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FULL PAPER

Syntheses and characterisation of methyltrioxorhenium adducts of low-valence organometallic Lewis bases

Ana M. Santos, Fritz E. Kühn,* Wen-Mei Xue and Eberhardt Herdtweck

*Anorganisch-Chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4,
D-85747 Garching b. München, Germany. Fax: 0049(0)89 289 13473;
E-mail: fritz.kuehn@ch.tum.de*

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Methyltrioxorhenium(VII) forms air and moisture stable trigonal-bipyramidal adducts with several organometallic Lewis bases having a pyridine nitrogen atom as the donor moiety. These complexes have been isolated and fully characterised. A single-crystal structure of one of the products has been determined. Whilst the Re–N interaction is weaker than in some simple organic Lewis base adducts of $Re(CH_3)O_3$, *e.g.* with pyridine or 4-*tert*-butylpyridine, the more pronounced stability of the complexes described in this work is probably due to steric crowding and the moderate donor capability of the organometallic ligands. The donor capability of the ligands applied increases in the order $Re(CO)_3Br(4,4'\text{-bpy})_2$ < 1,1′-bis(4-pyridylethynyl)ferrocene < ferrocenyl-4-pyridylacetylene.

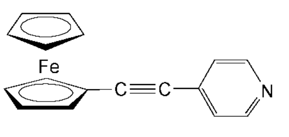
Introduction

Methyltrioxorhenium(VII) **1** has been found to be a very useful catalyst for a broad variety of processes during the last decade.[1] Among the best examined of these is the epoxidation of olefins.[2] The most important drawback was the concomitant formation of diols instead of the desired epoxides, most notably in the case of more sensitive substrates.[3] It has been found that the use of organic Lewis base adducts of complex **1** significantly decreases the formation of diols as a consequence of the reduced Lewis acidity of the catalytic system. Especially pyridine derivatives and pyrazole are very useful Lewis bases for this purpose.[4] Only recently Lewis base adducts of compound **1** were characterised properly. Despite the sensitivity of complexes of that type these attempts have been quite successful for organic Lewis bases.[5] Organometallic Lewis base adducts of **1**, still being very rare and in principle interesting as charge transfer complexes, turned out to be even more sensitive in several cases and therefore no structurally characterised example is known to date.[6] All known organometallic Lewis base adducts of **1** are unstable towards oxidation of the organometallic ligand. In some cases an intramolecular redox reaction can be observed. Since we have recently worked on stable, one dimensional organometallic chain molecules utilising the Lewis bases ferrocenyl-4-pyridylacetylene **2**, 1,1′-bis(4-pyridylethynyl)ferrocene **3** and $Re(CO)_3Br(4,4'\text{-bpy})_2$ **4** as interconnecting units of metal–metal bonded molecules, we applied the same organometallic ligands for reactions with compound **1**.

In this work we shall present the first stable and fully characterised organometallic Lewis base adducts of **1**. These compounds will be compared to the known reaction products of **1** with organic Lewis bases mentioned above.

Results and discussion

Preparation and characterisation



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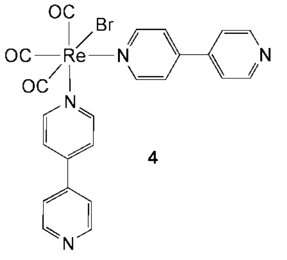

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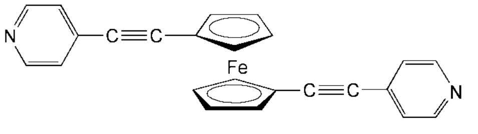

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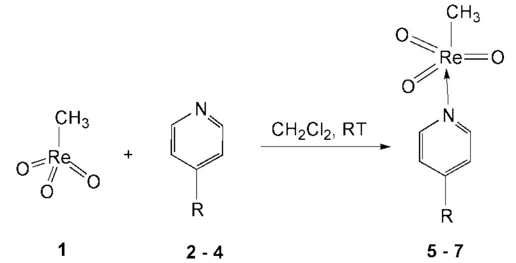

(1)

1 **2 - 4** **5 - 7**

The addition of one equivalent of compound **2** to **1** in diethyl ether or CH_2Cl_2 at room temperature (eqn. 1) immediately leads to the formation of complex **5**, which can be isolated from the orange suspension as a light orange solid in good yield. This compound is stable at room temperature and shows no signs of decomposition when exposed to air for several hours. It is soluble in polar organic solvents, *e.g.* THF and acetonitrile.

The IR active C≡C stretching vibration occurs at 2208 cm^{-1}, with a deviation within the measurement error range (4 cm^{-1}) in comparison to that of the “free” ligand (2210 cm^{-1}). The pyridyl ring stretching vibration appears at 1603 cm^{-1}, the corresponding band of **2** at 1594 cm^{-1}. The Re=O stretching vibrations are shifted from 958 (asym.) and 1005 cm^{-1} (sym.) in the case of **1** to 920 and 960 cm^{-1} in the case of complex **5**, reflecting the donor capacity of ligand **2**. From these IR vibrational frequencies the force constant of the Re=O vibration can be calculated according to ref. 7 to be 7.55 mdyn $Å^{-1}$. This value indicates a weakening of the Re–O bonds in comparison to that of complex **1** (f(Re=O) = 8.58 mdyn $Å^{-1}$) (Table 1). The additional electron density donated from the

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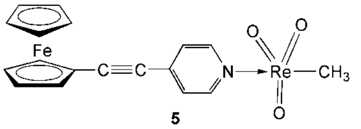
Table 1 Selected IR (in KBr), ^{1}H and ^{17}O NMR (in CD_2Cl_2) data, and calculated force constants *f*(ReO) for **5**–**7** and related complexes

Compound	ν(Re=O)/ cm^{-1}	$\delta(^1H)$	$\delta(^{17}O)$	*f*(ReO)/ mdyn Å^{-1}
1	958, 1005	2.67	829	8.58
5	920, 960	2.01	865	7.55
6	925, 964	2.11	860	7.63
7	930, 964	2.27	855	7.68
$Re(CH_3)O_3$–4-*t*-butylpyridine	921, 929	1.80	868	7.38
$[Re(CH_3)O_3]_2$bpy	928, 940		863	7.53



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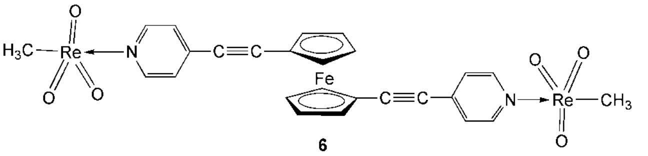

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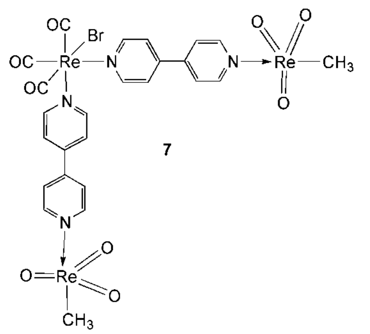

7

ligand to the Re^{VII} significantly weakens the Re–O bonds. It has been argued that the formally 14e system **1** should be regarded as an 18e system with three Re–O bonds of order $2^{2}/_{3}$.[8] If additional electron density is introduced in the system, for example by a Lewis base ligand, the Re–O bond order is reduced and less electron density is withdrawn from the terminal oxygen ligands. The value obtained for the force constant is also in accordance with the ^{17}O NMR shift of $\delta(^{17}O)$ 865 which is observed at significantly lower field than for free ^{17}O-labelled **1** ($\delta^{17}O$), 829.[9a,b] The pyridyl protons of **5** [$\delta(H_\alpha)$ 8.24, $\delta(H_\beta)$ 7.42] differ in their chemical shift also notably from those free **2** [$\delta(H_\alpha)$ 8.53, $\delta(H_\beta)$ 7.32]. The ferrocene proton resonances are comparable to those of the "free" ligand, because they are far apart from the Re^{VII}. The proton NMR signal corresponding to the methyl group of **5** appears at δ 2.01 which is shifted upfield with regard to the un-coordinated compound **1** (δ 2.67) as a result of the electron density donated by the N-donor ligand to the Lewis acidic Re^{VII}.

The addition of one equivalent of ligand **3** to two of **1** affords the high yield formation of complex **6** in CH_2Cl_2 at room temperature as a dark orange solid, soluble in polar organic solvents (CH_3CN, CH_2Cl_2, THF) and stable at room temperature. Complex **6** does not show signs of decomposition when exposed to air for several hours. Its solid state IR spectrum exhibits the characteristic C≡C stretching vibration at 2213 cm^{-1}. In relation to free **3** [ν(C≡C) 2208 cm^{-1}] the deviation is not significant. The strong band at 1592 cm^{-1} of free **3** attributed to the pyridyl ring is shifted to 1603 cm^{-1} after co-ordination. The IR bands corresponding to the Re=O stretching vibrations appear at 925 (asym.) and 964 cm^{-1} (sym.), the force constant being in this case $f = 7.63$ mdyn Å^{-1}, in good accordance with values obtained for other bis(CH_3ReO_3) complexes.[5] The ^{1}H NMR chemical shifts of the ferrocene protons of complex **6** are similar to those of free **3**. The pyridyl protons [$\delta(H_\alpha)$ 8.21, $\delta(H_\beta)$ 7.25] also do not show a significant difference compared to the free ligand **3** [$\delta(H_\alpha)$ 8.25, $\delta(H_\beta)$ 7.19]. Concerning the ^{17}O NMR shift a significant difference between the chemical shift of compound **1** (δ ^{17}O 829) and **6** (δ ^{17}O 860) is evident, reflecting the fact that Lewis base adducts show a strong low field shift due to the pronounced σ donor character of the co-ordinating nitrogen.[9]

Table 2 Crystallographic data comparison for complex **5**, **1** and two known organic pyridine adducts of **1**

Compound	Σ O–Re=O/°	Re–N/pm	Re–C/pm
5	355.2(3)	241.7(6)	208.9(8)
$Re(CH_3)O_3$–4-*t*-butylpyridine	355.9(2)	240.7(5)	208.3(7)
$[Re(CH_3)O_3]_2$bpy	353.2(3)	250.4(5)	207.9(7)
1	338.8(1)		206.3(2)

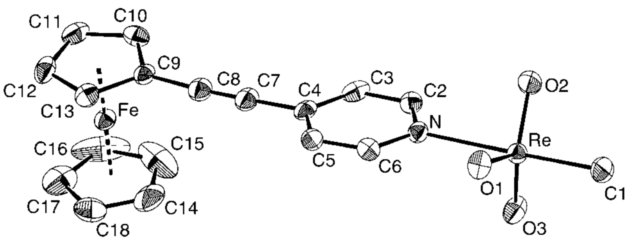

Fig. 1 PLATON[12b] plot of the solid state structure of complex **5**. Thermal ellipsoids are at the 50% probability level. Hydrogens omitted for clarity.

The reaction of one equivalent of ligand **4**[10] with two of **1** in CH_2Cl_2 at room temperature affords promptly complex **7** as a yellow solid soluble in common polar organic solvents, *e.g.* THF. Compound **7** does not decompose when exposed to air for some hours. In the IR spectrum the bands corresponding to the CO stretching vibrations, 1903 and 1887 cm^{-1}, show no significant difference from the non-co-ordinated **4**, indicating that the effect of the co-ordination of **1** to the 4,4′-bipyridine does not influence significantly the back donation to the CO ligands by the Re^I. This would be expected if the pyridine rings are twisted and therefore in different planes. Although in this case we have not obtained single crystal X-ray data for the complex, this is known to happen in similar rhenium(I) complexes.[11] The values $\nu(Re{=}O)_{asym}$ 930 and $\nu(Re{=}O)_{sym}$ 964 cm^{-1} show a similar deviation from those of free **1** as found for complex **5** (see Table 1). The ^{1}H NMR chemical shift of the CH_3 group of **7** is shifted to higher field $\delta(^1H)$ 2.27 in comparison to complex **1**, $\delta(^1H)$ 2.67.

Table 2 gives a comparison of the crystallographic data for the complexes examined here and the two known organic pyridine adducts of **1**.[5] It can be seen that all of the Lewis base ligands used in complexes **5**–**7** have a weaker influence on the CH_3ReO_3 moiety than the organic ligand 4-*tert*-butylpyridine. The complex of **1** with 4-*tert*-butylpyridine shows the weakest Re=O force constant, the most pronounced low field shift in ^{17}O NMR and the strongest high field shift in ^{1}H NMR. The values obtained for the complexes **5**–**7** are closer to the values of the not ligated **1**, but still well within the range for Lewis base adducts of **1**. The results obtained are quite similar to that of $(CH_3ReO_3)_2$–4,4′-bipyridine.[5] In this complex the donor capability of the organic ligand is relatively weak due to its co-ordination to two electron withdrawing molecules of compound **1**. It is interesting that the organometallic ligands utilised here to coordinate to **1** do not have a stronger electron donor capability than simple organic ligands, especially since the $C_5H_4C{\equiv}CC_5H_4N$ unit is not tilted. The two rings are coplanar as can be seen from the X-ray crystal structure of **5** (Fig. 1). The structural data of this complex are very similar to those of the 4-*tert*-butylpyridine adduct of **1**; within the given error range the Re–C and the Re–N bond distances as well as the sum of the O–Re=O angles can be regarded as identical. This again shows the significantly larger sensitivity of IR and NMR spectroscopy to small, but important interaction differences compared to X-ray crystallography. We therefore regarded the failed attempt to crystallise compounds **6** and **7** as of little consequence since spectroscopic methods give a closer insight on the donor capabilities of the ligands applied. The Re–N interaction is strongest in **5** and weakest in **7** according to both NMR(^{17}O, ^{1}H) and IR spectroscopy (see Table 1). Accordingly, complex **7** has the largest Re=O force constant, the most high field shifted Re–CH_3 ^{1}H NMR signal and the most low field shifted Re=O ^{17}O NMR signal. Additionally, ligand **3** is a slightly stronger donor than **4** according to Table 1. However, since both complexes **6** and **7** show co-ordination to two electron withdrawing CH_3ReO_3 units the ligands are weaker donors than **2**, interacting with only one molecule of complex **1**. Forming stable Lewis base adducts of **1** seems to be a difficult task. Strong donor ligands shift too much electron density to the Re^{VII} causing disruption of the Re–C bond (usually recognised by the formation of dark residues of ReO_3), whereas too weakly co-ordinating ligands can be exchanged quite easily by the moisture of the air (usually recognised by the formation of colourless residues of "$HOReO_3$"(perrhenic acid)).[4a,6,9,13] The complexes described in this work are quite obviously on the borderline between these two decomposition pathways and therefore comparatively stable.

It should be emphasised in this context that the relatively weak interaction between the organometallic Lewis base ligands and the Re^{VII} is very likely due to the large distance between the Re^{VII} and the Fe^{II} or Re^{I} and not to the lack of similar orbitals at the Re and N atoms, enabling charge transfer. The possibility of the formation of charge transfer complexes of this type has been stated in a theoretical work.[14]

Thermogravimetry

Complexes **5**–**7** and the precursors for which no literature data were available were examined by thermogravimetry (TG). Compound **1** sublimes below 100 °C under TG conditions,[15] ligand **2** starts decomposing at 229 °C and ligand **3** at 480 °C.[16] Complex **5** decomposes below 100 °C, in the same temperature range in which **1** sublimes. Obviously Re–N rupture leads to an immediate sublimation of the now un-coordinated **1**.

Table 3 UV/Vis Absorption spectral data measured in CH_2Cl_2 at room temperature

Compound	λ_{max}/nm (ε/M^{-1} cm^{-1})
1	236 (1700), 258 (980)
2	252 (13700), 304 (12800), 352 (2320), 449 (760)
3	261 (26100), 281 (20900), 311 (19600), 350 (4160), 457 (1040)
4	246 (38700), 320 (14100)
5	252 (15700), 304 (13800), 351 (2760), 449 (950)
6	262 (33700), 282 (27000), 311 (24800), 350 (5680), 456 (1510)
7	245 (43000), 320 (15000)

Complex **6** decomposes in four steps, the onset temperature of the first decomposition step being 50 °C above the sublimation onset temperature for **1**, which denotes increased stability of **6**.

Complex **7** starts decomposing at 134 °C; this value is situated between the decomposition onset temperatures of **1** and **4** (222 °C).[17] The decomposition follows in 6 steps of which the first can be regarded as loss of one molecule of **1** corresponding to *ca.* 24% weight loss. At 730 °C only 17% remains as residual weight.

Electronic absorption spectroscopy and cyclic voltammetry

The adducts **5**–**7** show their characteristic absorptions at similar wavelengths to those of their Lewis base precursors. Not only the absorption energies but also the absorption coefficients of the adducts are not significantly different (see Table 3).

Mixed-valence compounds, which contain a metal in low oxidation state and another metal in a high oxidation state, may be intriguing in their electronic communications between metal centres. A unique property of these species is the presence of a metal-to-metal charge-transfer (MM′CT) band in their electronic spectra which is absent from the spectra of the pure starting materials. However, for the binuclear and trinuclear compounds investigated here no MM′CT bands are identified from their electronic spectra even on scanning a concentrated solution of *ca.* 5×10^{-3} M in CH_2Cl_2 over 1100 nm. It seems that no significant intramolecular electronic communication occurs between the metal centres.

The cyclic voltammograms of the adducts were measured and the data are summarised in Table 4. According to the electronic spectra and cyclic voltammograms, the co-ordination of the organometallic Lewis bases utilised in this investigation to compound **1** does not significantly change the electronic structures from those of the parent molecular fragments; the high-valence metal (Re^{7+})[18] and low-valence metal (Fe^{2+}, Re^{+}) are obviously not communicating electronically. This is in good accordance with the spectroscopic and crystallographic results described above.

Conclusions

Organometallic Lewis-base adducts of compound **1** can be prepared very easily by treating organometallic Lewis bases with **1** at room temperature. The adducts with ligand **2** (mono-adduct) and with **3** and **4** (bis adducts) are stable against air and moisture for several hours. Most of the known organic Lewis base adducts of **1** are significantly less stable. However, no detectable charge transfer between the two involved metal centres in different oxidation states can be observed. The organometallic Lewis base ligands applied in this work are weaker donors than simple organic molecules like pyridine, 4-*tert*-butylpyridine and 4-methylpyridine, according to our spectroscopic data. This is probably due to the distance between the metal centres which hampers proper electron transfer from the electron rich to the electron deficient metal atom. Anyway,

Table 4 Cyclic voltammetric data[a] measured in deoxygenated CH_2Cl_2 solutions at room temperature

Compound	$Re^{7+/6+}$	$Fe^{3+/2+}$	$Re^{2+/+}$	Reduction of pyridyl
1	−1.24(ir)			
2		0.12(72)		
3				
4			+1.39(ir)	−1.66(103), −1.98(100), −2.16(ir)
5	−1.33(ir)	0.20(83)		
6	−1.38(ir)			
7	−1.27(ir)		+1.37(ir)	−1.68(107), −1.99(103), −2.17(ir)

[a] Potentials in volts *vs.* the ferrocene–ferrocenium couple; scan rate is 50 mV s^{-1}; $\Delta E_p = E_{pa} - E_{pc}$ (mV) are included in parentheses.

the apparent lack of communication between the metal centres together with the steric crowding of the rhenium(VII) core might be responsible for the enhanced stability of these adducts that enables easy handling and characterisation. More work to synthesize complexes with shorter bridges between the metal centres in order to get measurable charge transfer between them is currently underway in our laboratories.

Experimental

General

All preparations and manipulations were carried out under an oxygen and water free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard procedures, distilled and kept under argon over 4 Å molecular sieves. Complexes **1**,[19] **2**,[15,20] **3**[15,21] and **4**[10] were prepared according to the literature. All the other chemicals mentioned were used as received from Aldrich. Elemental analyses were performed in the Mikroanalytisches Labor of the TU München in Garching. ^1H, ^{13}C and ^{17}O NMR spectra were recorded using a FT-JEOL GX 400 spectrometer, IR spectra on a Perkin-Elmer FT-IR spectrometer using KBr pellets as matrix. TGA was performed using a Perkin-Elmer TGA 7 Thermogravimetric Analyzer. Electronic absorption spectra were run using a Perkin-Elmer Lambda 2 UV/VIS spectrometer. Cyclic voltammograms were recorded with a computer-controlled Model 173 Potentiostat/Galvanostat (EG&G Princeton Applied Research) in argon saturated and dried solutions with tetrabutylammonium hexafluorophosphate (0.1 M) as supporting electrolyte. The working electrode was platinum and the reference electrode was silver wire. Potentials are quoted *vs.* the ferrocene–ferrocenium couple as an internal standard.

Preparations

(4-Ferrocenylethynylpyridine)methyltrioxorhenium 5. To a solution of $Re(CH_3)O_3$ (200 mg, 0.8 mmol) in 10 mL of diethyl ether, ferrocenyl-4-pyridylacetylene (222 mg, 0.8 mmol) was added. An orange precipitate formed immediately. After stirring for 30 min the diethyl ether was removed by oil pump vacuum and the precipitate washed with n-hexane. Yield: 380 mg (90%). Calc. for $C_{18}H_{16}FeNO_3Re$: C 40.31, H 3.01, N 2.61%. Found: C 40.20, H 3.20, N 2.40%. Selected IR (KBr): 2208s (C≡C), 1603s, 1436s, 1109s, 997m, 960m, 920s and 884s. ^1H NMR (CD_2Cl_2, RT): δ 2.01 (CH_3ReO_3, s, 3 H), 4.26 (C_5H_5, s, 5 H), 4.35 (H_β of C_5H_4, t, 2 H), 4.57 (H_α of C_5H_4, t, 2 H), 7.42 (H_β of C_5H_4N, d, 2 H) and 8.24 (H_α of C_5H_4N, d, 2 H). ^{13}C NMR ($CDCl_3$, RT): δ 27.7 (CH_3ReO_3), 71.6, 72.6, 74.4 (C_5H_5 and C_5H_4), 85.3 ($C_5H_4\mathit{C}C$), 100.2 ($C\mathit{C}C_5H_4N$), 128.8 (C_β of C_5H_4N), 137.5 (C_γ of C_5H_4N) and 149.1 (C_α of C_5H_4N). ^{17}O NMR (CD_2Cl_2, RT): δ 865.

[μ-1,1′-Bis(4-pyridylethynyl)ferrocene]-bis(methyltrioxorhenium) 6. To a solution of $Re(CH_3)O_3$ (200 mg, 0.8 mmol) in 15 mL of CH_2Cl_2, 1,1′-bis(4-pyridylethynyl)ferrocene (155 mg, 0.4 mmol) was added. The solution became dark red; after *ca.* 15 min an orange solid started to precipitate. The solvent was removed by oil pump vacuum. The resulting orange powder was washed twice with diethyl ether. Yield 315 mg (88%). Calc. for $C_{26}H_{22}FeN_2O_6Re_2$: C 35.22, H 2.50, N 3.16%. Found: C 35.17, H 2.48, N 3.16%. Selected IR (KBr): 2213s (C≡C), 1603vs and 925vs. ^1H NMR (CD_2Cl_2, RT): δ 2.11 (CH_3ReO_3, s, 6 H), 4.43 (H_β of C_5H_4, t, 4 H), 4.61 (H_α of C_5H_4, t, 4 H), 7.25 (H_β of C_5H_4N, d, 4 H) and 8.21 (H_α of C_5H_4N, d, 4 H). ^{13}C NMR (CD_2Cl_2, RT): δ 23.7 (CH_3ReO_3), 65.8, 72.1, 73.9 (C_5H_4), 84.3 ($C_5H_4\mathit{C}C$), 95.2 ($C\mathit{C}C_5H_4N$), 126.4 (C_β of C_5H_4N), 134.5 (C_γ of C_5H_4N) and 147.7 (C_α of C_5H_4N); ^{17}O NMR (CD_2Cl_2, RT): δ 860.

Table 5 Summary of data for crystal structure analysis of compound **5**

Formula	$C_{18}H_{16}FeNO_3Re$
M	536.38
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/pm	598.09(6)
b/pm	1149.5(2)
c/pm	1371.9(2)
α/°	68.94(2)
β/°	77.44(2)
γ/°	75.59(1)
V/10^6 pm^3	843.9(2)
Z	2
μ/mm^{-1}	8.040
λ/pm	71.073
T/K	173
No. reflections collected	11532
No. independent/observed $I > 2\sigma I$	2945/2654
$R1$, $wR2$ indices [$I > 2\sigma I$]	0.0276, 0.0653
(all data)	0.0329, 0.0663

$Re(CO)_3Br[(4,4'\text{-bipy})Re(CH_3)O_3]_2$ 7. To a solution of $Re(CH_3)O_3$ (100 mg, 0.4 mmol) in 10 mL of CH_2Cl_2, $Re(CO)_3Br(4,4'\text{-bipy})_2$ (132 mg, 0.2 mmol) was added. The solvent was removed by oil pump vacuum and the resulting yellow precipitate washed twice with hexane. Yield 195 mg (84%). Calc. for $C_{25}H_{22}BrN_4O_9Re_3$: C 25.86, H 1.91, N 4.83%. Found C 25.77, H 1.92, N 4.80%. Selected IR (KBr): 2022s, 1903s, 1887s, 1607s, 930s and 814s. ^1H NMR (CD_2Cl_2, RT): δ 2.27 (CH_3ReO_3, s, 6 H), 7.64 (H_β of $C_{10}H_8N_2$, m, 8 H), 8.57 (H_α of $C_{10}H_8N_2Re^{VII}$, d, 4 H) and 8.98 (H_α of $C_{10}H_8N_2Re^{I}$, d, 4 H). ^{13}C NMR (CD_2Cl_2, RT): δ 23.8 (CH_3ReO_3), 122.3 (C_β of $C_{10}H_8N_2$), 146.6 (C_γ of $C_{10}H_8N_2$), 148.7 (C_α of $C_{10}H_8N_2$) and 155.2 (CO). ^{17}O NMR (CD_2Cl_2, RT): δ 855.

Crystal structure determination

Details are given in Table 5. Preliminary examination and data collection on compound **5** were carried out on an imaging plate diffraction system (IPDS; STOE&CIE) equipped with a rotating anode (NONIUS FR591; 50 kV; 80 mA; 4.0 kW) and graphite monochromated Mo-Kα radiation. Data were corrected for Lorentz and polarisation effects.[12a] Corrections for absorption (DIFABS)[12b] and decay effects (DECAY)[12a] were applied. The unit cell parameters were obtained by full-matrix least-squares refinements of 5000 reflections (CELL).[12a] The structure was solved by a combination of direct methods[12c] and Fourier-difference syntheses All non-hydrogen atoms of the asymmetric unit were refined anisotropically. All hydrogen atoms were placed in ideal geometry and allowed to ride on the parent carbon atom. Full-matrix least-squares refinements were carried out by minimising $\Sigma w(F_o^2 - F_c^2)^2$ with the weighting scheme of SHELXL-97.[12d,e]

CCDC reference number 186/2167.

See http://www.rsc.org/suppdata/dt/b0/b004640j/ for crystallographic files in .cif format.

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