Tricarbonyl Complexes of Rhenium(I) with Acetylpyridine Benzoylhydrazone and Related Ligands

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Received November 15th, 2002.

Dedicated to Professor Alfonso Castiñeiras on the Occasion of his 60th Birthday

Abstract. Novel rhenium(I) tricarbonyl complexes have been prepared by reactions of $(Et_4N)_2[Re(CO)_3Br_3]$ with acetylpyridine benzoylhydrazone, Hapbhyd, di(2-pyridyl)ketone benzoylhydrazone, Hpy₂bhyd, bis(2-pyridine)ketone, py₂CO, and pyridinealdehyde terephtalaldehydebishydrazone, pytehyd. The ligands remain protonated when no supporting base is added and the following complexes have been isolated: [Re(CO)_3Br(Hapbhyd)], [Re(CO)_3-Br(Hpy_2bhyd-py,hyd)], [Re(CO)_3Br(Hpy_2bhyd-py^1,py^2)], [Re(CO)_3-Br(py_2CO-N,N)] and [Re(CO)_3Br(pytehyd)]. Addition of triethyl amine results in deprotonation of Hapbhyd and the formation of [Re(CO)₃(OH₂)(apbhyd)], whereas Hpy₂bhyd is hydrolysed and a rhenium complex with the monoanionic bis(2-pyridyl)hydroxymethanolato ligand, {py₂C(OH)O}⁻, is formed. The same compound, [Re(CO)₃{py₂C(OH)O}], is obtained when triethyl amine and water are added to a mixture of $(Et_4N)_2$ [Re(CO)₃Br₃] and py₂CO. The air-stable products have been studied by spectroscopic methods

and X-ray crystallography.

Keywords: Rhenium; Benzoylhydrazones; Carbonyls; Crystal structure

Tricarbonylkomplexe von Rhenium(I) mit Acetylpyridinbenzoylhydrazon und verwandten Liganden

Inhaltsübersicht. Durch Reaktionen von $(Et_4N)_2[Re(CO)_3Br_3]$ mit Acetylpyridinbenzoylhydrazon, Hapbhyd, Di(2-pyridyl)ketonbenzoylhydrazon, Hpy₂bhyd, Bis(2-pyridyl)keton, py₂CO, und Pyridinaldehydterephtalaldehydbishydrazon, pytehyd, wurden neue Rhenium(I)-Tricarbonylkomplexe hergestellt und charakterisiert. Ohne Zugabe von Hilfsbasen koordinieren die Hydrazone als Neutralliganden und es konnten folgende Produkte isoliert werden: [Re-(CO)₃Br(Hapbhyd)], [Re(CO)₃Br(Hpy₂bhyd-py,hyd)], [Re(CO)₃-Br(Hpy₂bhyd-py¹,py²)], [Re(CO)₃Br(py₂CO-N,N)] und [Re(CO)₃-Br(pytehyd)]. Durch die Zugabe von Triethylamin erfolgt eine Deprotonierung von Hapbhyd, was zur Bildung von $[Re(CO)_3-(OH_2)(apbhyd)]$ führt. Eine analoge Reaktion mit Hpy₂bhyd führt zur Hydrolyse des Proliganden und es entsteht ein Rheniumkomplex mit dem monoanionischen Bis(2-pyridyl)hydroxymethanolato-Liganden, {py₂C(OH)O}⁻. Die gleiche Verbindung, [Re(CO)₃-{py₂C(OH)O}], entsteht nach Zugabe von Triethylamin und Wasser zu einer Mischung aus (Et₄N)₂[Re(CO)₃Br₃] und py₂CO.

Die luftstabilen Produkte wurden mit spektroskopischen Methoden und durch Röntgenkristallstrukturanalysen untersucht.

Introduction

The co-ordination chemistry of rhenium and technetium attract a considerable interest due to the nuclear medical applications of the γ - and β ⁻-emitting nuclides of the elements. ^{99m}Tc (pure γ -emitter, $E\gamma = 300$ keV, half-life $T_{1/2} = 6.0$ h) is the "working horse" in the diagnostic nuclear medicine [1]. More than 80 per cent of the routine studies in this field are done with this artificial element [2]. The β ⁻-emitting rhenium isotopes ¹⁸⁶Re ($E_{max} = 1.1$ MeV, $T_{1/2} = 90.64$ h) and ¹⁸⁸Re ($E_{max} = 2.1$ MeV, $T_{1/2} = 16.98$ h) are under discussion for radioimmuno therapy [3].

A facile approach to carbonyl complexes of the elements by a normal pressure synthesis [4] opened the door to the application of low-valent carbonyl compounds for nuclear medical purposes. The co-ordination behaviour of the $[M(CO)_3]^+$ cores (M = Tc, Re) has been studied in numerous papers [4–6]. Knowledge of preferred co-ordination sites and donor atom arrangements is important for the designing of new metal-based radiopharmaceuticals independent of the preferred labelling concept (direct labelling or bifunctional approach) [6]. Particularly stable bonds have been found between the $[M(CO)_3]^+$ core (M = Re, Tc) and nitrogen donor ligands of aromatic rings [7] which make multidentate ligands containing pyridine or imidazole substituents interesting for further studies.

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In the present paper we report the complex formation of the rhenium(I) tricarbonyl moiety with acetylpyridine benzoylhydrazone, Hapbhyd, and the related ligands bis(2-pyridyl)ketone benzoylhydrazone, Hpy₂bhyd, bis(2-pyridine)ketone, py₂CO, and pyridinealdehyde terephtalaldehydebishydrazone, pytehyd.



Results and Discussion

The reaction of $[\text{Re}(\text{CO})_3\text{Br}_3]^{2-}$ with Hapbhyd yields different products depending on the conditions applied. This is mainly due to the protonation/deprotonation of the NH function of the hydrazone ligands. All reactions have been performed on air in solvents which have not been dried unless otherwise stated.

Orange-red crystals of $[Re(CO)_3Br(Hapbhyd)]$ are formed when equimolare amounts of $(Et_4N)_2[Re(CO)_3Br_3]$ and the ligand are dissolved in methanol and heated under reflux. Increasing the amount of hydrazone ligand does not yield another product but causes problems during the isolation of a pure compound.

The complex is soluble in organic solvents like CHCl₃ or acetone. Its infrared spectrum shows the typical pattern for a facial tricarbonyl moiety with bands at 2020, 1895 and 1870 cm⁻¹. The position of the benzovl C=O band is almost the same as in the unco-ordinated hydrazone. A bathochromic shift has been found for the C=N band, while the NH band is still present in the spectrum of the complex. This suggests a co-ordination of the potentially tridentate Hapbhyd only via the pyridine/hydrazone site without deprotonation. The spectroscopic results are verified by the structure analysis of the compound. An ellipsoid representation of the complex molecule is given in Fig. 1 showing the rhenium atom in [Re(CO)₃Br(Hapbhyd)] in a distorted octahedral environment. Main distortions from an ideal octahedron are due to the small bite angle of the 5-membered chelate ring which is only 73.1°. The Re-N and Re-Br bond lengths are in the same range as previously observed for other fac-Re(CO)₃ complexes [6]. A summary of selected bond lengths and angles are summarised in Table 1.

Deprotonation of the Hapbhyd ligand can be achieved when triethyl amine is added. The reaction with $(Et_4N)_2[Re-(CO)_3Br_3]$ then gives $[Re(CO)_3(OH_2)(apbhyd)]$. The water ligand is taken from the solvent, which has not been dried for the reactions reported in this paper. Applying dried methanol decreases the yield of the product. No evidence was found for the cleavage of the C-N bond to the benzoyl



Figure 1 Ellipsoid presentation [21] of [Re(CO)₃Br(Hapbhyd)]. Thermal ellipsoids represent 50 per cent probability.

Table 1 Selected bond lengths/Å and angles/° for $[Re(CO)_3-Br(Hapbhyd)]$ and $[Re(CO)_3(OH_2)(apbhyd)]$

	[Re(CO) ₃ Br(Hapbhyd)]	[Re(CO) ₃ (OH ₂)(apbhyd)]
Re-C10	1.899(8)	1.89(1)
Re-C20	1.907(8)	1.925(8)
Re-C30	1.904(8)	1.913(9)
Re-Br/O1	2.6183(8)	2.175(6)
Re-N1	2.158(5)	2.168(6)
Re-N2	2.167(5)	2.175(6)
C6-C7	1.475(9)	1.44(1)
C7-C8	1.48(1)	1.48(1)
C7-N2	1.290(8)	1.296(9)
N2-N3	1.403(7)	1.394(9)
N3-C27	1.374(9)	1.30(1)
C27-O28	1.215(9)	1.300(9)
Re-N1-C6	116.8(4)	115.6(5)
N1-C6-C7	114.8(6)	116.5(6)
C6-C7-N2	114.0(6)	115.7(6)
C7-N2-Re	119.6(4)	117.9(5)
Br/O1-Re-C10	179.6(2)	174.1(3)
Br/O1-Re-C20	92.2(2)	93.1(3)
Br/O1-Re-C30	91.2(2)	96.6(3)
Br/O1-Re-N1	87.7(1)	82.1(2)
Br/O1-Re-N2	82.2(2)	79.4(2)
C10-Re-C20	87.8(3)	88.2(4)
C10-Re-C30	89.1(3)	89.2(4)
C10-Re-N1	95.3(3)	95.9(3)
C10-Re-N2	97.5(3)	94.7(3)
C20-Re-C30	90.1(3)	88.6(4)
C20-Re-N1	170.2(3)	172.3(3)
C20-Re-N2	97.4(3)	99.3(3)
C30-Re-N1	99.2(3)	98.0(3)
C30-Re-N2	170.2(2)	171.3(3)
N1-Re-N2	73.1(2)	73.9(2)

group and the formation of benzoic acid as has been observed for a formylpyridine benzoylhydrazone complex of technetium [6], neither the formation of anionic species or complexes with co-ordinated methanol ligands instead of water has been detected. The bonding situation in [Re-(CO)₃(OH₂)(apbhyd)] (Fig. 2) is very similar to that in [Re-(CO)₃Br(Hapbhyd)]. Deprotonation of the hydrazone does not cause significant changes in the bond lengths inside the chelate rings. The C=N bond length is only slightly lengthened by 0.005 Å. However, a shortening of the N3-C27



Figure 2 Ellipsoid presentation [21] of [Re(CO)₃(OH₂)(apbhyd)]. Thermal ellipsoids represent 50 per cent probability.



Scheme 1

bond together with the lengthening of the C27-O28 bond is observed which suggests that the negative charge of the ligand is widely delocalised over the benzoyl moiety which does not contribute to the co-ordination of the metal. A comparison of the bond length situation in the acetylpyridine benzoylhydrazone moieties in [Re(CO)₃Br(Hapbhyd)] and [Re(CO)₃(OH₂)(apbhyd)] is given in Scheme 1. The values in brackets represent those in the aqua complex. More bond lengths and angles are summarised in Table 1. An intramolecular hydrogen bond between O1 and O28 (see Fig. 2) causes a change in the conformation of the complex molecule. The crystallographic results are confirmed by the spectroscopic data. While the IR bands of the C=O vibrations occur at almost the same position, the C=N band of the agua complex is bathochromically shifted which indicates a weakening of the double bond. FAB⁺ mass spectra of both complexes show no evidence for the molecular ion peaks. Preferably the bonds to the Br⁻ or the H₂O ligands are cleaved giving evidence for the peaks at m/z = 510. Subsequently the three carbonyl ligands are lost.

The fact that the benzoyl moieties of the Hacpbhyd or acpbhyd⁻ ligands do not contribute to the co-ordination of rhenium is not unexpected and underlines the high tendency of the $[\text{Re}(\text{CO})_3]^+$ core to bind to nitrogen donors and provides a reactive site in the complexes which can be used for the coupling of biomolecules. The facial arrangement of

the carbonyl ligand requires a more flexible ligand system to realise a three-dentate N,N,O co-ordination as has been demonstrated for [Re(CO)₃(histidinate)] [6] or [Tc(CO)₃-(picac)] (picac- = picolineamine-N-acetato-N-acetic acid)] [7]. The C=N double bonds in the hydrazones under study, however, require a planar co-ordination as has been found in numerous transition metal complexes.

Three different products have been isolated from reactions of (Et₄N)₂[Re(CO)₃Br₃] with Hpy₂bhyd. As with Hapbhyd, the ligand remains protonated when no supporting base is added. The second pyridine donor site, however, allows two different bidentate co-ordination modes using the nitrogen donor atoms exclusively. The sp² hybridisation of the central carbon atom (C7) prevents from a tridentate N,N,N co-ordination mode and the results with Hapbhyd described above make a complex formation of the benzoyl group with the rhenium(I) tricarbonyl core less probable. No obvious preference of one of the possible donor site combinations (pyridine/pyridine or pyridine/hydrazone) has been observed. Products of the composition [Re(CO)-Br(Hpy₂bhyd-py¹,py²] and [Re(CO)₃Br(Hpy₂bhyd-py,hyd)] are formed parallely when $(Et_4N)_2[Re(CO)_3Br_3]$ and Hpy₂bhyd are heated on reflux in methanol without the addition of a supporting base. The percentage of their formation approximately agrees with the expected 1:2 ratio. The two isomers can be separated applying their different solubility. Yellow blocks of [Re(CO)₃Br(Hpy₂bhyd-py¹,py²] deposit directly from the reaction mixture upon concentration whereas the second product can be isolated from the oily residue which is obtained upon complete removal of the solvent. Re-dissolution in THF and overlayering with nhexane gives orange-red crystals of [Re(CO)₃Br(Hpy₂bhyd py^{1} , hyd] · THF. The infrared spectra of both complexes show the typical pattern of the fac-[Re(CO)₃]⁺ core and suggest non-co-ordinating benzoyl groups by the presence of C=O frequencies at 1680 cm⁻¹ which resembles with the value of the carbonyl band in Hpy₂bhyd. FAB⁺ mass spectra of both isomers show no significant differences.

The molecular structure of [Re(CO)Br(Hpy2bhyd py^{1} , py^{2}] is illustrated in Fig. 3. The co-ordination sphere of the rhenium atom is a distorted octahedron. Main distortions are due to the restricting geometric parameters of the chelating ligand. The six-membered chelate ring causes an N1-Re-N31 angle of 83.1(3)°. The bonding parameters of the hydrazone unit are almost uninfluenced by the complex formation. The Re-N bond lengths are 2.217(7) and 2.204(7) A which is somewhat longer than those in the acetylpyridine hydrazone complexes discussed above. This can be attributed to the different sizes of the chelate rings and has also been found for the other few examples of rhenium tricarbonyl complexes with six-membered N,N chelate rings [8,9]. The angular strain inside the six-membered ring can clearly be derived from the angles around the carbon atom C7. The chelate ring is in boat conformation to minimize the strains (Scheme 2). This, however is restricted by repulsions between the bulky hydrazone unit and the pyridine rings.



Figure 3 Ellipsoid presentation [21] of $[Re(CO)_3Br(Hpy_2bhyd-py^1, py^2)]$. Thermal ellipsoids represent 50 per cent probability.



Scheme 2



Figure 4 Ellipsoid presentation [21] of [Re(CO)₃Br(Hpy₂bhyd-py, hyd)]. Thermal ellipsoids represent 50 per cent probability.

Fig. 4 shows the molecular structure of $[Re(CO)-Br(Hpy_2bhyd-py^1,hyd]$. The compound co-crystallises with a molecule of solvent THF and a hydrogen bond between H3 and the oxygen atom of the solvent is established. The rhenium atom is six-co-ordinate with the same extend of

Table	2	Selected	bond	lengths/A	and	angles/°	for	$[Re(CO)_3-$
Br(Hp	y ₂ ł	ohyd-py,hy	yd)] and	d [Re(CO) ₃	Br(H)	py2bhyd-j	py ¹ ,p	y ²)]

	[Re(CO) ₃ - Br(Hpy ₂ bhyd-py ¹ ,py ²)]	[Re(CO) ₃ - Br(Hpy ₂ bhyd-py,hyd)]*		
Re-C10	1.904(9)	1.93(1)		
Re-C20	1.93(1)	1.911(8)		
Re-C30	1.92(1)	1.90(1)		
Re-Br	2.602(1)	2.615(1)		
Re-N1	2.217(7)	2.167(7)		
Re-N2/N31	2.204(7)	2.197(7)		
C6-C7	1.49(1)	1.44(1)		
C7-C36	1.48(1)	1.49(1)		
C7-N2	1.30(1)	1.29(1)		
N2-N3	1.360(9)	1.39(1)		
N3-C27	1.38(1)	1.36(1)		
C27-O28	1.22(1)	1.20(1)		
Re-N1-C6	121.2(5)	115.5(6)		
N1-C6-C7	116.5(7)	116.2(7)		
C6-C7-N2	113.5(7)	115.4(7)		
C7-N2-Re	_	117.5(5)		
C6-C7-C36	117.4(7)	121.2(8)		
C7-C36-N31	118.9(7)	112.8(9)		
C36-N31-Re	119.2(5)	_		
Br-Re-C10	177.7(3)	175.7(3)		
Br-Re-C20	88.8(3)	92.0(3)		
Br-Re-C30	93.9(3)	93.9(3)		
Br-Re-N1	85.7(2)	86.3(2)		
Br-Re-N2/N31	86.3(2)	81.3(2)		
C10-Re-C20	91.3(4)	89.4(4)		
C10-Re-C30	88.4(4)	90.2(5)		
C10-Re-N1	94.2(3)	91.8(3)		
C10-Re-N2/N31	91.3(3)	94.5(4)		
C20-Re-C30	88.3(4)	88.5(7)		
C20-Re-N1	174.5(3)	172.0(6)		
C20-Re-N2/N31	95.8(4)	98.4(6)		
C30-Re-N1	92.8(3)	99.4(4)		
C30-Re-N2/N31	175.9(3)	171.7(3)		
N1-Re-N2/N31	83.1(3)	73.7(3)		

Hydrogen bond: N3-H3...O40 (x, 1+y, z) d(D-H) 0.81(11) Å, d(H...A) 1.97(11) Å, d(D...A) 2.764(12) Å, <(DHA) 166(10)°

distortions of the octahedral co-ordination sphere by the influence of the 5-membered chelate ring as has been discussed previously for $[Re(CO)_3Br(Hacpybhyd)]$ and $[Re(CO)_3(OH_2)(acpybhyd)]$. Selected bond lengths and angles of $[Re(CO)Br(Hpy_2bhyd-py^1,hyd]$ and $[Re(CO)Br-(Hpy_2bhyd-py^1,py^2]$ are compared in Table 2.

In contrast to the reaction of (Et₄N)₂[Re(CO)₃Br₃] with Hapbhyd, where the addition of a supporting base results in the deprotonation of the hydrazone and the formation of [Re(CO)₃(OH₂)(apbhyd)], Hpy₂bhyd is hydrolysed upon addition of Et₃N and finally $[Re(CO)_3 \{py_2C(O)OH\}]$, a complex with a tridentately bonded bis(2-pyridyl)hydroxymethanolato ligand is obtained. The compound can also be isolated from reactions of (Et₄N)₂[Re(CO)₃Br₃] with bis(2pyridyl)ketone and Et₃N or (in less yields) from the hydrolysis of [Re(CO)₃Br(Hpy₂bhyd-py¹,py²)]. This, and the fact that hydrolysis of neat Hpy₂bhyd or py₂CO under comparable conditions proceeds very slowly and under decomposition of the products, suggest that the nucleophilic attack of water is metal-promoted in the cases described above. The hydrolysis or alcoholysis of py2CO in the presence of metalions and complex-formation with the resulting



Figure 5 Ellipsoid presentation [21] of [Re(CO)₃{py₂C(OH)O})]. Thermal ellipsoids represent 50 per cent probability.

diol is not without precedent. Besides numerous multiwith bridging $[py_2C(OH)_2]^0$, nuclear compounds $[py_2C(OH)O]^-$ and $[py_2CO_2]^{2-}$ units, a number of mononuclear complexes has been isolated containing bis(2-pyridyl)methanediol as neutral N,N'-bonded ligand [10]. Tridentate co-ordination of the neutral ligand has been observed for Cu²⁺ and Ni²⁺ complexes [11], whereas its singly deprotonated forms is present in chromium, cobalt, ruthenium or antimony compounds [12] as well as in the rhenium(V) complex [ReOCl₂{ $py_2C(OH)O$ }] which has been prepared from [ReOCl₃(Ph₃P)₂] and py₂CO in THF [13]. The formation of $[Re(CO)_3 \{py_2C(OH)O\}]$ from the hydrolysis of [Re-(CO)₃Cl(py₂CO)] has been studied spectroscopically and an extended electrochemical report has bee given [14].

The ready metal-promoted hydrolysis of Hpy₂bhyd may be attributed to the angular strain in $[Re(CO)_3Br-(Hpy_2bhyd)]$ which is induced by the formation of the nonplanar six-membered chelate ring (Fig. 3) and can also be seen from the lengthening of the Re-N(pyridine) bond length. The hybridisation of the carbon atom C7 is changed to sp³ upon hydrolysis and the resulting bond angles at C7 come close to the tetrahedral angle. A representation of the structure of $[Re(CO)_3\{py_2C(OH)O\}]$ is given in Fig. 5. Selected bond lengths and angles are summarised in Table 3 and compared with the corresponding values in [Re-(CO)_3Br(py_2CO)].

The latter compound is obtained when equivalent amounts of $(Et_4N)_2[Re(CO)_3Br_3]$ and py_2CO are heated on reflux in acetonitrile. Hydrolysis and the formation of $[Re(CO)_3\{py_2C(OH)O\}]$ is only observed when considerable amounts of water are added. This is remarkable since attempts to prepare $[ReOCl_3\{py_2CO\}]$ with an intact and unco-ordinated ketone group failed even when unaerobic conditions were applied [13a]. $[Re(CO)_3Br(py_2CO)]$ is an



Figure 6 Ellipsoid presentation [21] of $[Re(CO)_3Br(py_2CO)]$. Thermal ellipsoids represent 50 per cent probability. A disorder of 50 per cent occupancy between the Br atom and the carbonyl group C10/O10 have been omitted for clarity.



Figure 7 Ellipsoid presentation [21] of [Re(CO)₃Br(pytehyd)]. Thermal ellipsoids represent 50 per cent probability.

air-stable orange-red solid which is readily soluble in polar organic solvents. The IR frequency of the keto group can be assigned at 1685 cm⁻¹ which is slightly shifted compared with the value of the unco-ordinated py₂CO (1675 cm⁻¹). The FAB⁺ mass spectrum shows a less intense peak for the molecular ion at m/z = 534/536 (corresponding to the 1:1 isotopic pattern of ^{79,81}Br) and a fragment peak representing [Re(CO)₃(py₂CO)]⁺. The solid state structure of [Re(CO)₃Br(py₂CO)] is one of the few examples where py₂CO is chelate bonded to a single metal atom. To our knowledge there are only two other examples, a platinum(II) complex with an additional cyclobutanedicarboxylato ligand [15] and a chlorobridged ruthenium(II) dimer [16].

Table	3	Selected	bond	lengths/Å	and	angles/°	foi
[Re(CO) ₃ {p	y ₂ C(OH)O	}] and [R	Re(CO) ₃ Br(py	² CO)]		

	$[Re(CO)_3\{py_2C(OH)O\}]$	[Re(CO) ₃ Br(py ₂ CO)]
Re-C10	1.892(7)	1.85(3)
Re-C20	1.925(8)	1.897(8)
Re-C30	1.923(7)	- ``
Re-O71/Br	2.101(4)	2.573(6)
Re-N1	2.185(5)	2.201(6)
Re-N11	2.180(5)	-
C7-O71/O7	1.397(7)	1.30(2)
C7-O72	1.388(7)	-
Re-N1-C6	112.4(4)	121.8(5)
N1-C6-C7	111.6(5)	120.1(7)
C6-C7-C16/C6'	106.2(5)	121.0(9)
C16-N11-Re	111.9(4)	_*
O71/Br-Re-C10	170.1(3)	178.9(9)
O71/Br-Re-C20	97.9(2)	90.9(3)
O71/Br-Re-C30	96.6(2)	_*
O71/Br-Re-N1	75.3(2)	88.0(2)
O71/Br-Re-N11	74.5(2)	_*
C10-Re-C20	89.1(3)	89.9(6)
C10-Re-C30	90.3(3)	_*
C10-Re-N1	97.5(3)	91.2(6)
C10-Re-N11	98.0(3)	_*
C20-Re-C30	91.5(3)	_*
C20-Re-N1	172.9(2)	93.6(3)
C20-Re-N11/N1'	94.5(2)	176.6(3)
C30-Re-N1	91.3(3)	_*
C30-Re-N11	169.8(2)	_*
N1-Re-N11/N1'	81.8(2)	83.2(3)

Table 4 Selected bond lengths/Å and angles/° for $[Re(CO)_3-Br(pytehyd]]$

1.900(7)	C30-O30	1.125(9)
1.919(8)	N1-C6	1.355(8)
1.909(9)	C6-C7	1.447(9)
2.620(1)	C7-N2	1.276(9)
2.165(5)	N2-N3	1.399(7)
2.195(5)	N3-C27	1.260(9)
1.147(8)	C27-C21	1.46(1)
1.126(9)		
87.7(3)	Br-Re-N2	83.8(1)
90.5(3)	N1-Re-N2	74.1(2)
93.8(3)	Re-C10-O10	1176.3(7)
94.6(3)	Re-C20-O20	178.1(8)
168.6(3)	Re-C30-O30	179.2(6)
90.7(4)	Re-N1-C6	116.8(4)
91.3(3)	N1-C6-C7	113.6)6)
175.5(3)	C6-C7-N2	119.8(6)
103.5(3)	Re-N2-C7	115.5(4)
175.3(2)	Re-N2-N3	132.7(4)
93.2(2)	N2-N3-C27	114.9(6)
91.6(2)	C7-N2-C3	111.1(5)
84.6(1)		-
	$\begin{array}{c} 1.900(7)\\ 1.919(8)\\ 1.909(9)\\ 2.620(1)\\ 2.165(5)\\ 2.195(5)\\ 1.147(8)\\ 1.126(9)\\ 87.7(3)\\ 90.5(3)\\ 93.8(3)\\ 94.6(3)\\ 168.6(3)\\ 90.7(4)\\ 91.3(3)\\ 175.5(3)\\ 103.5(3)\\ 175.3(2)\\ 93.2(2)\\ 91.6(2)\\ 84.6(1)\\ \end{array}$	1.900(7) C30-O30 1.919(8) N1-C6 1.909(9) C6-C7 2.620(1) C7-N2 2.165(5) N2-N3 2.195(5) N3-C27 1.147(8) C27-C21 1.126(9) 87.7(3) 87.7(3) Br-Re-N2 90.5(3) N1-Re-N2 93.8(3) Re-C10-O10 94.6(3) Re-C30-O30 90.7(4) Re-N1-C6 91.3(3) N1-C6-C7 175.5(3) C6-C7-N2 103.5(3) Re-N2-C7 175.3(2) Re-N2-N3 93.2(2) N2-N3-C27 91.6(2) C7-N2-C3

Symmetry operation: (') x, 0.5-y, z; * symmetry related atoms

An ellipsoid representation of the structure of [Re-(CO)₃Br(py₂CO)] is given in Fig. 6. A summary of selected bond lengths is contained in Table 3. The co-ordination environment of the rhenium atom is a distorted octahedron in which the distortions are due to the limiting bite angle of the chelate ligand (N1-Re-N1': 83.2(3)°). As discussed above for [Re(CO)₃Br(Hpy₂bhyd-py¹,py²)], the Re-N bonds are slightly longer than the other Re-N(pyridine) bonds. The six-membered chelate ring is in boat conformation minimising the angular strain at the carbon atom C7. This strain is less than in [Re(CO)₃Br(Hpy₂bhyd-py¹,py²)] as can be derived from the bond angles around C7. The values of 118.6, 118.6 and 121.0° for [Re(CO)₃Br(py₂CO)] come much closer to the ideal value of 120° for an idealised sp² hybridised atom than the corresponding angles in the hydrazone complex: 113.5, 117.4 and 128.7°. This should be addressed to sterical interactions with the non-co-ordinated hydrazone substituent and limits the synthetic potential of the ketone moiety in [Re(CO)₃Br(py₂CO)] for derivatisation reactions with biomolecules which should weaken the rhenium ligand bonds and finally lead to solvolysis.

However, the formation of inert complexes with the functionalised hydrazones and hydrazonato ligands described above encouraged us to attempt reactions with hydrazone ligands containing additional reactive sites for coupling reactions with proteins. Exemplarily the complex formation of the tricarbonylrhenium(I) core with pyridinealdehyde terephtalaldehydebishydrazone, pytehyd, is described.

Orange-red crystals of [Re(CO)₃Br(pytehyd)] were obtained when equivalent amounts of $(Et_4N)_2[Re(CO)_3Br_3]$ and pytehyd were heated under reflux in ethanol. As with the ligands described above, chelate formation is obtained with pytehyd. A 5-membered chelate ring is obtained using the pyridine and hydrazone donor sites as has been observed $[Re(CO)_3Br(Hapbhyd)], [Re(CO)_3(OH_2)$ for (apbhyd)] or [Re(CO)₃Br(Hpy₂bhyd-py,hyd)]. Thus the environment is very similar to the situation in these complexes. The molecular structure of [Re(CO)₃Br(pytehyd)] is illustrated in Fig. 7. Selected bond lengths and angles are summarised in Table 4. The most remarkable feature of the compound is the presence of the reactive formyl group which allows further substitution reactions at the co-ordinated ligand. This favours this compound for coupling reactions with biomolecules.

Summary and Conclusions

The rhenium(I) tricarbonyl core readily reacts with acetylpyridine hydrazone and related ligands under formation of chelate complexes. A summary of the performed reactions and obtained products is given in Scheme 3. The pyridine site of the ligands always contributes to the complex formation whereas the benzoyl moiety remains unco-ordinated. Deprotonation of Hacpybhyd is achieved when a supporting base is added. The same procedure decomposes Hpy₂bhyd under formation of bis(2-pyridine)methanediol which represents the product of hydrolysis of bis(2-pyridine)ketone. It reacts as mononegative, tridentate chelate ligand under formation of $[Re(CO)_3 \{py_2C(OH)O\}]$. A rhenium complex with intact bis(2-pyridine)ketone, [Re(CO)₃- $Br(py_2CO)$], is obtained from direct reactions between (Et₄N)₂[Re(CO)₃Br₃] and the ketone. This compound is more resistant against hydrolysis than the complex with the hydrazone derivative, [Re(CO)₃Br(Hpy₂bhyd-py,hyd)].





Appropriate substitution of the chelating hydrazone ligands allows the synthesis of functionalised rhenium complexes which can be used for the coupling of biomolecules and represent an interesting approach for nuclear medical labelling experiments. An example has been given with [Re-(CO)₃Br(pytehyd)].

Experimental

Hapbhyd has been prepared by heating equivalent amounts of benzoylhydrazone and acetylpyridine (ALDRICH) in refluxing ethanol. Pytehyd has been prepared by heating formylpyridine hydrazone with terephtalaldehyde in boiling methanol in a 2:1 ratio. The compounds have been characterised by elemental analysis and standard spectroscopic methods. Hpy₂bhyd and py₂CO have been purchased commercially (ALDRICH). All reactions have been performed on air without special precautions against moisture.

Infrared spectra have been recorded for KBr pellets on a Shimadsu instrument. Routine FAB⁺ spectra have been measured with a TSQ spectrometer (Finnigan) with nitrobenzylalcohol as matrix. A 400MHz JEOL spectrometer has been used for the NMR measurements.

 $[Re(CO)_3Br(Hapbhyd)]$. (Et₄N)₂[Re(CO)₃Br₃] (77 mg, 0.1 mmol) and Hapbhyd (24 mg, 0.1 mmol) were dissolved in 20 ml methanol and heated under reflux for 2 h. The solvent was removed in vacuum and the oily residue was re-dissolved in acetonitrile. This solution was overlayered with diethyl ether. Slow diffusion of the ether into the acetonitrile layer gave orange-red crystals of [Re(CO)₃Br(Hapbhyd)]. Yield: 35 mg (55%). Elemental analysis, Found: C, 34.7; H, 2.5; N, 6.9%; Calcd. for C₁₇H₁₃N₃O₄BrRe: C, 34.6; H, 2.2; N, 7.1%.

IR (v_{max} /cm⁻¹): 2020, 1895, 1870sh (C≡O), 1675 (C=O), 1480 (C=N). FAB⁺-MS m/z (assignment, %B): 510 ([M−Br]⁺, 8), 482 ([Re(CO)₂(apbhyd)]⁺, 5), 454 ([Re(CO)(apbhyd)]⁺, 5), 426 ([Re(apbhyd)]⁺, 7). ¹H-NMR (acetone): 10.6 s NH (1H), 7.4-9.2 m phenyl, pyridine (13H), 1.4 CH₃ s (3H).

 $[Re(CO)_3(OH_2)(Hapbhyd)]$. Hapbhyd (24 ml, 0.1 mmol) was dissolved in 20 ml methanol and 0.2 ml Et₃N was added. This mixture

was added to a solution of $(Et_4N)_2[Re(CO)_3Br_3]$ (77 mg, 0.1 mmol) in 10 ml methanol. After heating for 2 h on reflux the solvent was removed and the oily residue was re-dissolved in THF. Overlayering with diethyl ether and standing for some days gave yellow-orange crystals of [Re(CO)_3(OH_2)(apbhyd)]. Yield: 39 mg (75%). Elemental analysis, Found: C, 38.4; H, 3.0; N, 7.8%; Calcd. for $C_{17}H_{14}N_3O_5Re:$ C, 38.7; H, 2.7; N, 8.0%.

 $\begin{array}{l} \label{eq:result} \mbox{IR} (v_{max}/cm^{-1}\ 2017,\ 1900,\ 1895sh\ (C=O),\ 1670\ (C=O),\ 1480\ (C=N).\ FAB^+-MS\ m/z\ (assignment,\ \%B):\ 510\ ([M\ -H_2O]^+,\ 20),\ 481\ ([Re(CO)_2(apbhyd)]^+,\ 10),\ 454\ ([Re(CO)(apbhyd)]^+,\ 10),\ 426\ ([Re(apbhyd)]^+,\ 5).\ ^1\ H-NMR\ (acetone):\ 11.3\ s\ OH\ (1H),\ 7.3\ -9.1\ m\ phenyl,\ pyridine\ (13H),\ 1.3\ s\ CH_3\ (3H). \end{array}$

[$Re(CO)_3Br(Hpy_2bhyd-py^1,py^2)$]. (Et₄N)₂[Re(CO)₃Br₃] (77 mg, 0.1 mmol) and Hpy₂bhyd (30 mg, 0.1 mmol) were dissolved in 20 ml methanol and heated on reflux for 2 h. The resulting orangered solution has been reduced in volume to about 5 ml and stored at about 5 °C for 5 days. During this time yellow blocks of [Re-(CO)₃Br(Hpy₂bhyd-py¹,py²)] deposited which have been filtered off and washed with a minimum amount of cooled methanol. Yield: 20 mg (30%). Elemental analysis, Found: C, 38.5; H, 2.0; N, 8.6 %; Calcd. for C₂₁H₁₄N₄O₄BrRe: C, 38.6; H, 2.1; N, 8.6%.

IR (v_{max} /cm⁻¹): 2005, 1910, 1895 (C=O), 1680 (C=O), 1475 (C=N). FAB+MS m/z (assignment, %B): 651 ([M]⁺, 30), 595 ([M-2(CO)]⁺, 25), 546 ([M-PhCO]⁺, 25).

 $[Re(CO)_3Br(Hpy_2bhyd-py,hyd)] \cdot THF$. This compound has been isolated from the orange-red filtrate obtained during the preparation of $[Re(CO)_3Br(Hpy_2bhyd-py^1,py^2)]$. The solvent has been removed in vacuum and the oily liquid has been re-dissolved in THF. Overlayering with n-hexane gave orange-red crystals of $[Re(CO)_3Br(Hpy_2bhyd-py,hyd)] \cdot THF$.

Yield: 42 mg (60%). Elemental analysis, Found: C, 41.2; H, 3.3; N, 7.7 %; Calcd. for $C_{25}H_{22}N_4O_5BrRe:$ C, 41.4; H, 3.0; N, 7.7%. The crystals lost solvent upon standing at ambient temperatures for several weeks.

IR (v_{max}/cm^{-1}): 2005, 1915sh, 1895 (C=O), 1680 (C=O), 1475 (C=N). FAB⁺-MS m/z (assignment, %B): 652 ([M]⁺, 32), 623 ([M-CO]⁺, 30), 595 ([M-2(CO)]⁺, 25), 546 ([M-PhCO]⁺, 25).

 $[Re(CO)_3Br\{py_2C(OH)O\}]$. a) Hpy₂bhyd (30 mg, 0.1 mmol) has been dissolved in 20 ml methanol and 2 ml Et₃N has been added. (Et₄N)₂[Re(CO)₃Br₃] (77 mg, 0.1 mmol) has been added and the resulting solution has been heated on reflux for 2 h. Finally the volume has been reduced to about 3 ml and yellow crystals deposited upon cooling. Yield: 16 mg (35%).

b) $(Et_4N)_2[Re(CO)_3Br_3]$ (77 mg, 0.1 mmol) and py_2CO (19 mg, 0.1 mmol) have been dissolved in 20 ml acetonitrile. 2 ml Et_3N and 0.1 ml H_2O have been added. The colour of the solution changed to yellow upon heating on reflux and a yellow solid of $[Re(CO)_3Br\{py_2C(OH)O\}]$ precipitated upon cooling. Yield 30 mg (65%). Elemental analysis, Found: C, 35.6; H, 1.9; N, 5.9%; Calcd. for $C_{14}H_9N_2O_5Re:$ C, 35.6; H, 1.9; N, 5.9%.

IR (ν_{max} /cm⁻¹): 2008, 1910, 1861 (C≡O), 3048 (OH). FAB⁺-MS m/z (assignment, %B): 473 ([M+H]⁺, 5), 472 ([M]⁺, 5), 444 ([M-(CO)]⁺, 3), 416 ([M-2CO]⁺, 3). ¹H-NMR: pyridine 7.4 m (1H), 7.8 m (1H), 8.8 m (1H); OH 7.75 s (1H).

 $[Re(CO)_3Br(py_2CO)]$. (Et₄N)₂[Re(CO)₃Br₃] (77 mg, 0.1 mmol) and py₂CO (19 mg, 0.1 mmol) have been dissolved in 20 ml acetonitrile. The mixture has been heated on reflux for 2 h. Orangered crystals of [Re(CO)₃Br(py₂CO)] deposited upon reducing the volume of the solvent to about 3 ml and cooling. Yield: 30 mg (55%). Elemental analysis, Found: C, 31.4; H, 1.6; N, 5.0 %; Calcd. for C₁₄H₈N₂O₄Re: C, 31.4; H, 1.5; N, 5.2%.

IR (ν_{max} /cm⁻¹): 2010, 1915, 1880sh (C≡O), 1685 (C=O). FAB⁺-MS m/z (assignment, %B): 534/536 ([M]⁺, 4), 455 ([M-Br]⁺, 10). ¹H-NMR: pyridine 7.9 m (1H), 8.2 m (1H), 8.4 m (1H), 9.3 m (1H).

	[Re(CO) ₃ Br- (Hapbhyd)]	[Re(CO) ₃ - (OH ₂)(apbhyd)]	[Re(CO) ₃ Br(Hpy ₂ - bhyd-py ¹ ,py ²)]	[Re(CO) ₃ Br(Hpy ₂ - bhyd-py,hyd)]THF ^{a)}	[Re(CO) ₃ - {py ₂ (OH)O}]	[Re(CO) ₃ Br- (py ₂ CO)]	[Re(CO) ₃ Br- (aptehyd)] ^{b)}
Crystal dimensions (mm ³)	$1 \cdot 1 \cdot 0.2$	0.20 · 0.20 · 0.05	0.2 · 0.15 · 0.15	0.20 · 0.10 · 0.10	0.2 · 0.15 · 0.05	$0.2 \cdot 0.2 \cdot 0.1$	0.60 · 0.15 · 0.02
Formula	C17H13N3BrO4Re	C ₁₇ H ₁₄ N ₃ O ₅ Re	C ₂₁ H ₁₄ BrN ₄ O ₄ Re	C25H22BrN4O5Re	C ₁₄ H ₉ N ₂ O ₅ Re	C14H8BrN2O4Re	C ₁₇ H ₁₁ BrN ₃ O ₄ Re
$M (g mol^{-1})$	589.41	526.51	652.47	724.58	471.43	534.33	587.40
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	P2 ₁ /c	ΡĪ	P2 ₁ /c	P21	C2/c	Pnma	P2 ₁ /c
Unit cell	a = 11.777(2) Å	a = 8.270(2)	a = 13.480(1) Å	a = 10.961(3)Å	a = 27.569(4) Å	a = 8.253(2) Å	a = 7.510(2) Å
	b = 11.760(1) Å	b = 9.378(2)	b = 11.248(1) Å	b = 9.791(1) Å	b = 7.800(1) Å	b = 13.020(2) Å	b = 17.158(2) Å
	c = 13.513(2) Å	c = 11.722(2) $\alpha = 76.99(2)$	c = 14.368(2) Å	c = 12.779(2) Å	c = 16.157(3) Å	c = 12.532(2) Å	c = 14.059(4) Å
	$\beta = 100.78(1)^{\circ}$	$\beta = 87.15(2)$ $\gamma = 79.54(3)$	$\beta = 104.26(1)$	$\beta = 101.40(2)^{\circ}$	$\beta = 125.55(1)$	$\beta = 92.56(2)^{\circ}$	
V (Å ³)	1839.6(4)	870.7(3)	2111.3(3)	1344.4(5)	2826.6(8)	1450.0(5)	1809.8(7)
z	4	2	4	2	8	4	4
$D_c (g \text{ cm}^{-3})$	2.128	2.008	2.053	1.790	2.216	2.448	2.156
Measuring temperature (°C)	20	20	20	20	-100	20	20
Scan type	ω scans	ω scans	@-scans	ω-scans		ω-scans	@-scans
Linear absorption coefficient (mm ⁻¹)	8.804	7.012	13.793	6.046	8.623	11.154	8.949
Absorption correction	DELABS [19]	DELABS [199]	ψ scans	ψ scans	SADABS [20]	DELABS [19]	ψ scans
T _{min}	0.0412	0.3345	0.7810	0.8347	0.6006	0.300	0.6659
T _{max}	0.2719	0.7206	0.9752	0.9955	0.9077	0.740	0.9040
Measured reflections	4562	5925	4536	6743	16326	5197	4402
Independent reflections/R _{int}	3980/0.0354	5064/0.0566	3584/0.0609	5826/0.0337	4134/0.0649	2150/0.0476	3556/0.0373
Refined parameters	287	291	282	313	235	127	279
R1 (F)/wR2 (F ²) (I > 2σ (I))	0.0372/0.0729	0.0229/0.0518	0.0479/0.1300	0.0437/0.0961	0.0353/0.0666	0.0511/0.1260	0.0333/0.0686
GooF	1.053	1.020	1.032	1.043	0.913	1.187	1.063
Programs used	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]	SHELXS97 [17], SHELXL97 [18], PLATON, HELENA [19]

Table 5 X-ray structure data collection and refinement parameters

a) Flack parameter: 0.008(16)

 $[Re(CO)_3Br(pytehyd)]$. (Et₄N)₂[Re(CO)₃Br₃] (77 mg, 0.1 mmol) and pytehyd (24 mg, 0.1 mmol) were dissolved in 20 ml methanol and heated under reflux. The solution turned yellow-orange within 30 min. Orange-red crystals of [Re(CO)₃Br(pytehyd)] precipitated after reducing the solvent to about 2 ml and cooling. Yield: 40 mg (63%). Elemental analysis, Found: C, 34.5; H, 2.2; N, 7.2%; Calcd. for C₁₇H₁₁N₃O₄BrRe: C, 34.6; H, 2.2; N, 7.1%.

 $IR \ (v_{max}/cm^{-1}): 2025, 2000, 1875sh \ (C=O), 1695 \ (C=O), 1485 \ (C=N). FAB^+-MS \ m/z \ (assignment, %B): 508 \ ([M-Br]^+, 15), 480 \ ([Re(CO)_2(pytehyd)]^+, 10), 452 \ ([Re(CO)(pytehyd)]^+, 5).$

X-Ray structure determinations

The intensities for the X-ray determinations were collected on an automated single crystal diffractometer of the type CAD4 (Enraf-Nonius) or a SMART CCD (Bruker) with Mo K α ($\lambda = 0.71073$ Å) or Cu K α radiation ($\lambda = 1.54184$ Å). Standard procedures have been applied for data reduction and absorption correction. Structure solutions and refinements have been performed with SHELXS97 and SHELXL97 [17, 18]. More details on data collection and structure calculation are contained in Table 5.

The refinements have been done with anisotropic thermal parameters for all non-hydrogen atoms. The positions of the hydrogen atoms binding on carbon atoms have been calculated using the "riding model" option of SHELXL97. H atoms on nitrogen atoms which are mentioned in the text (e.g. for the discussion of hydrogen bonds or to derive the protonation of the NH function in the ligands) have been obtained from the Fourier maps.

The position of the bromine atom in $[Re(CO)_3Br(py_2CO)]$ is disordered with the carbonyl group in *trans* position. This has been regarded during the refinement with an approximate 64/36per cent occupancy of each site.

Further details of the crystallographic data have been deposited with the Cambridge Crystallographic Data Centre under the deposition numbers CCDC-195113 (([Re(CO)₃Br(Hapbhyd)]), CCDC-195114 ([Re(CO)₃(OH₂)(apbhyd)]), CCDC-195115 ([Re(CO)₃Br-(Hpy₂bhyd-py,hyd)]), CCDC-195116 ([Re(CO)₃Br(Hpy₂bhyd-py¹,py²)]), CCDC-195117 ([Re(CO)₃{py₂(OH)O}]), CCDC-195118 ([Re(CO)₃Br(py₂CO)]) and CCDC-195119 ([Re(CO)₃Br(aptehyd)]).

Acknowledgements. We thank the Hermann Starck AG (Goslar) for a generous gift of rhenium metal and Professor J. Strähle (Tübingen) for the opportunity to collect the X-ray data set of [Re-(CO)₃Br(Hpy₂bhyd-py¹,py²)].

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