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Synthesis, Characterisation and Ligand Properties of Novel Bi-1,2,3-triazole Ligands

Uwe Monkowius,*[a] Stefan Ritter,[b] Burkhard König,*[b] Manfred Zabel,[b] and Hartmut Yersin[c]

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Three 1,1′-disubstituted 4,4′-bi-1*H*-1,2,3-triazols [R-bta; R = Bn (**1**), Ph (**2**), CH_2COOH (**3**)] have been synthesised as bidentate, nitrogen-based ligands by a Cu^I-catalysed "click" reaction between 1,3-butadiyne and organic azides. Their ligand properties were investigated by preparation of the complexes $[Ru^{II}(R\text{-bta})_3]Cl_2$ [R = Bn (**4**), Ph (**5**), CH_2COOH (**6**)], $[(Bn\text{-bta})Cu^I(DPEPhos)]$ (**7**) [DPEPhos = bis{2-(diphenylphosphanyl)phenyl} ether] and $[(Bn\text{-bta})Re^I(CO)_3Cl]$ (**8**) following standard reaction procedures. All compounds were analysed by elemental analysis, mass spectrometry and NMR, IR, UV/Vis and luminescence spectroscopy. In addition, the molecular structures of **1**–**4**, **7**, and **8** have been determined by X-ray crystallography. In all complexes the Bn-bta acts as a bidentate ligand with structural features comparable to the analogous 2,2′-bipyridine complexes. In their electronic absorption spectra the Ru^{II} and Re^I complexes exhibit a lowest energy band at around 300 nm, which is substantially higher in energy than in analogous complexes with bpy ligands. All R-bta ligands yield complexes that are not luminescent in solution or in the solid state, which makes these ligands particularly suited for use as spectator ligands.

Introduction

A large number of transition metal complexes based on the 2,2′-bipyridine (bpy) ligand and its derivatives have been investigated in different fields of chemistry due to their high stability and remarkable (electro)chemical and photophysical properties. More than 4200 entries were found in the Cambridge Structural Database when searching for complexes with byp (February 2007). There have been many reports about the application of these metal complexes in opto-electronic devices, as redox- and photo-catalysts, as building blocks of supramolecular structures and for medical and analytical purposes.[1–4] Prominent examples are $[Ru(bpy)_3]^{2+}$ and related octahedral d^6 transition metal complexes, which are frequently employed in studies that take advantage of the properties of their excited state, such as in photochemistry, chemoluminescence, electro-chemoluminescence and electron-transfer chemistry.[5–8]

New chromophoric ligands that are capable of generating emissions in the blue region of the spectrum are in demand due to the rapid development of OLED (organic light emitting device) technology. It has been shown that the emission energy increases with decreasing size of the chromophoric π-system, and this strategy has been successfully applied by Thompson et al. in the case of cyclometallated Ir^{III} complexes, where replacement of the pyridine moiety by the five-membered ring of a pyrazolyl group led to a hypsochromic shift of the emission wavelength.[9] Chelating ligands with high energy electronic states are also useful as auxiliary, ancillary, spectator or innocent ligands in light-emitting complexes.[10] De Cola et al. recently reported a blue light emitting heteroleptic Ir^{III} complex (λ_{max} = 461 nm), where the anionic 1,2,4-triazolyl ligand (Figure 1) does not participate directly in the electronic transition.[11–13]

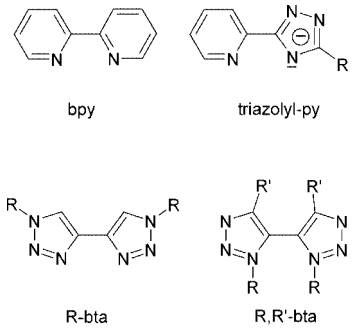

Figure 1. Bpy and triazolyl-py, R-bta and R,R′-bta ligands.

1,1′-R_2-4,4′-Bi(1,2,3-triazole) ligands (R-bta, R = organic group) seem to be promising alternatives to bipyr-

[a] Institut für Anorganische Chemie, Johannes Kepler Universität Linz,
4040 Linz, Austria
E-Mail: Uwe.Monkowius@jku.at
[b] Institut für Organische Chemie, Universität Regensburg,
93040 Regensburg, Germany
E-Mail: Burkhard.Koenig@chemie.uni-regensburg.de
[c] Institut für Physikalische Chemie, Universität Regensburg,
93040 Regensburg, Germany

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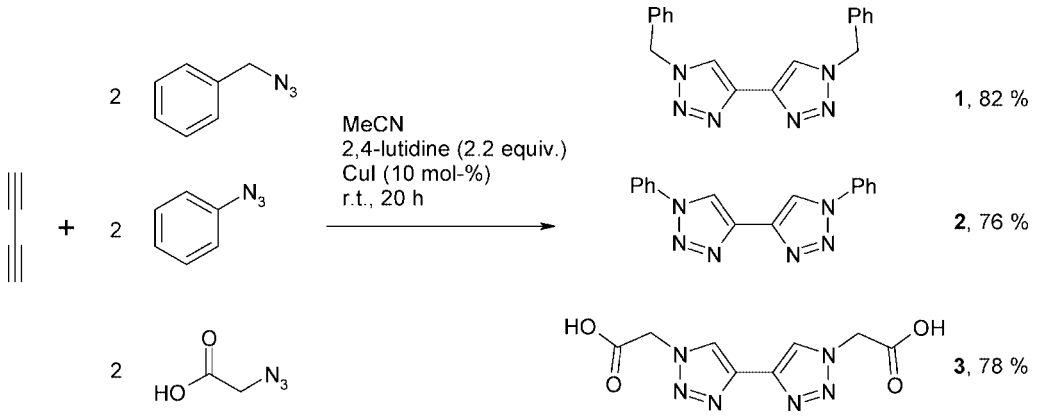


Scheme 1. Synthesis of the bitriazoles **1**–**3**.

idine ligands in transition metal complexes (Figure 1). In addition, functionalisation with a wide range of different substituents is possible using the "click chemistry" approach for the preparation of novel R-bta ligands.[14] Compared to bpy, where substitution with certain organic groups is usually cumbersome,[4,15] this may facilitate ligand preparation significantly. CuAAC (copper-catalysed azide-alkyne cycloaddition) has been used recently to synthesise 1,4-disubstituted 1,2,3-triazole ligands,[16] and the oxidative coupling products R,R′-bta (Figure 1) have been observed as major products under basic conditions in the CuAAC.[17]

Complexes of Ru^{II}, Re^{I} and Cu^{I} have been synthesised to evaluate the ligand properties of R-bta and the spectroscopic behaviour of these ligands and complexes investigated by UV/Vis and luminescence spectroscopy.

Results and Discussion

Synthesis of Triazole Ligands

The desired R-bta ligands **1**–**3** were synthesised by a Cu^{I}-catalysed cycloaddition between 1,3-butadiyne and the organic azides (benzyl azide, phenyl azide[14] and β-azidoacetic acid). The 1,3-butadiyne was freshly prepared from 1,4-dichlorobutyne[18] and treated immediately with the azide compound in basic acetonitrile solution in the presence of a catalytic amount of copper iodide (Scheme 1). Workup with aqueous H_2O_2 (3%) and saturated aqueous EDTA was necessary to remove the Cu^{I} salt as it could form a complex with the synthesised R-bta ligands. Compounds **1**–**3** were obtained in acceptable yields as colourless powders after purification. All compounds are sparingly soluble in most organic solvents and insoluble in water.

Spectroscopic Characterisation

The spectroscopic properties of compounds **1**–**3** were investigated by UV/Vis and luminescence spectroscopy. The compounds absorb in the UV region between 220 and 260 nm (Figure 11, Figures S3 and S4 in the Supporting Information). Compound **3** shows a very weak emission signal at 414 nm (λ_{ex} = 267 nm) in the luminescence spectrum.

Structural Studies

All free ligands were structurally characterised by single-crystal X-ray experiments. Ligand **1** crystallises in two different modifications, namely prisms (monoclinic space group $P2_1/c$, with two molecules in the unit cell) and needles (monoclinic space group *Cc*, with four molecules in the unit cell). Whereas the prisms crystallise as the more stable form from most organic solvents used (e.g. CH_2Cl_2, $CHCl_3$, MeCN), needles are obtained as the major fraction only by slow crystallisation from methanol. Because each of the equivalent molecules in crystals of the first modification of **1** has an inversion centre, the asymmetric unit contains only one half of the formula unit (Figure 2). The individual molecules in the latter modification show no crystallographically imposed symmetry, but they approach closely the symmetry of the molecules in the prismatic crystal (Figure 3).

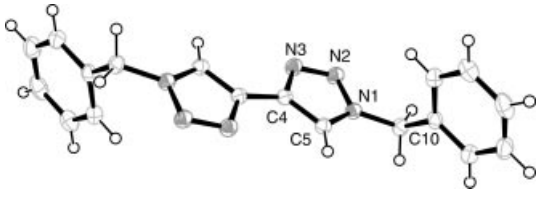


Figure 2. ORTEP drawing of the molecular structure of compound **1** (prismatic crystals) with 50% probability ellipsoids. Selected bond lengths [Å], angles [°] and torsion angles [°]: N1–N2 1.3476(15), N2–N3 1.3195(15), N3–C4 1.3643(17), N1–C5 1.3522(15), C4–C4′ 1.4666(16), C4–C5 1.3764(17); N1–N2–N3 107.26(10), N2–N3–C4 108.71(10), N3–C4–C5 108.54(10), C4–C5–N1 104.45(11), N2–N1–C5 111.05(10), C4′–C4–C5 129.85(11); N3–C4–C4′–N3′ 180.00(11).

Compounds **2** and **3** were obtained as colourless needles. Compound **2** crystallises in the triclinic space group $P\bar{1}$ with three molecules in the unit cell and 1.5 formula units

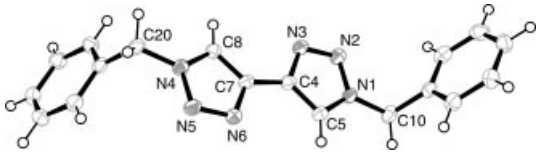


Figure 3. Molecular structure of compound **1** (needles). Selected bond lengths [Å], angles [°] and torsion angles [°]: N1–N2 1.344(4), N2–N3 1.328(4), N3–C4 1.368(4), C4–C5 1.374(4), N1–C5 1.356(4), N4–N5 1.353(4), N5–N6 1.331(4), N6–C7 1.371(4), C7–C8 1.372(4), C8–N4 1.354(4), C4–C7 1.463(3); N2–N1–C5 111.6(2), N1–N2–N3 107.0(2), N2–N3–C4 108.4(3), N3–C4–C5 108.9(3), C4–C5–N1 104.1(3), C5–C4–C7 130.6(3), N5–N4–C8 11.6(2), N4–N5–N6 106.7(2), N5–N6–N7 108.4(2), N6–C7–C8 109.0(2), C7–C8–N4 104.3(2), C4–C7–C8 129.2(3); N3–C4–C7–N6 174.9(3).

per asymmetric unit. This means that there are two independent molecules present, one of which is centrosymmetric and the other roughly C_2-symmetric (Figure 4). Crystals of compound **3** are monoclinic (space group $P2_1/c$ with two molecules in the unit cell). Again, the molecules in crystals of compound **3** are centrosymmetric and the asymmetric unit consists of one half of the formula unit (Figure 5). The carboxylate proton exhibits an intermolecular hydrogen bond with the N3 atom of a neighbouring molecule to form helices [*d*(O1–H) 0.80(6), *d*(H–N3) 1.88(6), *d*(O1–N3) 2.670(4) Å; ∠(O1–H–N3) 171(4)°; Figure 6]. Each discrete helical subunit is connected to two others by the second carboxylate group of the molecule to yield a layered structure of interconnected helices (Figure S1).

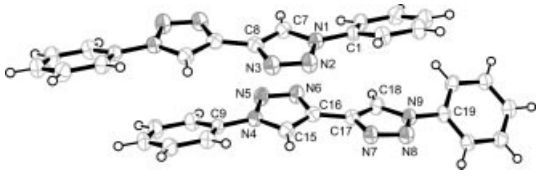


Figure 4. Structure of the two independent molecules in crystals of compound **2**. Selected bond lengths [Å], angles [°] and torsion angles [°]: C8–C8′ 1.452(2), N1–N2 1.357(3), N2–N3 1.310(3), N3–C8 1.365(4), C7–C8 1.372(4), N4–N5 1.358(3), N5–N6 1.312(3), N6–C16 1.368(4), C15–C16 1.372(4), C16–C17 1.449(4), C17–C18 1.374(4), C17–N7 1.368(4), N7–N8 1.310(3), N8–N9 1.362(3); N2–N1–C7 110.5(2), N1–N2–N3 107.4(2), N2–N3–C8 108.7(2), N1–C7–C8 105.1(2), N3–C8–C7 108.3(2), C7–C8–C8′ 129.6(2), N5–N4–C15 110.6(2), N4–N5–N6 107.3(2), N5–N6–C16 108.9(2), N4–C15–C16 105.0(2), N6–C16–C15 108.3(2), N8–N7–C17 108.9(2), N7–N8–N9 107.3(2), N8–N9–C18 110.4(2), N7–C17–C18 108.1(2), C15–C16–C17 130.5(2), C16–C17–C18 129.7(2), C17–C18–N9 105.3(2); N3–C8–C8′–N3′ 180.0(2), N6–C16–C17–N7 173.3(2).

The bitriazole units of molecules **1**–**3** are planar with an (*E*)-configuration of the 3,3′-N atoms. This configuration is also found in all solid-state structures of the free ligand 2,2′-bipyridine.[19] All bond lengths and angles of the triazole moiety lie in a very narrow range and are comparable to those of previously published structures of 1,2,3-triazole compounds.[20] The C–C bonds between the triazole groups have lengths of between 1.449 and 1.466 Å and are therefore shorter than the analogous bond in 2,2′-bipyridine [1.4881(13) Å] (Table 1).[19]

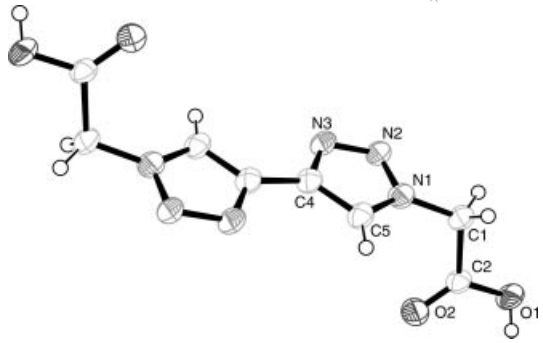


Figure 5. Molecular structure of compound **3**. Selected bond lengths [Å], angles [°] and torsion angles [°]: N1–N2 1.339(4), N2–N3 1.328(5), N3–C4 1.359(5), N1–C5 1.345(5), C4–C4′ 1.446(5), C4–C5 1.377(5); N1–N2–N3 106.1(3), N2–N3–C4 109.5(3), N3–C4–C5 107.9(3), C4–C5–N1 104.6(3), N2–N1–C5 112.0(3), C4′–C4–C5 130.0(3); N3–C4–C4′–N3′ 180.0(4).

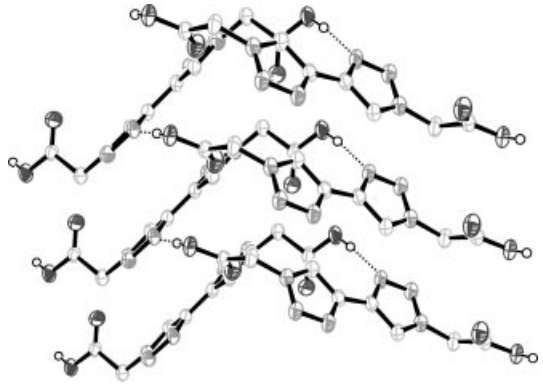


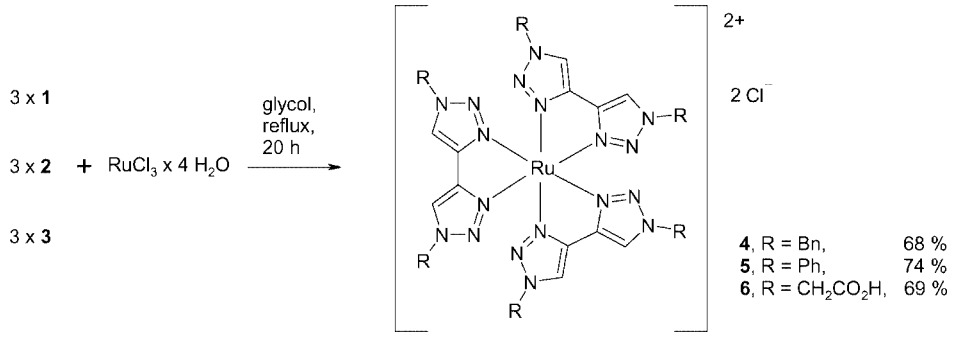
Figure 6. Excerpt from a cell plot of the crystalline phase of compound **3** depicting the helix formed by the intermolecular hydrogen bonds (dotted lines) between the carboxylate protons and the N3 atoms of the neighbouring molecules. Only the participating H atoms are shown for clarity.

Synthesis of Complexes

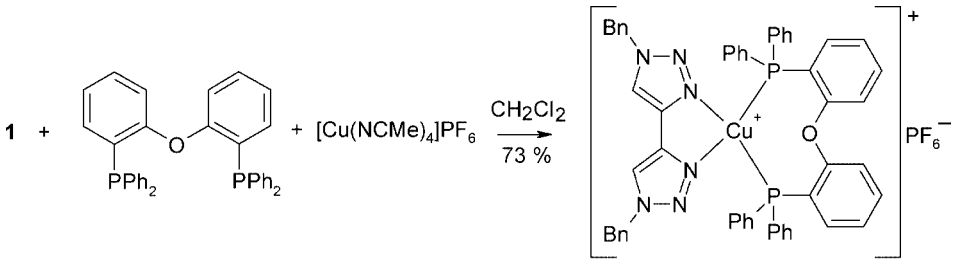
The synthesis of homoleptic Ru^{II} complexes of ligands **1**–**3** was carried out with $RuCl_3 \cdot 4H_2O$ in boiling ethylene glycol solution. Precipitation of complexes **4**–**6** was provoked by addition of ethanol or diethyl ether (Scheme 2).

The synthesis of a heteroleptic Cu^{I} complex (**7**) was performed with ligand **1**, bis[2-(diphenylphosphanyl)phenyl] ether (DPEPhos) and $[Cu^{I}(NCMe)_4]PF_6$ (Scheme 3). The DPEPhos ligand was chosen as related heteroleptic Cu^{I} complexes with a 1,10-phenanthroline (phen) ligand show high quantum yields.[21] The colourless crystals of this complex are only modestly soluble in polar organic solvents. Complex **7** is perfectly stable in solution and the solid state in air at room temperature; no oxidation to Cu^{II} occurs.

The heteroleptic carbonylrhenium(I) complex **8** was obtained from ligand **1** and $[Re^{I}(CO)_5]Cl$, after reaction in toluene and recrystallisation from $MeCN/Et_2O$, as colourless crystals in almost quantitative yield (Scheme 4). This complex is modestly soluble in hot MeCN and, as is the case for its bpy and phen analogs, it is stable in solution and the solid state in air.



Scheme 2. Synthesis of the homoleptic complexes **4**–**6**.



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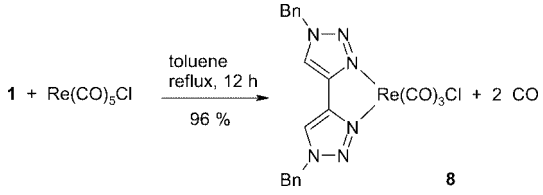
Scheme 3. Synthesis of heteroleptic copper(I) complex **7**.



8

Scheme 4. Synthesis of heteroleptic rhenium(I) complex **8**.

Structural Studies

Recrystallisation from ethylene glycol/ethanol or MeCN/Et_2O yielded complexes **4**–**6** as light yellow crystals, although only the crystals of complex **4** were of sufficient, though still low, quality for an X-ray structure refinement (Figure 7). The quality of the structural data is less accurate because crystals of **4** contain an unspecified number and type of solvent molecules (Figure S2 in the Supporting Information). Complex **4** crystallises in the monoclinic space group $P2_1/a$ with four molecules in the unit cell. The Ru^{II} atom shows a distorted octahedral coordination geometry with both the Λ and Δ enantiomers present in the unit cell. The benzyl substituents have a random orientation and do not approach a symmetrical pattern. The average Ru–N distances of the cations in **4** [*d*(Ru–N) 2.05(3) Å] and $[Ru(bpy)_3]^{2+}$ [*d*(Ru–N) 2.056(2) Å] are roughly the same within experimental error. The average bite angles of the bpy ligand in $[Ru(bpy)_3]^{2+}$ are 79° compared to 77.7(12)° and 77.9(11)° (N7–Ru1–N10 and N13–Ru1–N16, respectively) for the bta ligand in complex **4**.[22] A further discussion of the structural data and a comparison with the free ligand **1** is not meaningful due to the inaccuracy of the experimental data.

The crystals of **7** obtained upon cooling of a dichloromethane solution to –35 °C are triclinic (space group $P\bar{1}$ with four molecules in the unit cell). The asymmetric unit contains two independent complexes with both copper atoms coordinated by **1** and DPEPhos in a distorted tetrahedral environment (Figures 8 and 9). There are no sub van der Waals contacts between the oxygen of the phosphane ligands and the copper centres. Both cations differ in their geometrical parameters, with one benzyl group being disordered over two positions in the cation containing Cu2 (occupation 55:45). Furthermore, the bta ligand deviates significantly from planarity in the case of the cation containing Cu1 [Cu1: ∠(N3–C45–C46–N4) 14.9(8)°; Cu2: ∠(N10–C106–C107–N9) 3.0(6)°]. There is a high degree of asymmetry in the bitriazole coordination [Cu1–N3 2.118(4), Cu1–N4 2.201(5), Cu2–N9 2.233(5), Cu2–N10 2.075(6) Å], as was also found, although less pronounced, for bpy in the crystal structure of the complex $[(bpy)Cu(PPh_3)_2]ClO_4$.[23] The bite angle of bpy in the latter complex and of the bi-triazoles in **7** are comparable [78.53(18)/78.7(2)° vs. 79.6(4)°].[23] The asymmetric coordination of the copper atoms in the crystal structure of **7** arises due to the steric restraints of the bta and DPEPhos ligand, and the differences between the two cations are caused by the disordered benzyl group and packing forces.

Crystals of **8** were obtained from MeCN/Et_2O. The compound crystallises in the orthorhombic space group *Pnma* with four molecules in the unit cell. The complexes in the crystals possess a mirror plane including Re1, Cl1 and C1, thus the asymmetric unit contains only one half of the formula unit. The Re^{I} atom exists in a distorted octahedral

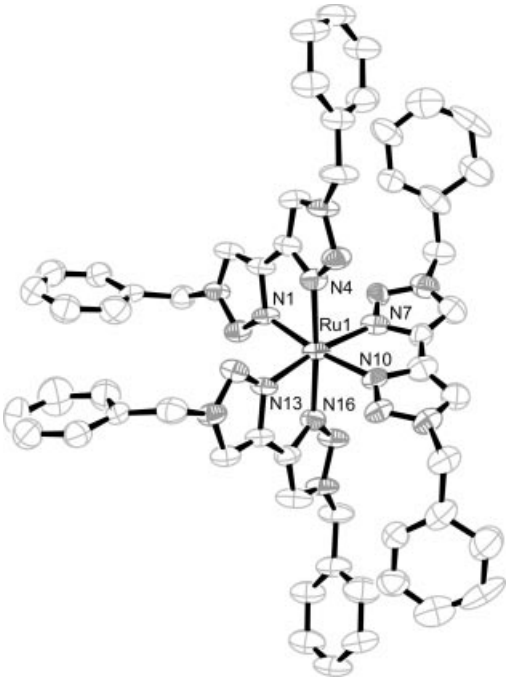


Figure 7. Crystal structure of the homoleptic Ru^{II} complex cation of **4** (H atoms, chloride anions and solvent molecules have been omitted for clarity). Because of the low quality of the structure no atom distances or torsion angles are discussed (see text and Supporting Information). Bond angles [°]: N1–Ru1–N4 74.9(12), N7–Ru1–N10 77.7(12), N13–Ru1–N16 77.9(11), N4–Ru1–N10 100.7(11), N7–Ru1–N16 98.7(12), N1–Ru1–N10 167.5(10), N4–Ru1–N16 172.5(12), N7–Ru1–N13 172.1(11).

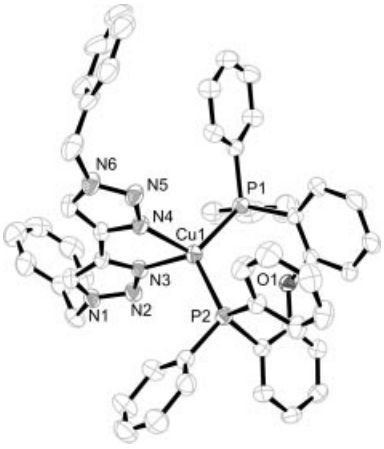


Figure 8. ORTEP drawing (30% probability ellipsoids) of the structure of the cation containing Cu1 in the crystals of **7**. Selected bond lengths [Å], angles [°] and torsion angles [°]: Cu1–P1 2.2631(17), Cu1–P2 2.3016(19), Cu1–N3 2.118(4), Cu1–N4 2.201(5); P1–Cu1–P2 115.44(7), P1–Cu1–N3 119.68(15), P2–Cu1–N4 113.05(13), N3–Cu1–N4 78.53(18); N3–C45–C46–N4 14.9(8).

environment defined by a *fac* arrangement of the three carbonyl groups, the chloride atom and the two nitrogen atoms of the bta ligand (Figure 10). The distortion from octahedral symmetry essentially arises from the steric demands of the chelating bta ligand. Again, the bite angle of the bitriazole [∠(N1–Re–N1′) 73.4(2)°] is very similar to the bite

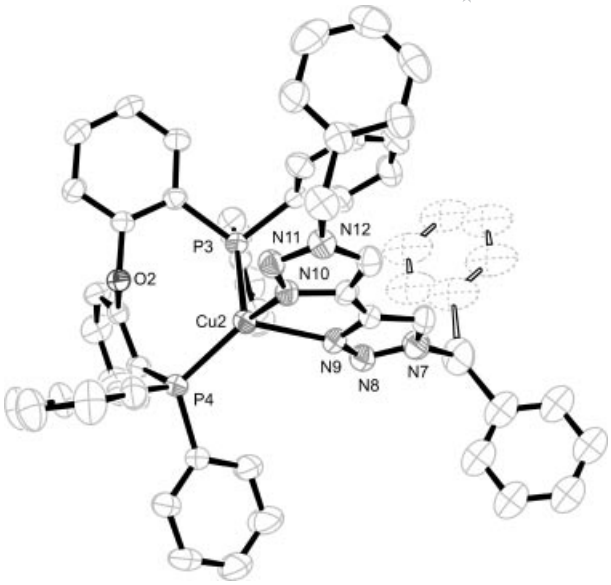


Figure 9. ORTEP drawing (30% probability ellipsoids) of the structure of the cation containing Cu2 in the crystals of **7**. Selected bond lengths [Å], angles [°] and torsion angles [°]: Cu2–P3 2.3079(18), Cu2–P4 2.2292(16), Cu2–N9 2.233(5), Cu2–N10 2.075(6); P3–Cu2–P4 114.39(7), P3–Cu2–N9 97.32(14), P4–Cu2–N10 130.61(14), N9–Cu2–N10 78.7(2); N10–C105–C106–N9 3.0(6). As indicated in the text, one benzyl group is disordered.

angles of several complexes of the type [(s-bpy)$Re^{I}(CO)_3X$] (X = anionic or neutral ligand) containing a substituted bpy ligand [∠(N1–Re–N1′) ca. 74°].[24] The bitriazole ligand is perfectly planar as a result of the mirror symmetry. The characteristic bond lengths and angles are normal and are similar to previously reported values in analogous bpy complexes.[24]

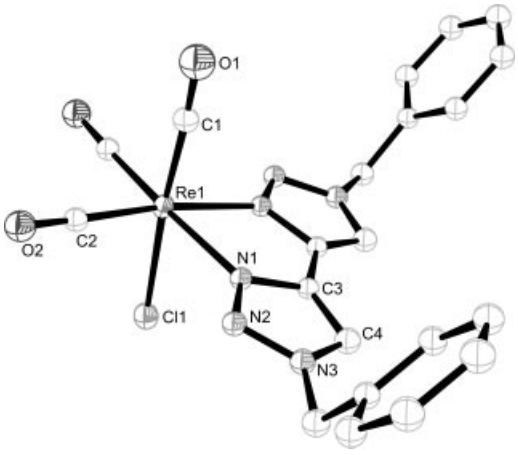


Figure 10. Crystal structure of **8** (H atoms have been omitted for clarity). Selected bond lengths [Å], angles [°] and torsion angles [°]: Re1–N1 2.176(6), Re1–Cl1 2.494(2), Re1–C1 1.890(12), Re1–C2 1.907(8), C1–O1 1.175(15), C2–O2 1.161(10); N1–Re1–N1 73.4(2), Cl1–Re1–N1 81.26(18), Cl1–Re1–C1 175.3(4), N1–Re1–C1 95.0(3), N1–Re1–C2 99.1(3), C1–Re1–C2 88.1(4), Re1–C2–O2 177.7(6), Re1–C1–O1 176.9(11); N1–C3–C3′–N1′ 0.0(9).

The present crystal structures display the strong similarities of the ligand properties of 2,2′-bipyridines and bi-1,2,3-triazoles in terms of steric features.

Spectroscopic Characterisation

All compounds were analysed by NMR, IR and UV/Vis spectroscopy (see Experimental Section). No ^{13}C NMR spectra could be recorded for complexes **4**, **7** or **8** due to their low solubility. The proton and carbon signals in the NMR spectra are in the usual regions, and the IR spectrum of **8** shows three intense signals at $\tilde{\nu}$ = 2018, 1906 and 1866 cm^{-1}, as expected for the vibrations of carbonyl groups in a facial conformation.[25]

The electronic absorption spectra of ligand **1** and its complexes with Ru^{II}, Re^{I} and Cu^{I} are depicted in Figure 11. Each complex exhibits a low-energy band at λ_{max} = 302 (**4**, log ε = 4.549), 272 (**7**, log ε = 3.883) and 302 (**8**, log ε = 3.918), and complexes **4** and **7** also exhibit a transition near the band of the free ligand absorption. The lowest energy band of complexes **5** and **6** appears at λ = 307 (log ε = 4.517) and 299 nm (log ε = 4.169), respectively (see Figures S3 and S4 in the Supporting Information). The complexes show absorption peaks between 270 and 370 nm, a region where no corresponding ligand absorption is found. We therefore tentatively assign these absorptions to MLCT bands. It is noteworthy that the maxima of the lowest absorptions in $[(bpy)Re^{I}(CO)_3Cl]$ (λ_{max} = 386 nm)[26] and $[(bpy)_3Ru]^{2+}$ (λ_{max} = 451 nm)[27] are substantially lower in energy than in the complexes of ligands **1**–**3**. Poor solubility in non-polar solvents precludes a more detailed study. None of the complexes is an emitter in solution or the solid state.

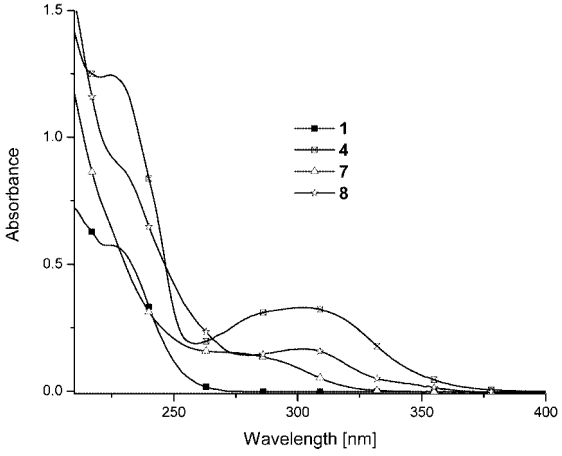


Figure 11. Electronic absorption spectra of compounds **1**, **4**, **7**, and **8** in acetonitrile (c = 20 μM).

Summary

New 1,1′-disubstituted 4,4′-bi-1,2,3-triazole compounds have been synthesised by a Cu^{I}-catalysed cycloaddition between 1,4-butadiyne and various alkyl and aryl azides. These compounds have been employed as ligands for transition metal complexes. Three homoleptic Ru^{II} complexes of the obtained ligands as well as one Cu^{I} and Re^{I} complex with one of the ligands have been synthesised. All of them are readily accessible by standard reactions and are perfectly stable. The steric properties of the ligands are similar to those of 2,2′-bipyridine, although the photophysical properties are not. The complexes show no luminescence. Application of these new compounds as bidentate and easy-to-modify "innocent" ligands may be envisaged. The ligand properties may be varied using established synthetic routes. For example, monosubstituted 4,4′-bitriazoles could be obtained from 1,4-butadiyne and a mixture of alkyl azide and trimethylsilyl azide.[28] This would allow the formation of a triazolyl anion after deprotonation of the unsubstituted triazole and asymmetric functionalisation. The use of 2,6-diethynylpyridine instead of 1,4-butadiyne would give access to terpyridine analogues, and substitution of the triazole-CH would allow introduction of further functionality at the ring carbon atom.[29]

Experimental Section

General Information: All reactions were performed under an inert atmosphere of N_2 using standard Schlenk techniques, unless otherwise stated. Melting points were determined on a Tottoli micro melting point apparatus and are uncorrected. TLC analyses were performed on silica gel 60 F-254 with a 0.2-mm layer thickness. Detection was by UV light at 254/366 nm or by discolouration with ninhydrin in EtOH. Merck Geduran SI 60 silica gel was used for preparative column chromatography. Commercially available solvents of standard quality were used. Unless otherwise stated, purification and drying was done according to accepted general procedures.[30] Elemental analyses were carried out by the Centre for Chemical Analysis of the Faculty of Natural Sciences of the University of Regensburg.

Safety Note: *Sodium azide is toxic and can generate the extremely hazardous hydrazoic acid (volatile, toxic, explosive) if it comes into contact with acids. Organic azides with a saturated carbon:azide ratio of less than 6 may be heat- and shock-sensitive and should be handled with care.*

Absorption spectra were recorded with a Varian Cary BIO 50 UV/Vis/NIR Spectrometer with a 1-cm quartz cell (Hellma) and Uvasol solvents (Merck or Baker). NMR spectra were recorded with a Bruker Avance 300 spectrometer (^1H: 300.1 MHz; ^{13}C: 75.5 MHz; T = 300 K). The chemical shifts are reported in ppm relative to external standards (solvent residual peak) and coupling constants are given in Hertz. The spectra were analysed as being first order. Assignment of signals in the ^{13}C NMR spectra was performed with the DEPT technique (pulse angle: 135°) and given as (+) for CH_3 or CH, (–) for CH_2 and (C_{quat}) for quaternary C. Error of reported values: chemical shift: 0.01 ppm for ^1H NMR, 0.1 ppm for ^{13}C NMR and 0.1 Hz for coupling constants. The solvent used is reported for each spectrum. Mass spectra were recorded with a Varian CH-5 (EI), Finnigan MAT 95 (CI, FAB and FD) or Finnigan MAT TSQ 7000 (ESI) spectrometer with xenon as the ionisation gas for FAB. IR spectra were recorded with a Bio-Rad FTS 2000 MX FT-IR or Bio-Rad FT-IR FTS 155 spectrometer.

Synthesis of Triazole Ligands and Complexes. General Procedures:

GP 1: Twofold "Click Reaction" with 1,3-Butadiyne: The freshly prepared butadiyne was condensed into 5 mL of acetonitrile at –40 °C and a solution of the azide (2.0 equiv.), 2,4-lutidine (2.2 equiv.) and CuI (10 mol-%) in 10 mL of acetonitrile was cooled to –40 °C and added. The reaction mixture was then warmed to room temperature. The reaction vessel was stored in a closed autoclave to prevent evaporation of the butadiyne. After stirring for

20 h, the mixture was poured into 50 mL of an aqueous solution of H_2O_2 (3%). The mixture was stirred until the generation of gas ceased, then 50 mL of a saturated aqueous solution of EDTA was added and the mixture was stirred for 30 min. Further purification was different for each compound.

GP 2: Synthesis of Homoleptic Ru^{II} Complexes: The bitriazole ligand (3 equiv.) and $RuCl_3·4H_2O$ were suspended in ethylene glycol (10 mL) in a round-bottomed flask (25 mL). The mixture was heated (oil bath temperature: 200 °C) to yield a dark-red solution, which slowly turned to brownish orange over 20 h. The solution was concentrated in vacuo with heating to 3 mL, then boiling ethanol was added to the solution at 80 °C until a white precipitate appeared. The mixture was stored at –20 °C overnight to complete precipitation, then the solid was separated by centrifugation and dried in vacuo.

1,1′-Dibenzyl-4,4′-bi-1*H*-1,2,3-triazolyl (1): Synthesised following GP 1 from butadiyne (563 mg, 11.3 mmol), benzyl azide (3.00 g, 22.5 mmol, 2 equiv.), 2,4-lutidine (2.65 g, 2.86 mL, 24.8 mmol, 2.2 equiv.) and CuI (214 mg, 1.13 mmol, 10 mol-%). After workup, the aqueous solution was extracted with $CHCl_3$ (3 × 100 mL) and the organic phase was dried with Na_2SO_4, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography with a dichloromethane/MeOH gradient from 99:1 to 96:4. This yielded 2.93 g of **4** as colourless crystals (82%). M.p. 228 °C. ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 5.67 (s, 4 H, CH_2), 7.31–7.40 (m, 10 H, CH), 8.58 (s, 2 H, triazole) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 52.8 (–, 2 C), 121.7 (+, 2 C, triazole), 127.9 (+, 4 C), 128.1 (+, 2 C), 128.7 (+, 4 C), 139.2 (1 C, C_{quat}), 142.2 (1 C, C_{quat}) ppm. MS (ESI, DCM/MeOH): *m*/*z* (%) 317.1 (100) [MH^+]. $C_{18}H_{16}N_6$ (316.37): calcd. C 68.34, H 5.10, N 26.56; found C 68.21, H 5.21, N 26.42. UV/Vis (MeCN): λ (log ε) = 225 nm (4.458). IR (KBr): $\tilde{\nu}$ = 3133, 3101, 3031, 2984, 2946, 2858, 1673, 1494, 1439, 1410, 1364, 1293, 1231, 1076, 1058, 949, 836, 722 cm^{-1}.

1,1′-Diphenyl-4,4′-bi-1*H*-1,2,3-triazolyl (2): Synthesised following GP 1 from butadiyne (335 mg, 6.7 mmol), phenyl azide (1.60 g, 13.4 mmol, 2 equiv.), 2,4-lutidine (1.58 g, 1.70 mL, 14.8 mmol, 2.2 equiv.) and CuI (127 mg, 0.67 mmol, 10 mol-%). After workup, the aqueous solution was heated to 40 °C and extracted with warm $CHCl_3$ (40 °C, 8 × 80 mL). The organic phase was dried with Na_2SO_4, filtered, concentrated at reduced pressure and dried in vacuo. The residue was dissolved in boiling $CHCl_3$, filtered through charcoal and Celite and concentrated again. The crude product was purified by recrystallisation from $CHCl_3$/petroleum ether. This yielded 1.47 g of **2** as colourless crystals (76%). M.p. 236 °C. ^{1}H NMR (300 MHz, $CHCl_3$): δ = 7.49 (t, ^3J = 7.7 Hz, 2 H, CH), 7.53–7.59 (m, 4 H, CH), 7.82 (d, ^3J = 7.6 Hz, 4 H, CH), 8.59 (s, 2 H, triazole) ppm. ^{13}C NMR (75.5 MHz, $CHCl_3$): δ = 118.9 (+, 2 C, triazole), 120.6 (+, 4 C), 129.0 (+, 2 C), 129.9 (+, 4 C), 136.9 (1 C, C_{quat}), 140.5 (1 C, C_{quat}) ppm. MS (ESI, DCM/MeOH): *m*/*z* (%) 289.1 (100) [MH^+]. $C_{16}H_{12}N_6$ (288.31): calcd. C 66.66, H 4.20, N 29.15; found C 66.57, H 4.31, N 29.01. UV/Vis (CH_3CN): λ (log ε) = 232 (4.480), 257 nm (4.366). IR (KBr): $\tilde{\nu}$ = 3132, 3093, 3065, 1654, 1597, 1504, 1464, 1396, 1257, 1234, 1034, 825, 756 cm^{-1}.

1,1′-Bis(carboxymethyl)-4,4′-bi-1*H*-1,2,3-triazolyl (3): Synthesised following GP 1 from butadiyne (541 mg, 10.8 mmol), β-azidoacetic acid (2.18 g, 21.6 mmol, 2 equiv.), 2,4-lutidine (2.55 g, 2.75 mL, 23.8 mmol, 2.2 equiv.) and CuI (206 mg, 1.08 mmol, 10 mol-%). After workup, the aqueous solution was acidified to pH 2 with 6 N aqueous HCl. The precipitate was filtered, washed with water and suspended in 10 mL of water. A 0.1 N aqueous solution of NaOH was then added dropwise until the solid dissolved completely. The solution was lyophilized to yield the sodium salt of **3** (2.50 g, 8.4 mmol, 78%). NMR, mass and UV spectra were recorded for this salt. The solid was dissolved in water (20 mL), the solution was heated to reflux and 0.5 N aqueous HCl was added dropwise until a precipitate appeared. After cooling to room temperature, 2 N aqueous HCl was added until no further product precipitated. The solid was filtered, washed with water and dried in vacuo. This yielded 2.12 g of **3** as colourless crystals (78%). M.p. > 215 °C (decomp.). ^{1}H NMR (300 MHz, D_2O): δ = 5.05 (s, 4 H, CH_2), 8.20 (s, 2 H, triazole) ppm. ^{13}C NMR (75.5 MHz, D_2O): δ = 53.3 (–, 2 C), 123.9 (+, 2 C, triazole), 138.6 (2 C, C_{quat}), 173.1 (2 C, C_{quat}) ppm. MS (ESI, H_2O/MeCN): *m*/*z* (%) 253.1 (100) [MH^+]. $C_8H_8N_6O_4$ (252.16): calcd. C 38.10, H 3.20, N 33.32; found C 37.97, H 3.32, N 33.17. UV/Vis (H_2O): λ (log ε) = 225 nm (4.092). IR (KBr): $\tilde{\nu}$ = 3435, 3151, 3117, 3013, 2947, 2792, 2708, 2594, 2511, 1930, 1794, 1724, 1496, 1420, 1347, 1295, 1257, 1223, 1151, 1109, 1064, 1011, 976, 896, 795 cm^{-1}.

Ru Complex 4: Ligand **1** (100 mg, 0.32 mmol) and $RuCl_3·3H_2O$ (28 mg, 0.11 mmol) were suspended in 20 mL of ethylene glycol in a round-bottomed flask fitted with a reflux condenser and the mixture was heated (oil bath temperature: 200 °C). This yielded a dark-red solution which slowly turned to brownish orange over 20 h. The solvent was removed in vacuo by heating. The remaining solid was dissolved in boiling MeCN and filtered. Et_2O was then added to the solution to precipitate the product. This yielded a light yellow powder, which was recrystallised from MeCN/Et_2O to give 84 mg of **7** as yellowish crystals (0.07 mmol, 68%). M.p. > 210 °C (decomp.). ^{1}H NMR (300 MHz, CD_3CN): δ = 5.55 (s, 12 H, CH_2), 7.12–7.18 (m, 12 H, CH), 7.28–7.36 (m, 18 H, CH), 8.54 (s, 6 H, triazole) ppm. MS (ESI, H_2O/MeCN): *m*/*z* (%) 525.4 (100) [$(L_3Ru^{2+})^{2+}$], 1185.5 (1) [$(L_3Ru^{2+} + Cl^-)^+$]. $C_{54}H_{48}Cl_2N_{18}Ru·4H_2O$ (1193.1): calcd. C 54.36, H 4.73, N 21.13; found C 54.46, H 4.62, N 20.47. UV/Vis (H_2O): λ (log ε) = 302 (4.549), 222 nm (5.143). IR (ATR): $\tilde{\nu}$ = 3116, 3032, 1446, 1456, 1426, 1356, 1340, 1276, 1112, 1078, 1042, 720, 694, 654 cm^{-1}.

Ru Complex 5: Synthesised following GP 2 from **2** (250 mg, 0.87 mmol) and $RuCl_3·4H_2O$ (78 mg, 0.29 mmol). This yielded 665 mg of **5** as colourless crystals (74%). M.p. > 210 °C (decomp.); ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 7.54–7.66 (m, 18 H, CH), 7.89 (d, ^3J = 7.1 Hz, 12 H, CH), 9.76 (s, 6 H, triazole) ppm. ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ = 120.1 (+, 2 C, triazole), 120.5 (+, 4 C), 129.9 (+, 2 C), 130.0 (+, 4 C), 135.6 (1 C, C_{quat}), 140.9 (1 C, C_{quat}) ppm. MS (ESI, H_2O/MeCN): *m*/*z* (%) 483.2 (100) [$(L_3Ru^{2+})^{2+}$], 1115.4 (5) [$(L_3Ru^{2+} + TfO^-)^+$]. UV/Vis (H_2O): λ (log ε) = 307 (4.517), 239 nm (5.012). IR (KBr): $\tilde{\nu}$ = 3102, 3062, 1595, 1499, 1464, 1422, 1313, 1271, 1065, 999, 760 cm^{-1}.

Ru Complex 6: Synthesised following GP 2 from **3** (250 mg, 0.99 mmol) and $RuCl_3·4H_2O$ (90 mg, 0.33 mmol). This yielded 634 mg of **6** as colourless crystals (69%). M.p. > 205 °C (decomp.). ^{1}H NMR (300 MHz, D_2O): δ = 5.22 (s, 12 H, CH_2), 8.50 (s, 6 H, triazole) ppm. ^{13}C NMR (75.5 MHz, D_2O): δ = 51.5 (–, 6 C), 122.0 (+, 6 C, triazole), 138.2 (6 C, C_{quat}), 171.0 (6 C, C_{quat}) ppm. MS (ESI, H_2O/MeCN): *m*/*z* (%) 478.2 (100), 507.2 (100), 521.3 (100), 955.3 (65). UV/Vis (H_2O): λ (log ε) = 299 (4.169), 225 nm (4.721). IR (KBr): $\tilde{\nu}$ = 3429. 3136, 2925, 1746, 1629, 1454, 1377, 1288, 1221, 1021 cm^{-1}.

Cu^I Complex 7: Ligand **1** (50 mg, 0.16 mmol), $[Cu^I(NCMe)_4]PF_6$ (59 mg, 0.16 mmol) and bis[2-(diphenylphosphanyl)phenyl] ether (85 mg, 0.16 mmol) were dissolved in degassed dichloromethane and heated to reflux for 3 h. The solution was concentrated and diethyl ether was added to precipitate the product. The suspension was filtered and the filtrate cooled to – 35 °C. This gave colourless

crystals of **7** suitable for X-ray crystallography. Complex **7** was obtained in an overall yield of 73% (123 mg). ^{1}H NMR (300 MHz, CD_3CN): δ = 5.59 (s, 4 H, CH_2), 6.66–6.75 (m, 2 H, CH), 6.90–7.02 (m, 4 H, CH), 7.25–7.47 (m, 32 H, CH), 8.12 (s, 2 H, triazole) ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ = –13.38 ppm. MS (ESI): *m*/*z* (%) 317.1 (8) [**1**$^+$], 601.2 (28) [(DPEPhos)Cu$^+$], 642.2 (100) [{(DPEPhos)Cu + MeCN}$^+$], 917.4 (51) [(DPEPhos)(**1**)Cu$^+$]. $C_{54}H_{44}CuN_6OP_2{\cdot}PF_6$ (1063.4): calcd. C 60.99, H 4.17, N 7.90;

Table 1. Crystal data, data collection and structure refinement for compounds **1**–**3**.

	1 (prisms)	**1** (needles)	**2**	**3**
Formula	$C_{18}H_{16}N_6$	$C_{18}H_{16}N_6$	$C_{16}H_{12}N_6$	$C_8H_8N_6O_4$
M_w	316.37	316.37	288.32	252.20
Crystal size [mm]	0.32 × 0.22 × 0.18	0.48 × 0.28 × 0.02	0.42 × 0.06 × 0.04	0.44 × 0.02 × 0.01
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	$P2_1/c$	Cc	$P\bar{1}$	$P2_1/c$
a [Å]	8.1669(10)	34.414(3)	5.729(4)	7.4088(4)
b [Å]	9.4871(13)	5.5439(5)	11.019(18)	4.5388(3)
c [Å]	10.3595(12)	8.4506(7)	16.744(14)	14.5860(9)
α [°]	90	90	101.38(11)	90
β [°]	94.135(14)	102.466(10)	93.17(7)	95.767(5)
γ [°]	90	90	102.51(11)	90
V [Å^3]	800.57(17)	1574.3(2)	1006(2)	488.00(5)
ρ_{calc} [g cm^{-3}]	1.311	1.335	1.428	1.716
Z	2	4	3	2
μ [mm^{-1}]	0.083	0.085	0.741	1.221
T [K]	123	123	150	123
Θ range [°]	2.50–26.80	2.42–26.80	2.71–50.31	6.10–62.10
Reflections collected	5365	6381	5716	1756
Unique reflections	1589 [R(int) = 0.0337]	3264 [R(int) = 0.0854]	2062 [R(int) = 0.0298]	748 [R(int) = 0.0298]
Observed reflections [$I > 2\sigma(I)$]	1166	2516	1411	558
Parameters refined/restraints	109/0	217/2	298/0	85/0
Absorption correction	none	none	semi-empirical from equivalents	semi-empirical from equivalents
T_{max}, T_{min}			0.6559, 1.0	0.4862, 1.0
σ_{fin} (max./min.) [e Å^{-3}]	0.238/–0.137	0.294/–0.248	0.146/–0.213	1.021/–0.299
R_1 [$I \geq 2\sigma(I)$]	0.0333	0.0565	0.0338	0.0773
wR_2	0.0805	0.1401	0.0754	0.2273
CCDC number	645041	645040	645044	645045

Table 2. Crystal data, data collection and structure refinement for compounds **4**, **7** and **8**.

	4	**7**	**8**
Formula	$C_{54}H_{48}Cl_2N_{18}RuS$[a]	$2(C_{54}H_{44}CuN_6OP_2)\ 2(PF_6)$	$C_{21}H_{16}ClN_6O_3Re$
M_w	–[a]	2124.87	622.06
Crystal size [mm]	0.36 × 0.11 × 0.06	0.34 × 0.22 × 0.14	0.11 × 0.026 × 0.015
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/a$	$P\bar{1}$	$Pnma$
a [Å]	16.3417(3)	13.742(1)	10.475(4)
b [Å]	23.1347(4)	14.425(1)	18.574(7)
c [Å]	18.0784(5)	29.195(2)	10.584(4)
α [°]	90	83.511(9)	90
β [°]	107.787(3)	86.160(9)	90
γ [°]	90	71.812(8)	90
V [Å^3]	6508.0(3)	5459.8(7)	2059.3(14)
ρ_{calc} [g cm^{-3}]	–[a]	1.294	2.006
Z	4	4	4
μ [mm^{-1}]	–[a]	0.551	13.070
T [K]	123	123	150
Θ range [°]	3.20–51.54	2.00–25.00	5.94–51.16
Reflections collected	32311	54865	4576
Unique reflections	6840 [R(int) = 0.0455]	18094 [R(int) = 0.0969]	1081 [R(int) = 0.0935]
Observed reflections [$I > 2\sigma(I)$]	4589	6873	889
Parameters refined/restraints	677/0	1252/0	75/0
Absorption correction	semi-empirical from equivalents	analytical from crystal shape	semi-empirical from equivalents
T_{min}, T_{max}	0.63090, 1.0	0.8458, 0.9441	0.25246, 1.0
σ_{fin} (max/min) [e Å^{-3}]	1.916/–0.698	0.796/–0.259	1.713/–1.067
R_1 [$I \geq 2\sigma(I)$]	0.0817	0.0562	0.0449
wR_2	0.2567	0.1461	0.1104
CCDC number	645042	645043	645046

[a] Crystals of **4** contain an unspecified number of solvents, which are highly disordered, thus no formula and no reliable values for the parameters or formula can be given.

found C 60.54, H 4.23, N 7.74; UV/Vis (MeCN): λ (log ε) = 272 nm (3.883). IR (ATR): $\tilde{\nu}$ = 3138, 2944, 2884, 2364, 2328, 2210, 2162, 2048, 1976, 1498, 1458, 1288, 1260, 1046, 814, 716 cm^{-1}.

Re^{I} Complex 8: Ligand **1** (50 mg, 0.16 mmol) and [Re^{I}(CO)$_5$]Cl (57 mg, 0.16 mmol) were dissolved in degassed toluene and heated to reflux for 12 h. After cooling to room temperature, the colourless precipitate was filtered and dried in vacuo. Recrystallisation from MeCN/Et$_2$O yielded **8** as colourless crystals (94 mg, 96%). ^{1}H NMR (300 MHz, CD$_3$CN): δ = 5.72 (s, 4 H, CH$_2$), 7.39–7.46 (m, 10 H, CH), 8.28 (s, 2 H, triazole) ppm. MS (ESI): *m/z* (%) 91.1 (100) [Bn$^+$], 503.0 (10) [(**1**)Re$^+$], 538.0 (1) [(M – 3CO + H)$^+$], 566.0 (2) [(M – 2CO + H)$^+$], 593.3 (2) [M – CO$^+$], 621.9 (1) [M$^+$]. IR (ATR): $\tilde{\nu}$ = 3136, 2944, 2886, 2018, 1906, 1866, 1494, 1448, 1422, 1292, 1266, 1178, 1158, 1108, 1082, 1050, 818, 744, 698, 660 cm^{-1}. UV/Vis (MeCN): λ (log ε) = 350 (sh), 302 (3.918), 228 nm (sh). $C_{21}H_{16}ClN_6O_3Re$ (622.05): calcd. C 40.55, H 2.59, N 13.51; found C 40.47, H 2.59, N 13.55.

Crystal Structure Determination: Diffraction data for crystals of compound **1** (needles and prisms) and complex **7** were collected with a STOE-IPDS diffractometer[31] with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å), whereas data for crystals of **2**, **3**, **4** and **8** were collected with an Oxford Diffraction Gemini Ultra CCD diffractometer[32] with multilayer optics and Cu-K_α radiation (λ = 1.5418 Å). Further crystallographic and refinement data can be found in Tables 1 and 2. The structures were solved by direct methods (SIR-97)[33] and refined by full-matrix least-squares on F^2 (SHELXL-97).[34] The H atoms were calculated geometrically and a riding model was applied during the refinement process. The structure solution of **4** and **8** was handicapped by poor crystal quality. For **4**, the obviously present solvent molecules could not be identified and were included in the refinement steps as C atoms (C100–C112) or as Cl atoms. For **8** only the heavy atoms could be refined with anisotropic displacement factors.

CCDC-645040–645046 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Cell plot of compound **3** (Figure S1), complete asymmetric unit of complex **4** (Figure S2), electronic absorption spectra of compounds **2**/**5** (Figure S3) and **3**/**6** (Figure S4).

Acknowledgments

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