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Ligand Variations in [ReX(diimine)(CO)$_3$] Complexes: Effects on Photocatalytic CO$_2$ Reduction

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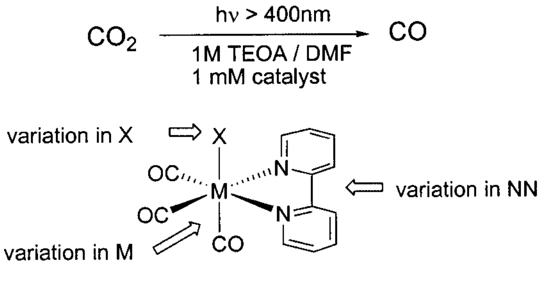
Two series of complexes [MX(diimine)(CO)$_3$] (M = Tc, Re) have been prepared, fully characterised and investigated for their ability to act as photocatalysts for the reduction of CO$_2$ to CO. One series consists of complexes with different aromatic diimine ligands while keeping X = Br$^-$ constant. The second series describes complexes with diimine = 2,2-bipyridine and variations in the anionic ligand X$^-$. Although numerous complexes of this type have been prepared and investigated before, a systematic study of their photocatalytic activity has not yet been carried out. Electrochemical and spectroscopic characterisation of these complexes has been performed with the objective of better understanding their respective activity in the photocatalytic CO$_2$ reduction. Despite various modifications, catalytic activity is retained for all compounds exhibiting fluorescence, including [^{99}TcCl(bipy)(CO)$_3$], whereas nonfluorescing compounds did not convert CO$_2$ to CO. The correlation of catalytic activity and spectroscopic or electrochemical properties such as absorption or emission wavelengths, redox potentials or Stern–Volmer constants for the reductive quenching of the excited complexes is difficult. Nevertheless, the study emphasises the possibility to obtain [ReX(CO)$_3$(diimine)] complexes with a wide range of physicochemical properties by ligand variations and the great potential of compounds of this class of complexes as inorganic photosensitisers.

Introduction

The development of a system for the conversion of solar energy into a chemical fuel is one of the most demanding challenges chemists face today. The choice of the photosensitiser performing the initial step of light absorption is of key importance. Complexes of the type [Ru(diimine)$_3$]$^{2+}$ have been most thoroughly studied in this respect.[1–4] Among further possible candidates, rhenium tricarbonyl diimine complexes [ReX(diimine)(CO)$_3$] have also attracted broad interest.[5–14] The complex [ReCl(phen)(CO)$_3$] was one of the first rhenium(I) carbonyl compounds ever synthesised.[15] Detailed studies have unveiled the remarkable photochemical properties of [ReCl(phen)(CO)$_3$] and related compounds such as [ReX(bipy)(CO)$_3$] (X = Cl$^-$ **1**, X = Br$^-$ **2**).[5,9,16,17] The excited state generated by visible light absorption at 450 to 500 nm has been identified as a metal to ligand charge transfer (MLCT) state, with the photoelectron ejected from a metal-centred π-d into a vacant ligand-centred π* orbital with up to µsec lifetimes. On the basis of the Rehm-Weller approximation[18] the photoexcited molecules are powerful oxidising agents with potentials of +500 to +1200 mV (vs. Ag/AgCl).[6] Thermodynamically, [ReX(diimine)(CO)$_3$] complexes can therefore oxidise very poor electron donors, even H$_2$O, in their excited states, which makes them very interesting compounds for light-energy conversion.

In a marked contrast to the large number of physicochemical investigations, there are only a few examples of light-driven reactions with these complexes as photosensitisers. Most prominent is a system for the photochemical reduction of CO$_2$ developed in Strasbourg over 20 years ago. Hawecker et al. found that **1** and **2** are both able to act as photosensitiser and reduction catalysts for the two-electron conversion of CO$_2$ to CO transferring reduction equivalents from poor reducing agents like triethanolamine (TEOA, $\Delta E°_{1/2}$ = +0.8 V) (Scheme 1).[10,19] In this “Strasbourg system”, the energetically uphill, two-electron reduction process is achieved using the energy of absorbed



Scheme 1. Photocatalytic conversion of CO$_2$ to CO and variation of the catalyst.

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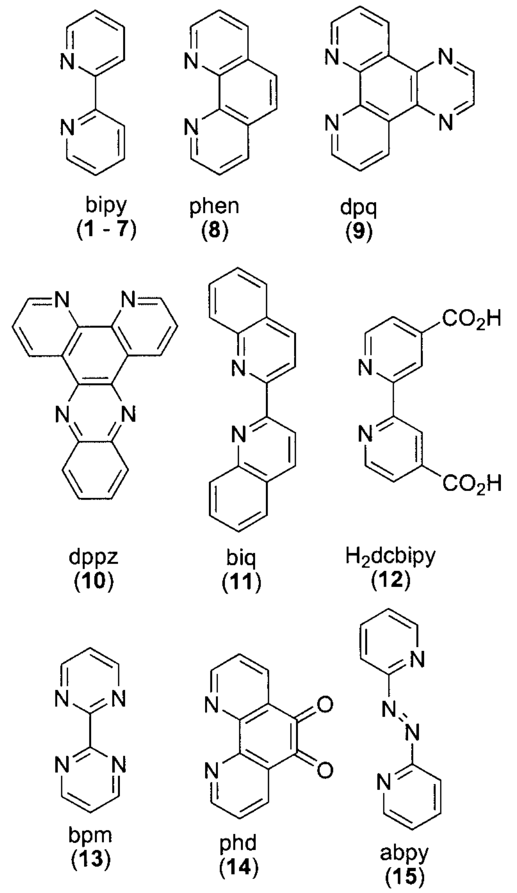
visible light. From the initial experiments on, the mechanism of this unprecedented reaction has been of great interest.[8,10,20,21] Many experiments have been carried out with the original catalysts **1** or **2**, but studies of the catalytic performance with variations in the anion X$^-$ or the diimine ligand N$^\cap$N are rare.[13,20]

We present in this study the synthesis and characterisation of two series of [ReX(diimine)(CO)$_3$] complexes and an investigation of the respective ligand effects on the photocatalytic activities. In a first series of complexes [ReX(bipy)(CO)$_3$] (**4**–**7**), also including the Tc(I) analogue [TcCl(bipy)(CO)$_3$] **3**, the bipy ligand is kept constant and X is varied. In a second series of [ReBr(diimine)(CO)$_3$] (**8**–**15**), the Br$^-$ ligand is kept constant but the diimine ligand is altered. The selected diimine ligands are depicted in Scheme 2. The detailed study of these series of complexes showed that the influence of both diimine and terminal X$^-$ ligands on physicochemical and catalytic properties is large. Nevertheless, catalytic activity is retained in most cases.



Scheme 2. Diimine ligands used for the synthesis of [ReBr(diimine)(CO)$_3$] complexes with the numbering of the corresponding complexes in brackets: 2,2′-bipyridine (bipy) (**1**–**7**); 1,10-phenanthroline (phen) (**8**); dipyrido[3,2-*f*:2′,3′-*h*]quinoxaline (dpq) (**9**); dipyrido[3,2-*a*:2′,3′-*c*]phenazine (dppz) (**10**); 2,2′-biquinoline (biq) (**11**); 2,2′-bipyridine-4,4′-dicarboxylic acid (H$_2$dcbipy) (**12**); 2,2′-bipyrimidine (bpm) (**13**); 1,10-phenanthroline-5,6-dione (phd) (**14**); 2,2′-azobispyridine (abpy) (**15**).

Results and Discussion

Synthesis and Characterisation: The complexes [ReBr(CO)$_5$] and (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] are convenient starting materials from which [ReBr(diimine)(CO)$_3$] complexes are directly afforded with the diimine ligands shown in Scheme 2. The Tc(I) complex **3** was prepared similarly from (NEt$_4$)$_2$[TcCl$_3$(CO)$_3$]. For the synthesis of the [ReX(bipy)(CO)$_3$] series, [Re(bipy)(CO)$_3$(sol)]$^+$ was prepared as an intermediate by halide precipitation and in a consecutive step the ligands X = OH$_2$ (**4**), SCN$^-$ (**5**) or CN$^-$ (**6**) were introduced. Treatment of **4** with only half an equivalent of cyanide gave the dinuclear complex **7** in which two Re centres are linked by a cyanide bridge with a Re–Re distance of 5.4 Å.[22]

Structures: All complexes depict an octahedral ligand arrangement with a facial tricarbonyl moiety, a bidentate diimine ligand and an anion X. The structure of the Tc surro-

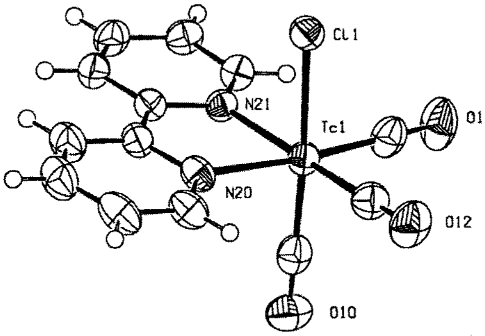


Figure 1. ORTEP drawing of one of the two independent molecules of [TcCl(bipy)(CO)$_3$] (**3**).

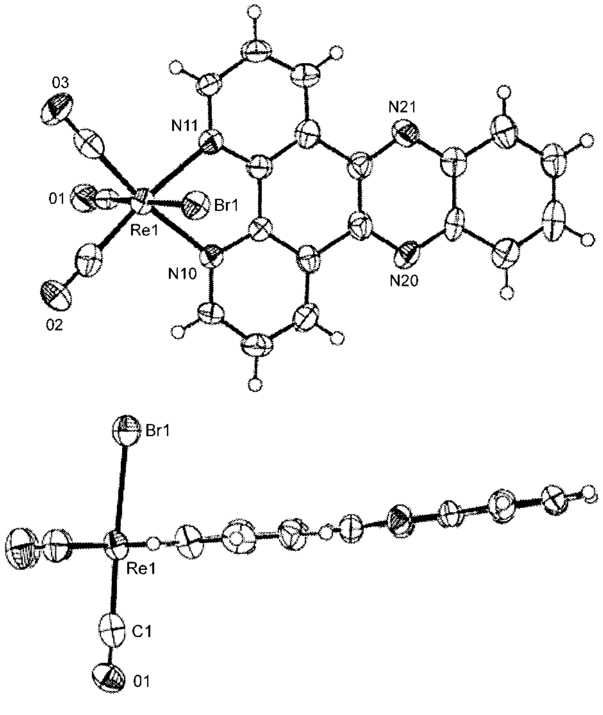


Figure 2. ORTEP representation of **10**, showing a view of the molecule from above and from the side.

gate **3** of the original photocatalyst **1** is shown in Figure 1 and complex **10** with the most extended ligand dppz in Figure 2. In all cases the two equatorial carbonyl ligands, the rhenium centre and aromatic rings of the diimine ligand are in a nearly ideal planar arrangement. Bond lengths and angles around the metal centres (see data deposited in The Cambridge Crystallographic Centre) are similar for all structures and comparable to those in closely related compounds.[23–25]

For the biquinoline (biq) complex **11** the usual planar arrangement of metal centre, diimine ligand and equatorial CO's was not observed. The aromatic rings of biq are displaced from the otherwise favoured $Re(CO)_2$- plane by 23 and 12°, respectively, due to steric strain between the hydrogen atoms of the outer aromatic rings and the equatorial carbonyl ligands (Figure 3). Similar biq complexes show comparable structural features.[26] The different twist angles for the two quinoline rings seem to be an effect of crystal packing since only six ^1H NMR signals are observed, indicating equivalence for the biq rings on the NMR timescale in solution.

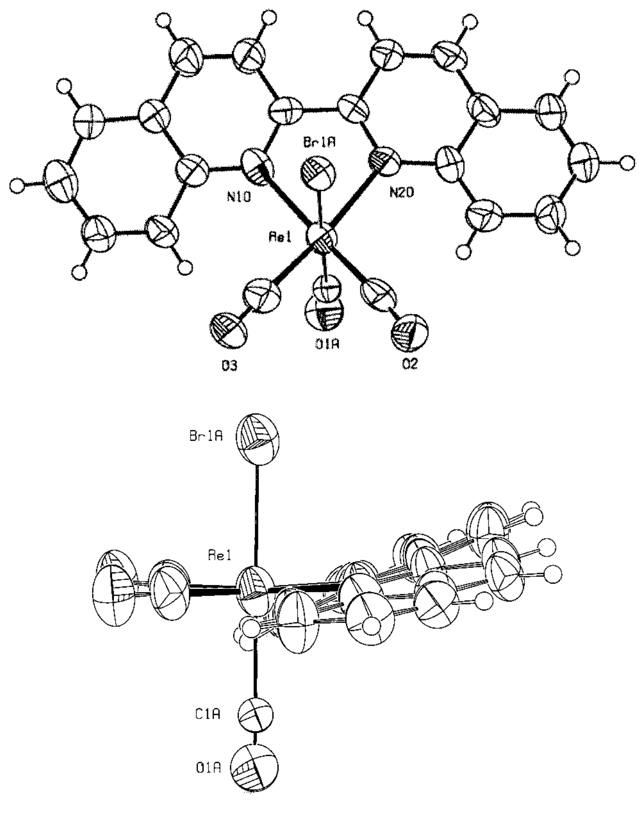


Figure 3. ORTEP drawings of a top and side view of **11**.

Spectroscopic Properties: Table 1 summarises analytical data obtained for the $[ReX(bipy)(CO)_3]$ series of complexes. Variation of ligand $X^{(-)}$ causes clear effects, but a correlation between $X^{(-)}$ and the spectroscopic or electronic data of the corresponding complexes is not readily obvious. The exchange of Br^- for water results in the formation of the cationic complex **4**. As a consequence of its charge, complex **4** has the series' lowest reduction potential and its light absorption shifts towards higher energy, as it is more difficult to excite an electron. The π- backbonding is reduced in **4** and the IR vibrations ν_{CO} shift to higher wavenumbers. The mono-cation **7** fits in this series with respect to the ν_{CO} frequencies, however, $E_{1/2}$ is larger than for example **5**. Considering ν_{CO}, the thiocyanate complex **5** appears to be about as low in electron density as **4**, yet its visible absorption is shifted the most towards lower energies. The lowest carbonyl vibration frequency of the series is observed for the cyano complex **6**. This indicates high electron density on Re^I, but is in contrast to the low wavelength of visible light absorption found for **6**.

Table 1. Spectroscopic and electrochemical properties of $[ReX(bipy)(CO)_3]$ complexes.

Ligand X	λ_{max} [nm][a]	λ_{em} [nm][a]	$\tilde{\nu}_{CO}$ [cm^{-1}][b]	$E_{1/2,red}$ [mV][c]
Cl (**1**)	370	580	2019, 1883	–1130
Br (**2**)	370	575	2019, 1905	–1190
H_2O (**4**)	350	540	2036, 1918	–1000
SCN (**5**)	375	580	2020, 1928	–1015
CN (**6**)	355	540	2006, 1878	–1125
M–CN–Re (**7**)	365	535	2025, 1910	–1050

[a] In DMF solution. [b] KBr pellets. [c] In DMF solution containing 0.1 M NBu_4PF_6.

Much larger differences in spectroscopic properties are observed when the diimine ligand is altered (Table 2). The carbonyl stretching frequencies vary by only about ±5 cm^{-1} for all the complexes, thus, the electron density on Re^I does not seem to be as greatly affected as in the case of the $[ReX(bipy)(CO)_3]$ series. The differences in the spectroscopic properties stem from the decreased energy of the diimine's LUMO when going to larger aromatic systems or heteroatom substitution.[1,16] The shift in λ_{max} towards smaller energies causes a larger part of the absorption to be in the visible spectrum for complexes like **10**, **11** or **15** (Figure 4). While all other compounds are orange yellow solids, **11** and **15** are deep red and dark blue-green, respectively. For **11**, this might be explained by the effect of the unusual coordination geometry on the electronics of the molecule. In the case of **15**, the exceptionally low-lying, par-

Table 2. Spectroscopic and electrochemical properties of $[ReBr(diimine)(CO)_3]$ complexes.

Diimine ligand	λ_{max} [nm][a]	λ_{em} [nm][a]	$\tilde{\nu}_{CO}$ [cm^{-1}][b]	$E_{1/2,red}$ [mV][c]
bipy (**2**)	370	575	2019, 1905	–1190
phen (**8**)	370	570	2018, 1933	–1090
dpq (**9**)	≈ 375[d]	585	2025, 1948	–975
dppz (**10**)	≈ 425[d]	520	2018, 1918	–705
biq (**11**)	435	[e]	2014, 1895	–735
Hdcbipy (**12**)	360	540	2024, 1896	–1250[f]
bpm (**13**)	385	[e]	2030, 1931	–860
phd (**14**)	375[d]	[e]	2033, 1943	–15, –755
abpy (**15**)	550, 360[d]	[e]	2020, 1924	+50

[a] In DMF solution. [b] KBr pellets. [c] In DMF solution containing 0.1 M NBu_4PF_6. [d] Absorption shoulder. [e] No fluorescence observed at room temperature in DMF solution. [f] Irreversible reduction.

ticularly stabilised LUMO of this ligand has already been reported to cause the unusual absorption properties of abpy- complexes.[27]

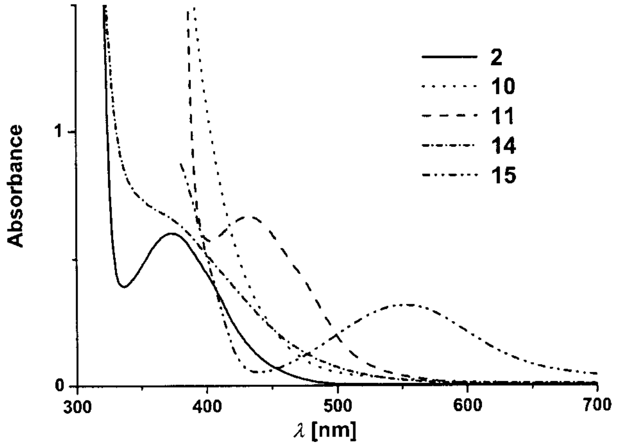


Figure 4. Absorption spectra for different [ReBr(diimine)(CO)$_3$] complexes in DMF (all solutions 0.2 mM).

According to Table 2, not all of the complexes exhibit room temperature fluorescence in DMF when irradiated with light between 350 and 450 nm (Figure 5). The emission maxima are between 520 and 585 nm for **2**, **8**, **9**, **10** and **12**, but **11**, **13**, **14** and **15** do not fluoresce. This behaviour is rationalised in **11** and **15** by the small energy gap between ground and excited states as indicated by the high values of $\lambda_{\max}$. Accordingly, radiationless decay to the ground state will be fast in accordance with the energy gap law.[18] Other reasons must account for the absence of fluorescence in **13** and **14** as the energy gap is similar to the structurally related complexes **2** and **8**, respectively. The emission of the dppz complex **10** is observed at much lower wavelengths (520 nm) than that of all other fluorescing complexes of this study. Because of the special nature of the dppz ligand, both diimine and phenazine centred excited states are theoretically possible,[28] resulting in the observation of MLCT or LC emissions, respectively. It was found in a recent study of closely related complexes of [Re(CO)$_3$Cl] with 11-substituted dppz that the ligand-centred emission dominates for two 11-X-dppz complexes of rhenium tricarbonyl,[25] thus explaining the unusual emission behaviour observed for **10**.

Electrochemistry: Reversible, one-electron reduction is observed for all complexes except **12**. This process has been assigned to a ligand-centred reduction resulting in the formation of what is best described as a rhenium(I) organic radical anion species [ReX(CO)$_3$(diimine$^-$)].[11] In agreement with the spectroscopic properties, the exchange of the ligand X influences the reduction potential $E_{1/2,\text{red}}$ of the complexes far less than the variation of the diimine ligand (Table 1 and Table 2).

Factors changing $E_{1/2,\text{red}}$ are the overall charge of the complex and the size of the aromatic system of the diimine. In the [ReX(CO)$_3$bipy] series, cationic **4** is the one most easily reduced. Similarly, the reduction of the cationic dinuclear cyano complex **7** is more facile compared to, for example, the neutral complex **6**. It is furthermore easier to place an additional electron into the LUMO of a large aromatic ligand, as seen for the [ReBr(CO)$_3$(diimine)] series for which the reduction potential of the complexes increases with the size of the diimine ligand.

Remarkable redox behaviour was found for **14** and **15**. Complex **15** shows a very high reduction potential of $E_{1/2,\text{red}}$ = +50 mV as the additional electron is localised in its unusual LUMO at the azo-bridge.[29] The electrochemistry of **14**, its molecular structure shown in Figure 6, is special since the phd ligand is formally an *ortho*-benzoquinone system. The first reduction already occurs at –15 mV and generates a strongly stabilised semiquinone radical. The diolate is formed at –755 mV in a second reversible step. Increasing concentrations of H_2O shift the second reduction to higher potentials, as direct two-electron reduction to the diol is known to occur in the presence of protons (Figure 7).[30] The phd complex **15** thus offers the possibility of a reversible storage of two electrons within a range of accessible potentials, which is unique within this series of rhenium diimine complexes.

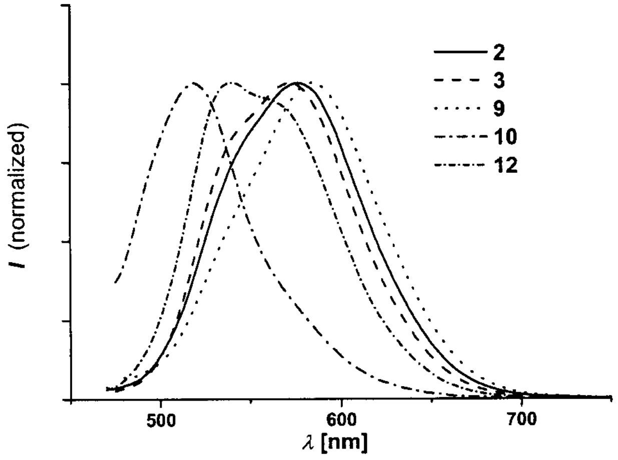


Figure 5. Emission spectra for different [ReBr(CO)$_3$(diimine)] complexes in DMF (all solutions 0.2 mM).

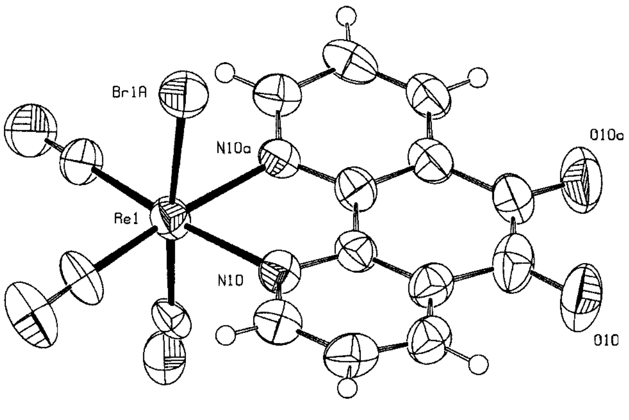


Figure 6. ORTEP drawing of **14**, which contains a mirror plane going through Re1, Br1A and the ligand between the nitrogen atoms.

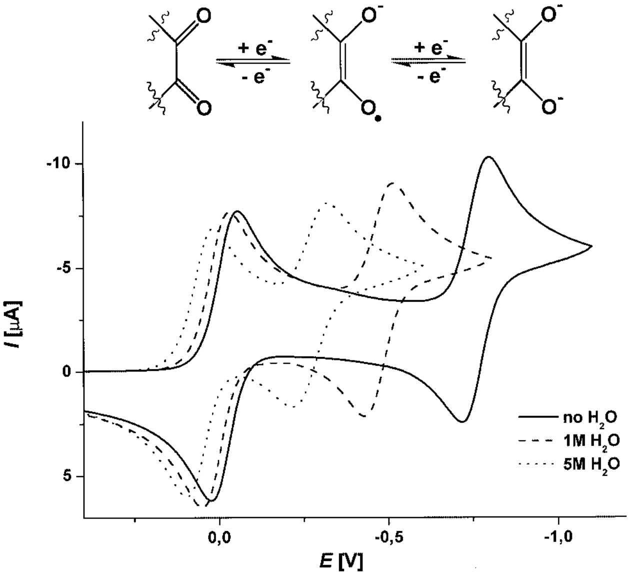


Figure 7. Cyclic voltammograms of the two reversible reduction steps observed for **14** in DMF containing increasing concentrations of water. A Scheme illustrating the successive reduction of the phd dione to form a semiquinone and then a diolate is shown above.

Reductive Fluorescence Quenching: The original work on the "Strasbourg system" suggested that the primary events of reaction are photoexitation of the complex followed by the reaction of the thexi- state with the electron donor.[8,10,21] It was therefore of interest how the synthetic modifications of the catalyst influence the ability of the excited complexes to react with the standard electron donor TEOA.

$$I_0/I = 1 + k_{q\ \tau}\ [Q] = 1 + K_{SV}\ [Q]$$

Fluorescence quenching is a good way to probe the reactions of the excited state with electron donors. For all fluorescing complexes, Stern–Volmer kinetics are observed for the reductive quenching by TEOA in DMF solutions. According to the Stern–Volmer equation, constants K_{SV} can be determined from plots of $(I_0/I) - 1$ versus quencher concentration (Figure 8).[18]

Table 3 summarises the determined K_{SV} values, which are indicators for the "success rate" of forming the reduced complex after photoexcitation in the presence of a quencher. The variations of diimine or X^- cause K_{SV} to vary by a factor of up to five. To explain this result, measurements of the excited state lifetimes τ would be necessary to estimate differences in the bimolecular quenching reaction rate k_q. It is known that the k_q of this reaction can vary by at least up to a factor of 2.5 for a series of much more closely related [ReX(CO)$_3$bipy] compounds.[13] Unfortunately, we did not have access to an instrument for fluorescence decay measurements.

A number of experiments were carried out to probe the possibility of finding a different solvent/donor combination for which reductive fluorescence quenching is observed. Fluorescence quenching of **2** by either TEOA or TEA is also found in acetonitrile or acetonitrile/water solutions, but the K_{SV} values found in these systems are smaller than in DMF by a factor of 2 and 5, respectively. The use of ternary amines as sacrificial electron donors restricts the reactions to alkaline conditions. This is a particular disadvantage for the goal of shifting the reactivity from CO_2 to H_2O reduction, as H_2O reduction is thermodynamically more difficult under basic or neutral conditions. Therefore other, nonbasic electron donors with irreversible oxidation between +0.5 and +1 V and solubility in DMF, MeCN or H_2O were studied. Well-suited candidates are oxalic acid, vitamin C, cystamine or EDTA.[31] None of these donors caused any quenching of [ReX(diimine)(CO)$_3$] fluorescence in solution, although all meet the requirements of a thermodynamically accessible, irreversible oxidation.[31]

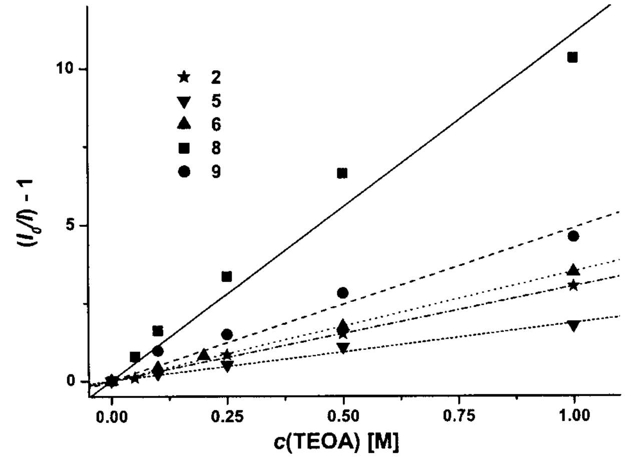


Figure 8. Stern–Volmer plots for the fluorescence quenching of the excited states of different [ReX(diimine)(CO)$_3$] complexes by TEOA.

Table 3. Stern–Volmer constants determined by linear fits of the data forced through zero together with the corresponding values of $E_{1/2,\text{red}}$ and λ_{em}.

Complex	K_{SV}	$E_{1/2,\text{red}}$ [mV]	λ_{em} [nm]
1	0.6	–1130	580
2	3.0	–1190	575
5	1.9	–1015	580
6	3.5	–1125	540
8	11.1	–1090	570
9	4.9	–975	585
10	13.5	–705	520
12	20.5	–1250	540

Photochemical CO_2 Reductions: Experiments to study the photocatalytic activity of these complexes in the Strasbourg system were carried out under conditions similar to the reported set-up.[10] Only CO with no detectable quantities of H_2 was found in the headspace of the reaction solutions.

The time course of produced CO per mol of catalyst for the [ReX(bipy)(CO)$_3$] series and the technetium homologue **3** are shown in Figure 9. All complexes of this series are active catalysts, though at very different rates (Table 4). It is most interesting to note that after a significant change of the metal centre – from rhenium to technetium – catalytic activity was retained. The thiocyanato complex **5** is a better catalyst than the original complexes **1** and **2** as it combines a rate as fast as **1**, but with improved long-term stability, as the turnover rate for **5** does not change over the first 2 h. The reason for this enhanced stability might be the suppression of the formation of the catalytically inefficient formato complex [Re(HCOO)(bipy)(CO)$_3$][10] as an undesired side product in reactions catalysed by **1** or **2**. The complexes of the larger diimines (**8**, **9** and **10**) are all active photocatalysts but at smaller rates than **2** (Table 4). No CO or any other gaseous products were detected for reactions using **11**, **13**, **14** or **15**. Thus, there is a strict correlation between the detection of room temperature fluorescence and catalytic activity: all fluorescing complexes are active catalysts for photocatalytic CO$_2$ reduction while the others are not.

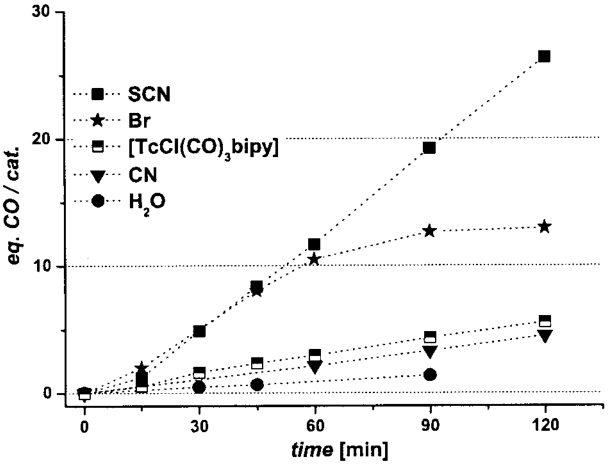


Figure 9. Formation of CO. Reactions with different [ReX(bipy)(CO)$_3$] and [TcCl(bipy)(CO)$_3$(bipy)] complexes.

Table 4. Formation of CO for reactions of photocatalysts of the [ReX(CO)$_3$(bipy)] series and [TcCl(bipy)(CO)$_3$].

Catalyst	CO after 30 min. [equiv./cat.]	CO after 120 min. [equiv./cat.]
1	4.6	8.2
2	4.0	13.0
3	1.6	5.5
4	0.5	1.8
5	4.9	26.4
6	1.1[a]	4.5
7	0.6[a]	2.6
8	4.8	11.5
9	0.5	1.1
12	2.2	7.7

[a] Extrapolated values.

In agreement with the fluorescence quenching experiments described earlier, the same experiments with different donors such as cystamine or vitamin C in DMF gave no CO. Furthermore, it has been claimed in the literature that the system would switch from CO$_2$ to H$_2$O reduction if the reaction was carried out in a THF/water mixture instead of DMF.[32] We tried to reproduce this result multiple times with our catalysts but no product at all, neither H$_2$ nor CO, was detected in a THF/water (4:1) mixture. On the other hand, about half the rate of CO production was observed with **2** in DMF/10% water.

These results support the original catalytic mechanism proposed by the Strasbourg group.[10] The well-established initial step is the absorption of a visible-light photon by the catalyst [Re^{I}X(diimine)(CO)$_3$] and subsequent MLCT to form the excited state [Re^{II}X(diimine^{-})(CO)$_3$]. This step occurs for all complexes discussed here but for **11**, **13**, **14** and **15** nonradiative relaxation pathways to the ground state are most probably so fast that no consecutive reactions can occur, as the absence of fluorescence for these compounds indicates. Hence, they are inactive as Strasbourg catalysts regardless of their electro- or photochemical properties.

According to our results, there is no evidence to support a carboxylate-bridged rhenium dimer as a key intermediate, as proposed in a recent study,[14] as this is in disagreement with the pronounced influence observed for the terminal ligands in the [ReX(bipy)(CO)$_3$] series. Also, the different compounds act both as photoactive and catalytic centres for the reduction of CO$_2$, but none show any reactivity to reduce water, as has been claimed before.[32]

Conclusions

We were able to show in this study that the [ReX(bipy)(CO)$_3$] catalysts could easily be modified for the Strasbourg system. The catalytic activity for photocatalytic reduction of CO$_2$ is retained in most cases or even enhanced, even though spectroscopic and electrochemical properties of the complexes are substantially altered. There are, however, limitations to the degree to which the diimine ligand can be varied. For a group of [ReBr(CO)$_3$(diimine)] compounds, catalytic activity is lost together with the ability of these complexes to fluoresce, indicating that a sufficiently long excited state life-time is of course a key prerequisite for photoreactivity. While many of the rhenium complexes are able to catalyse the two-electron photoreduction of CO$_2$, none show any reactivity for the reduction of the much more important substrate H$_2$O. Nevertheless, the unusual reactivity of [ReX(CO)$_3$(diimine)] compounds, observed once more in this study, justifies the idea that they should be considered as promising alternatives to the [Ru(diimine)$_3$]$^{2+}$ class of compounds.

Experimental Section

General: All chemicals were of reagent grade and used without further purification. Water was doubly distilled before use. Synthetic reactions were carried out under N$_2$ using standard Schlenk techniques. Abbreviations of the diimine ligands are according to Scheme 2. The complexes [ReBr(CO)$_5$],[33] (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$][34] and (NEt$_4$)$_2$[TcCl$_3$(CO)$_3$],[35] [ReCl(bipy)(CO)$_3$][36] (**1**), [ReBr(bipy)(CO)$_3$][36] (**2**), [ReBr(phen)(CO)$_3$][37] (**8**), [ReBr(biq)(CO)$_3$][38] (**11**) as well as the ligands abpy,[39] dpq,[40] dppz[41] and phd[42] were synthesised according to published procedures. Preparations of the complexes **4**,[43] **5**,[44] **6**,[45] **7**,[45] **13**[37] and **15**[46] have been reported before in the literature but for this study these compounds were obtained via the different, in most cases more facile, routes described below.

Caution! ^{99}Tc is a weak *β*-emitter with a half-life of $2.12{\cdot}10^5$ years. Although radiation from small amounts of material is absorbed completely by the walls of the glassware, reactions should only be carried out in specially equipped laboratories and under well-ventilated hoods.

[^{99}TcCl(bipy)(CO)$_3$] (3): (NEt$_4$)$_2$[^{99}TcCl$_3$(CO)$_3$] (33 mg, 0.06 mmol) was stirred in H_2O (5 mL) for 2 h, bipy (15.5 mg, 0.1 mmol) was added, dissolved in a mixture of EtOH (1 mL) and H_2O (2 mL). After 30 min a yellow precipitate started to form, which was filtered off after a reaction time of 12 h, washed with diethyl ether and dried in vacuo. Yield: 18 mg (80%). IR (KBr): $\tilde{\nu}_{CO}$ = 2031 (s), 1944 (s), 1920(s); $\tilde{\nu}_{bipy}$ = 1601 (m), 1469(m), 1441 (m), 771 (m) cm^{-1}. ^{1}H NMR ([D$_4$]MeOH): δ = 9.03 (br., 2 H), 8.63 (d, 2 H), 8.28 (m, 2 H), 7.75 (m, 2 H) ppm. ^{99}Tc NMR ([D$_4$]MeOH): δ = –1094.0 (s) ppm.

[Re(H_2O)(bipy)(CO)$_3$](OTf) (4): Complex **2** (150 mg, 0.3 mmol) was dissolved in acetone (15 mL) and AgOTf (76.1 mg, 1 equiv.) in acetone (5 mL) was added. The mixture was heated to 70 °C for 2 h. AgBr was filtered off and the solvent was removed in vacuo. The yellow residue was suspended in water (20 mL) and stirred at room temperature for 3 h. Insoluble parts were filtered off and the yellow solution was lyophilised to obtain the yellow, slightly hygroscopic product. Yield: 105 mg (60%). λ_{max} (DMF): 350 nm (sh, ε = 4000), 553 nm (ε = 1500). IR (KBr): $\tilde{\nu}_{CO}$ = 2036 (s), 1918 (s); $\tilde{\nu}_{bipy}$ = 1604 (m), 1475 (m), 1447 (m), 771 (m); $\tilde{\nu}_{OTf}$ = 1291 (m), 1230 (m), 1179 (m) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 426.87 [(M – H_2O)$^+$]. ^{1}H NMR ([D$_4$]MeOH): δ = 9.17 (m, 2 H), 8.70 (m, 2 H), 8.39 (m, 2 H), 7.82 (m, 2 H) ppm. ^{13}C NMR ([D$_4$]MeOH): δ = 155.3, 142.9, 129.7, 125.8 ppm. $C_{14}H_{10}F_3N_2O_7ReS_1$ (593.51): calcd. C 28.33, H 1.70, N 4.72; found C 28.99, H 1.79, N 5.08.

[Re(SCN)(bipy)(CO)$_3$] (5): 2 (50.6 mg, 0.1 mmol) was dissolved in acetone (5 mL) and AgOTf (17.1 mg, 1 equiv.) in acetone (2 mL) was added. The mixture was heated to 70 °C for 2 h. AgBr was filtered off and the solvent removed in vacuo. The residue was stirred MeOH (10 mL) for 1 h. KSCN (20 mg, 2 equiv.), dissolved in H_2O (2 mL), was added and the mixture heated to 70 °C for 4 h to obtain a clear yellow solution. The product precipitated after 1 d at 4 °C. The yellow compound was filtered off, washed with cold H_2O, MeOH and ether and dried in vacuo. Yield: 30 mg (60%). λ_{max} (DMF): 376 nm (ε = 2500). λ_{em} (DMF): 580 nm. IR (KBr): $\tilde{\nu}_{SCN}$ = 2093 (s); $\tilde{\nu}_{CO}$ = 2020 (s), 1928 (s), 1914 (s); $\tilde{\nu}_{bipy}$ = 1602 (m), 1471(m), 1444 (m), 765 (m) cm^{-1}. ESI-MS (acetone): *m/z* (%) = 426.87 [(M – SCN)$^+$]. ^{1}H NMR ([D$_6$]acetone): δ = 9.15 (m, 2 H), 8.77 (m, 2 H), 8.42 (m, 2 H), 7.86 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 154.4, 141.6, 129.1, 125.3 ppm.

[Re(CN)(bipy)(CO)$_3$] (6): (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] (100 mg, 0.13 mmol) was dissolved in H_2O (5 mL) and $AgNO_3$ (66.2 mg, 3 equiv.) in H_2O (3 mL) was added. The solution was stirred at room temperature for 30 min before AgBr was removed by filtration. Bipy (20.3 mg, 1 equiv.), dissolved in EtOH (2 mL) was added. HPLC analysis confirmed the quantitative formation of [Re(H_2O)(bipy)(CO)$_3$]$^+$ after 12 h. The addition of KCN (25.4 mg, 3 equiv.) and 20 h of stirring at 100 °C, resulted in the quantitative conversion to **6**, as detected by HPLC. The solvent was removed in vacuo and the product was obtained by extraction of the residue with three 5-mL portions of THF. Yield: 45 mg (75%). λ_{max} (DMF): 354 nm (ε = 2300). λ_{em} (DMF): 540 nm. IR (KBr): $\tilde{\nu}_{CN}$ = 2117 (w); $\tilde{\nu}_{CO}$ = 2006 (s), 1878 (s); $\tilde{\nu}_{bipy}$ = 1603 (m), 1473 (m), 1445 (m), 775 (m) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 453.60 [M$^+$]. ^{1}H NMR ([D$_6$]acetone): δ = 9.07 (d, 2 H), 8.21 (d, 2 H), 8.07 (m, 2 H), 7.54 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 154.4, 140.8, 128.8, 125.1 ppm.

[{Re(bipy)(CO)$_3$}$_2$(μ-CN)](ClO$_4$) (7): (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] (100 mg, 0.13 mmol) was dissolved in H_2O (10 mL) and $AgClO_4$ (80.8 mg, 3 equiv.) was added. AgBr was removed after 30 min by filtration. Bipy (20.3 mg, 1 equiv.), dissolved in EtOH (5 mL) was added. After 20 h at room temperature [Re(bipy)(CO)$_3$(H_2O)]$^+$ formed quantitatively, and KCN (4.2 mg, 0.5 equiv.) in H_2O (2 mL) was added. After 2 h at 100 °C, a yellow precipitate started to form which was filtered off after 20 h, washed with H_2O and diethyl ether and dried in vacuo. Yield: 28 mg (45%). λ_{max} (DMF): 363 nm (ε = 2000). λ_{em} (DMF): 535 nm. IR (KBr): $\tilde{\nu}_{CN}$ = 2151 (w); $\tilde{\nu}_{CO}$ = 2025 (s), 1910 (s), 1896 (s); $\tilde{\nu}_{bipy}$ = 1605 (m), 1473 (m), 1446 (m), 771 (m); $\tilde{\nu}_{ClO4}$ = 1121 (m) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 879.53 [M$^+$]. ^{1}H NMR ([D$_6$]acetone): δ = 8.83 (br., 4 H), 8.00 (br., 4 H), 7.60 (br., 4 H), 7.41 (br., 4 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 154.3, 154.1, 142.2, 141.8, 129.0 (2C), 125.9, 125.7 ppm.

[ReBr(dpq)(CO)$_3$] (9): A procedure similar to the published method for the preparation of [ReBr(phen)(CO)$_3$] was applied.[37] A suspension was prepared consisting of [ReBr(CO)$_5$] (50 mg, 0.12 mmol) and dpq (28.5 mg, 1 equiv.) in petroleum ether (10 mL, boiling range 100–130 °C). The suspension was heated to 100 °C for 2 h to obtain the product as a yellow precipitate. The powder was filtered off, washed with portions of petroleum ether and diethyl ether and then dried in vacuo to obtain the product as a yellow powder. Yield: 70 mg (quantitative). λ_{max} (DMF): 400 nm (sh, ε = 2500). λ_{em} (DMF): 585 nm. IR (KBr): $\tilde{\nu}_{CO}$ = 2025 (s), 1948 (s), 1902 (s); $\tilde{\nu}_{dpq}$ = 1402 (m), 1384 (m), 820 (w), 729(w), 631 (w) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 530.40 [M – Br + CO]$^+$, 502.80 [M – Br]$^+$. ^{1}H NMR ([D$_6$]acetone): δ = 9.96 (m, 2 H), 9.82 (m, 2 H), 9.38 (s, 2 H), 8.45 (m, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 155.8, 147.8, 136.5, 128.3 ppm. $C_{17}H_8BrN_4O_3Re$ (582.39): calcd. C 35.06, H 1.38, N 9.62; found C 35.38, H 1.53, N 9.69.

[ReBr(dppz)(CO)$_3$] (10): The same procedure as for [ReBr(dpq)(CO)$_3$] was applied, using [ReBr(CO)$_5$] (50 mg, 0.12 mmol) and dppz (33.8 mg, 1 equiv.), to obtain the complex as an orange powder. Yield: 50 mg (65%). λ_{max} (DMF): 400 nm (sh, ε = 5000). λ_{em} (DMF): 520 nm. IR (KBr): $\tilde{\nu}_{CO}$ = 2018 (s), 1918 (s), 1890 (s); $\tilde{\nu}_{dppz}$ = 1493 (m), 1418 (m), 1384 (m), 1360 (m), 822 (w), 773 (w), 729 (w) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 580.53 [M – Br + CO]$^+$, 553.00 [M – Br]$^+$. ^{1}H NMR ($CDCl_3$): δ = 10.04 (m, 2 H), 9.88 (m, 2 H), 8.47 (m, 2 H), 8.08 (m, 2 H), 7.26 (m, 2 H) ppm. $C_{21}H_{10}BrN_4O_3Re$ (632.45): calcd. C 39.88, H 1.59, N 8.86; found C 39.53, H 1.77, N 8.58.

(NEt$_4$)[ReBr(Hdcbipy)(CO)$_3$] (12): (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] (154 mg, 0.2 mmol) was dissolved in H_2O (15 mL) and H_2dcbipy (53.7 mg, 1.1 equiv.) was added as a solid. The pH of the solution was raised to pH ca. 6–7 by the careful addition of 10 mM NaOH. The mixture was stirred for 2 d at room temperature and some yellow precipitate formed, which was filtered off. The filtrate was lyophilised, triturated three times with CH_2Cl_2 (5 mL) to remove NEt$_4$Br and then dried in vacuo. Yield: 75 mg (50%). λ_{max} (DMF): 360 nm (sh, ε = 3000). λ_{em} (DMF): 540 nm. IR (KBr): $\tilde{\nu}_{CO}$ = 2024 (s), 1896 (s); $\tilde{\nu}_{dcbipy}$ = 1719 (w), 1619 (m), 1551 (w), 1366 (m), 1289 (m), 1071 (w), 766 (m), 682 (m) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 468.40 [(M – Br – COOH – H)$^-$]. ^{1}H NMR (D_2O/NaOH): δ = 9.02 (m, 2 H), 8.65 (s, 2 H), 7.81 (m, 2 H) ppm. ^{13}C NMR (D_2O/NaOH): δ = 151.6, 124.2, 120.7 ppm.

[ReBr(bpm)(CO)$_3$] (13): (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] (385 mg, 0.5 mmol) was dissolved in H_2O (20 mL) and bpm (87 mg, 1.1 equiv.), dissolved in EtOH (2 mL) was added. The mixture was stirred for 2 d at room temperature, after which a fine orange precipitate had formed. The solid was filtered off, washed with H_2O, cold EtOH and ether, and dried in vacuo. Yield: 210 mg (80%). λ_{max} (DMF): 383 nm (ε = 2500). IR (KBr): $\tilde{\nu}_{CO}$ = 2030 (s), 1931 (s), 1906 (s); $\tilde{\nu}_{bpm}$ = 1575 (m), 1547 (w), 1407 (s), 834 (w), 755 (w) cm^{-1}. ESI-MS ([D$_6$]acetone/MeOH): *m/z* (%) = 508.00 [M$^+$]. ^{1}H NMR ([D$_6$]-acetone): δ = 9.41 (dd, 2 H), 9.35 (dd, 2 H), 7.98 (dd, 2 H). ^{13}C NMR ([D$_6$]acetone): δ = 162.0, 161.4, 125.6 ppm. $C_{11}H_6BrN_4O_3Re$ (508.30): calcd. C 25.99, H 1.19, N 11.02; found C 26.24, H 1.05, N 10.87.

[ReBr(phd)(CO)$_3$] (14): The same procedure as for [ReBr(bpm)-(CO)$_3$] was applied, using (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] (500 mg, 0.65 mmol) and phd (163 mg, 1.2 equiv.) to isolate the orange complex. Yield: 350 mg (95%). λ_{max} (DMF): 375 nm (sh, ε = 3000). IR (KBr): $\tilde{\nu}_{CO}$ = 2033 (s), 1943 (s), 1885 (s); $\tilde{\nu}_{phd}$ = 1703 (m), 1573 (w), 1427 (m), 1298 (w), 1026 (w), 828 (w), 727 (w) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 512.73 [(M – Br + MeOH)$^+$], 480.73 [(M – Br)$^+$]. ^{1}H NMR ([D$_6$]acetone): δ = 9.34 (dd, 2 H), 8.81 (dd, 2 H), 8.05 (dd, 2 H) ppm. ^{13}C NMR ([D$_6$]acetone): δ = 158.0, 139.0, 129.8 ppm. $C_{15}H_6BrN_2O_5Re$ (560.33): calcd. C 32.15, H 1.08, N 5.00; found C 32.37, H 1.12, N 5.08.

[ReBr(abpy)(CO)$_3$] (15): The same procedure as for [ReBr(bpm)(CO)$_3$] was applied, using (NEt$_4$)$_2$[ReBr$_3$(CO)$_3$] (76 mg, 0.1 mmol) and abpy (27 mg, 1.5 equiv.) to isolate the violet-blue compound. Yield: 50 mg (95%). λ_{max} (DMF): 361 nm (ε = 5000), 553 nm (ε = 1500). IR (KBr): $\tilde{\nu}_{CO}$ = 2020 (s), 1924 (s), 1900 (s); $\tilde{\nu}_{abpy}$ = 1465 (w), 1433 (m), 1370 (w), 797 (m) cm^{-1}. ESI-MS (MeOH): *m/z* (%) = 454.67 [M – Br]$^+$. ^{1}H NMR ([D$_6$]acetone): δ = 9.33 (m, 1 H), 8.96 (m, 1 H), 8.87 (m, 1 H), 8.57 (td 1 H), 8.20 (br., 2 H), 8.00 (br., 1 H), 7.85 (br., 1 H) ppm. ^{13}C NMR ([D$_6$]-acetone): δ = 152.7, 149.7, 142.7, 140.3, 131.4, 130.9, 129.5, 115.7 ppm. $C_{13}H_8BrN_4O_3Re$ (534.34): calcd. C 29.22, H 1.51, N 10.49; found C 29.61, H 1.43, N 10.56.

Physical Measurements: UV/Vis spectra were measured with a Cary 50 spectrometer with solution samples in 1-cm quartz cells. If necessary, cells with silicon septa lids were used to keep samples under an inert gas atmosphere during measurements. Fluorescence measurements were performed with a Perkin–Elmer LS50B fluorescence spectrometer with argon purged solution samples in 1-cm cells. IR spectra were recorded with a Bio-Rad FTS-45 spectrometer with samples in compressed KBr pellets. ^{1}H NMR spectra were recorded with Varian Mercury and Varian Gemini-2000 spectrometers (^{1}H at 199.97 MHz and 300.08 MHz, respectively) and ^{13}C NMR spectra were recorded with Varian Gemini-2000 and Bruker DRX500 spectrometers (^{13}C at 75.47 MHz and 125.81 MHz, respectively). The chemical shifts are reported relative to residual solvent protons as a reference. ^{99}Tc NMR spectra were recorded with a Varian Gemini-2000 spectrometer (^{99}Tc resonance 67.40 MHz), referenced to [^{99}TcO$_4$]$^-$. Electrospray ionisation mass spectra (ESI-MS) were recorded with a Merck–Hitachi M-8000 spectrometer, reported are the values of the ^{187}Re isotope. Elemental analyses were performed with a Leco CHNS-932 elemental analyser. It was found that cyano- and thiocyanato compounds analysed by this instrument often show elemental analyses differing greatly from the expected calculated percentages. This analytical problem was also observed for commercial, analytical grade chemicals like NaCN, K$_3$[Fe(CN)$_6$] or CuSCN. Electrochemical measurements were carried out in DMF containing 0.1 M TBA PF$_6$ as conducting electrolyte. A Metrohm 757 VA Computrace electrochemical analyser was used with a standard three-electrode setup of glassy carbon working and auxiliary electrodes and a Ag/AgCl reference electrode. All potentials are given vs. Ag/AgCl (NHE: +221 mV). Gas chromatograms were recorded with a Varian CP-3800 gas chromatograph with helium as the carrier gas. The permanent gases CO, N_2, O_2 and H_2 were separated by a 3 m × 2 mm column packed with Varian molecular sieves 13X. The gases were detected using a thermal conductivity detector (Varian). Calibrations were performed by the injection of known quantities of pure gases.

Photochemical Carbon Dioxide Reductions: Reactions catalysed by [Re(CO)$_3$(diimine)X] complexes were tested in 50 mL septum capped Schlenk tubes. Exact volumes were determined gravimetrically. 10 mL of a solution containing TEOA (1 M) and the catalyst (1 mM) in DMF were prepared, wrapped in black foil and degassed using a CO_2-purged Schlenk-line. The mixture was equilibrated under 1.5 bar CO_2 pressure for 15 min and then transferred to a dark room for illumination. The light source was a Leica Pradovit S AF slide projector equipped with a 250-W Osram Xenophot HLX lamp. The light was filtered by a 400-nm cut-off filter (Schott GG 400) before reaching the sample at 40 cm distance from the projector. Light intensities illuminating the sample were determined by a TES 1332A luxmeter to be 46.000 lux. 100-µL gas samples were

Table 5. Crystal and structure refinement data for **1**, **3**, **10**, **11** and **14**.

Compound No.	**1**	**3**	**10**	**11**	**14**
Formula	$C_{13}H_8ClN_2O_3Re$	$C_{13}H_8ClN_2O_3Tc$	$C_{21}H_{10}BrN_4O_3Re$	$C_{21}H_{12}BrN_2O_3Re$	$C_{15}H_6BrN_2O_5Re$
M_r	461.86	373.67	632.44	606.44	560.33
Crystal system	monoclinic	triclinic	triclinic	triclinic	orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	*Pnma*
a [Å]	6.8740(5)	10.9879(8)	6.9955(7)	7.5081(10)	7.2858(5)
b [Å]	15.0038(9)	11.5003(9)	12.9547(11)	9.7573(10)	12.7348(6)
c [Å]	13.5114(11)	11.1203(9)	13.2653(12)	12.9934(18)	16.7641(9)
α [°]		93.703(10)	111.200(10)	94.697(15)	
β [°]	96.494(10)	103.282(9)	98.272(11)	94.288(16)	
γ [°]		86.214(9)	95.110(11)	106.434(14)	
V [Å^3]	1384.57(17)	1362.87(18)	1096.10(17)	905.1(2)	1555.43(15)
Z	4	4	2	2	4
D_c [g cm^{-3}]	2.216	1.821	1.916	2.225	2.393
μ(Mo-K_α) [mm^{-1}]	8.976	1.259	7.394	8.946	10.409
Goodness-of-fit on F^2	0.882	0.867	0.926	1.042	1.047
R$^{[a,b]}$	0.0464	0.0426	0.0593	0.0749	0.0701
$wR_2$$^{[a,c]}$	0.0702	0.0990	0.1685	0.1893	0.1835
Max., min. peaks [e·Å^{-3}]	3.433, –1.822	0.661, –0.970	3.063, –1.710	2.066, –2.314	2.002, –1.804

[a] Observation criterion: $I > 2\sigma(I)$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

drawn from the headspace above the solution and injected into the GC-TCD gas analyser.

X-ray Diffraction Studies: Suitable crystals were covered with Paratone N oil, mounted on top of a glass fibre and immediately transferred to a Stoe IPDS diffractometer. Data was collected at 183(2) K using graphite-monochromated Mo radiation (0.71073 Å). Data was corrected for Lorentz and polarisation effects as well as for absorption. Structures were solved with direct methods using SHELXS-97[47] or SIR97[48] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[49] ORTEP plots were generated by the PLATON software package[50] and are drawn at 50% probability. The crystal data and refinement parameters of the presented structures are summarised in Table 5.

CCDC-299061 to -299065 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Centre via www.ccdc.cam.ac.uk/datarequest/cif.

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