energy of the metal-to-ligand charge transfer (MLCT) transition varies strongly in the order **3** > **4** > **1** (Table 5); the reason for this is the d orbital stabilization for the tetracarbonylmethyl cations, especially for M = Re. Tentatively, the second band at 348 nm of **1** may be attributed to a $d_{xy} \rightarrow \pi^*(acetyl)$ MLCT transition.

Since the reduction potentials and the EPR spectra [11] do not clearly indicate a sizable participation of the acetyl substituent at the primary reduction process we studied the conversion $[fac-Re(bpy)(CO)_3(CO-CH_3)]^{(0) \rightarrow (-)}$ by infrared spectroelectrochemistry, following the behavior of the acetyl and metal-carbonyl stretching bands. Fig. 5 illustrates the experiment with the use of an OTTLE cell [16]. Whereas the three metal-carbonyl bands shift by an average of 30 cm^{-1} ($2001 \rightarrow 1979$, $1900 \rightarrow 1865$, $1889 \rightarrow 1856\text{ cm}^{-1}$) the acetyl carbonyl band shifts only by 16 cm^{-1} from 1591 to 1575 cm^{-1} .

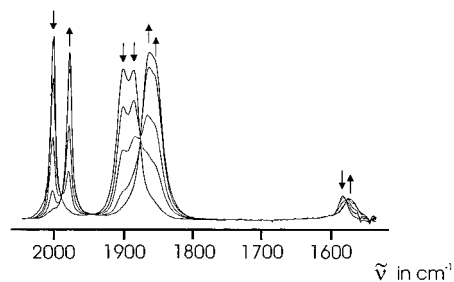


Fig. 5. IR spectroelectrochemistry (reduction) of compound **1** in $CH_2Cl_2/0.1\text{ M Bu}_4NPF_6$.

In conclusion, both the structural and IR-spectroelectrochemical results confirm [11] the non-participation of the acetyl ligand as a direct acceptor of the first added electron; the structurally established orthogonality of $d_{xz}/\pi^*(bpy)$ and $d_{xy}/\pi^*(acetyl)$ orbital systems disfavors orbital mixing and leaves only charge effects. The data presented here are thus adding another facet to the highly variegated chemistry of the $[Re(bpy)(CO)_3]^+$ fragment with simple carbon ligands such as CO_2 , $COOH$, $COOR$, COH , COR , CH_2OH or CH_3 [1–3,11,20,21].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 127450 (**1**), 127449 (**3**) and 127448 (**4**). Copies of the information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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