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Synthesis and Reactivity of the 17 e^- Complex $[Re^{II}Br_4(CO)_2]^{2-}$: A Convenient Entry into Rhenium(II) Chemistry

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The reduction of $(Et_4N)[Re^{III}Br_4(CO)_2]$ (**1**) by 0.5 equiv of *tetrakis*-dimethylaminoethylene in acetonitrile yields directly the air-stable, 17-electron Re^{II} synthon $(Et_4N)_2[Re^{II}Br_4(CO)_2]$ (**2**) in nearly quantitative yield. The versatility of **2** as a synthon for Re^{II} chemistry was demonstrated by substitution reactions of $[Re^{II}Br_4(CO)_2]^{2-}$ with different mono-, bi-, and tridentate ligands. The resulting Re^{II} complexes form highly crystalline compounds, and the solid state structures of the neutral *trans*−*cis*-$[Re^{II}Br_2(CO)_2(X)_n]$ species (where X = imidazole, pyridine, or phenanthroline) could be determined. All complexes are stable under aerobic conditions, both as solids and in solution, and showed fully reversible one-electron $Re^{II} \rightarrow Re^{I}$ reductions between ca. −70 and −120 mV. Carbonyl stretching frequencies (ν_{CO}) of this new family of Re^{II} complexes are observed in the 1990 cm^{-1} (A_1) and 1830 (E_g) cm^{-1} regions. With complex **2**, a wide variety of fundamental but so far unknown Re^{II} complexes become accessible via facile substitution reactions.

Introduction

Rhenium (and technetium) complexes in the oxidation state II (d^5 configuration) are rare as compared to complexes of the other oxidation states of these elements. This is unexpected since the related paramagnetism together with the attractive open-shell electronic configuration make such complexes highly interesting for various applications in magnetochemistry or catalysis. This has recently been shown by, for example, Dunbar et al. with the synthesis of pseudo-cubic metal cyanide clusters comprising Re^{II} and exhibiting single molecule magnetism (SMM).[1−3] Complexes of Re^{II} are also assumed to be transient species in the photocatalytic $CO_2 \rightarrow CO$ conversion, although no intermediates could be identified unambiguously, so far.[4−6]

When inspecting Re^{II} chemistry in a recent review,[7] it becomes obvious that Re^{II} complexes widely rely on phosphine, nitrile, or isocyanide ligands with π-accepting properties. Some examples of complexes with aromatic or aliphatic amines have also been described.[8−12] Furthermore, Re^{II} chemistry is dominated by the dinuclear $\{Re_2\}^{4+}$ building block, a nice example being $[Re_2(NCCH_3)_8]^{4+}$ which served as a source for triphos complexes of the form $[(triphos)Re(CN)_3]^-$ or $[(triphos)Re(NCCH_3)_3]^{2+}$ prepared via homolytic bond scission of dinuclear precursors.[13,14] The latter two complexes were versatile mononuclear 17-electron building blocks for the design of molecular materials or molecular magnets with tunable electronic properties.[1−3]

A few Re^{II} carbonyl complexes have been described;[15−20] of particular note are the unusual complexes

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$[(Cp^*)Re^{II}(CO)_3]^{+}$[21] and $[Re^{II}Br(CO)_2(tacn)]^+$, the latter being prepared by ligand-mediated decarbonylation of a Re^{III} precursor and subsequent reoxidation with Fc^+ (ferrocenium).[22] As illustrated by the last two examples, mononuclear Re^{II} complexes have generally been received by either oxidation[23] of Re^I or reduction of Re^{III} precursor complexes[24-26] but rarely by direct ligand substitution from a common precursor. The scarcity of mononuclear Re^{II} species is also surprising in view of the well-developed Mn^{II} chemistry but mirrors the differences in the chemical behavior of first, second, or third transition element series.

For a more systematic development of Re^{II} chemistry, it would be convenient to have a stable but substitution labile precursor. Conceptually, such a Re^{II} synthon would comprise a number of halides, fully or partially replaced in coordinating solvents and undergoing substitution reactions with a broad variety of ligands. A prototype for this concept is the Re^I complex $[ReBr_3(CO)_3]^{2-}$, the availability of which enabled a systematic development of fundamental and applied chemistry of the *fac*-$[Re^I(CO)_3]^+$ building block.[27] The convenience of $[Re^IBr_3(CO)_3]^{2-}$ begged the question of whether a comparable complex would exist for Re^{II} chemistry. The Re^{III} complex $[Re^{III}Br_4(CO)_2]^-$ was in support of this hypothesis and made a corresponding Re^{II} complex likely. We present in this paper the synthesis of the Re^{II} synthon $[Re^{II}Br_4(CO)_2]^{2-}$, some of its fundamental properties in coordinating solvents, and substitution reactions with selected ligand types to underscore the convenience of $[Re^{II}Br_4(CO)_2]^{2-}$ as an entry into Re^{II} chemistry.

Experimental Section

Chemicals and solvents were purchased from standard sources. Solvents were distilled and degassed prior to use. The syntheses of **2**, **4** (method a), **8b**, and **9** were performed in a glovebox; **4** (method b) through **7** were synthesized under nitrogen with standard techniques. Compound **1** was synthesized according to literature methods.[28] Elemental analyses were performed on a Leco CHNS-932 elemental analyzer. IR spectra were recorded on a PerkinElmer Spectrum BX FT-IR spectrometer. Crystallographic data were collected at 183(2) K with Mo Kα radiation ($\lambda = 0.7107$ Å) that was monochromated with the help of graphite on an Oxford Diffraction Xcalibur system with a Ruby detector. Suitable crystals were covered with oil (Infineum V8512), mounted on top of a glass fiber, and immediately transferred to the diffractometer. The program suite CrysAlis^{Pro} was used for data collection, semiempirical absorption correction, and data reduction.[29] Structures were solved with direct methods using SIR97[30] and were refined by full-matrix least-squares methods on F^2 with SHELXL-97.[31] The structures were checked for higher symmetry with help of the program Platon.[32] CCDC 730937−730942 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.

Synthesis of $(Et_4N)_2[Re^{II}Br_4(CO)_2]$ (2). A total of 400 mg of $(Et_4N)[Re^{III}Br_4(CO)_2]$ (**1**) (0.580 mmol) and 1.2 g of Et_4NBr (10 equiv) were dissolved in 10 mL of CH_3CN. After 5 min of stirring, 68 μL (0.5 equiv) of *tetrakis*-dimethylaminoethylene (TDAE) in 2 mL of CH_3CN was added in 200 μL portions. The solution turned from dark red to a bright red/orange color. After 1 h of stirring, a white precipitate was removed by filtration and the solution dried. The light orange powder was stirred in 30 mL of CH_2Cl_2 for 15 min and then filtered, yielding **2** as a bright red solid which was dried in vacuo. Yield: 435 mg, 92%. Anal. Calcd for $C_{18}H_{40}Br_4N_2O_2Re$ (822.4): C, 26.29%; H, 4.90%; N, 3.41%. Found: C, 26.22%; H, 4.96%; N, 3.31%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1972, 1796.

Synthesis of $[Re^{II}Br_2(CO)_2(py)_2]$ (4). Method a. A total of 200 mg of **1** (0.290 mmol) was dissolved in 10 mL of dimethoxyethane (DME). A total of 20 equiv (500 μL) of pyridine (py) was added, followed by 34 μL (0.5 equiv) of TDAE. After 1 h of stirring, the precipitate was removed by filtration and the solution dried. The brown powder was washed with a few milliliters of MeOH, filtered, and dried in vacuo to yield 90 mg of **4** (50%). Anal. Calcd for $C_{12}H_{10}Br_2N_2O_2Re$ (560.2): C, 25.73%; H, 1.80%; N, 5.00%. Found: C, 25.62%; H, 1.92%; N, 5.31%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1990, 1825.

Method b. A total of 100 mg of **2** (0.122 mmol) was suspended in 5 mL of DME, and 10 equiv of pyridine (105 μL) was added. After stirring overnight, the brownish precipitate was filtered off and dried in vacuo to yield **4** (55 mg, 80%). Anal. Calcd for $C_{12}H_{10}Br_2N_2O_2Re$ (560.2): C, 25.73%; H, 1.80%; N, 5.00%. Found: C, 26.00%; H, 1.69%; N, 4.88%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1990, 1825. Single crystals suitable for X-ray diffraction were grown by the slow diffusion of pentane into a CH_2Cl_2 solution of the compound.

Synthesis of $[Re^{II}Br_2(CO)_2(Im)_2]$ (5). A total of 100 mg of **2** (0.122 mmol) was suspended in 15 mL of DME, and 27 mg of imidazole (Im; 0.39 mmol, 3 equiv) was added. The mixture was heated to 60 °C for 3.5 h and stopped when the red suspension had become a yellow solution and a yellow precipitate had formed. The mixture was filtered while still hot. A bright yellow solid of **5** was collected, dried in vacuo, and recrystallized from a CH_2Cl_2/hexane mixture, giving dark red crystals. Yield: 53 mg, 81%. Anal. Calcd for $C_8H_8Br_2N_4O_2Re$ (538.2): C, 17.85%; H, 1.50%; N, 10.41%. Found: C, 17.49%; H, 1.32%; N, 10.46%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1988, 1826. Single crystals suitable for X-ray diffraction were grown by slow evaporation of a CH_2Cl_2 solution of the compound.

Synthesis of $(Et_4N)[Re^IBr_2(CO)_2(Im)_2]$ (5a). A total of 200 mg of **1** (0.290 mmol) was dissolved in 5 mL of DME. A total of 100 mg of imidazole (10 equiv) was added, followed by 68 μL (1 equiv) of TDAE. The red solution became colorless, and a precipitate appeared. After 30 min of stirring, the precipitate was collected by filtration and dried. The residue was then suspended in 3 mL of water and stirred for 1 h. After filtration, the solid was washed with water, giving **5a** as a light brown solid. Yield: 104 mg, 49%. Anal. Calcd for $C_{16}H_{28}Br_2N_5O_2Re$ (668.5): C, 28.75%; H, 4.22%; N, 10.48%. Found: C, 28.35%; H, 3.99%; N, 10.77%. ^{1}H NMR, 500 MHz (CD_3OD, δ ppm): 7.90 (s, 2H), 7.20 (t, 2H, J = 1.4 Hz), 7.02 (t, 2H, J = 1.4 Hz), 3.30 and 1.29 (m, 8H and 12H, from Et_4N^+). IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1870, 1775. Single crystals

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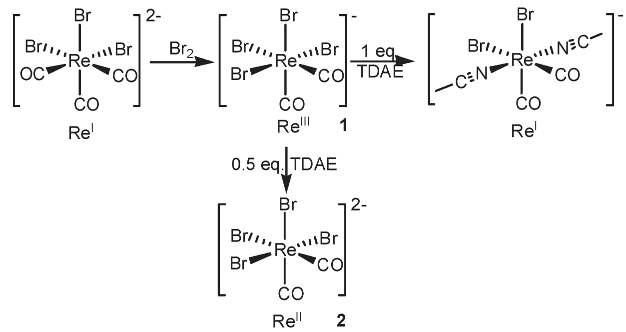
Scheme 1. Synthesis of the Re^{II} Synthon **2**[a]



[a] Reactions in acetonitrile and at room temperature.

suitable for X-ray diffraction were grown by the slow diffusion of hexane into a methanol solution of the compound.

Synthesis of [$Re^{II}Br_2(CO)_2$(bipy)] (6). A total of 100 mg of **2** (0.122 mmol) was suspended in 15 mL of DME, and 25 mg (1.25 equiv) of 2,2′-bipyridine (bipy) was added. The suspension was heated to 60 °C for 3.5 h and stopped when the red suspension had become a deep red solution. The mixture was allowed to cool to room temperature (RT) and then was filtered. The dark red solution was dried in vacuo, leaving **6** as a dark red solid. This was recrystallized from a CH_2Cl_2/hexane mixture, giving dark red crystals. Yield: 65 mg, quantitative. Anal. Calcd for $C_{12}H_8Br_2N_2O_2Re$ (558.2): C, 25.82%; H, 1.44%;, N, 5.02%. Found: C, 25.54%; H, 1.22%; N, 5.56%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1989, 1837.

Synthesis of [$Re^{II}Br_2(CO)_2$(phen)] (7). A total of 100 mg of **2** (0.122 mmol) was suspended in 15 mL of DME, and 27 mg (1.25 equiv) of phenanthroline (phen) was added. The suspension was heated to 60 °C for 3.5 h and stopped when the red suspension had become a deep red solution. The mixture was allowed to cool to RT and then was filtered. The dark red solution was dried in vacuo, leaving **7** as a dark red solid. This was recrystallized from a CH_2Cl_2/hexane mixture, giving dark red crystals. Yield: 70 mg, quantitative. Anal. Calcd for $C_{14}H_8Br_2N_2O_2Re$ (582.2): C, 28.88%; H, 1.83%; N, 4.81%. Found: C, 28.61%; H, 1.73%; N, 4.98%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1993, 1862. Single crystals suitable for X-ray diffraction were grown by the slow evaporation of a CH_2Cl_2 solution of the compound.

Synthesis of [$Re^{I}Br(CO)_2$(tacn)] (8b). A total of 100 mg of **2** (0.122 mmol) was dissolved in 5 mL of CH_3CN, and 24 mg (1.5 equiv) of 1,4,7-triazacyclononane (tacn) was added. Within 30 min, the solution became dark brown and then a light brown/orange color. After stirring overnight, a colorless precipitate (**8b**) was separated from the solution, washed with CH_2Cl_2, and dried under a vacuum. Yield: ca. 50%. Analytical data are in agreement with what was previously reported.[22] IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1883, 1770.

Synthesis of [$Re^{I}Br(CO)_2$(9S3)] (9). A total of 100 mg of **2** (0.122 mmol) was dissolved in 4 mL of CH_3CN/CH_2Cl_2 (1:1), and 17 mg (2 equiv) of 1,4,7-trithiacyclononane (9S3) was added. After 2 days, the colorless precipitate was separated from the solution, washed with CH_2Cl_2, and dried under a vacuum. Yield: 25 mg, 40%. Anal. Calcd for $C_8H_{12}BrO_2S_3Re$ (502.5): C, 19.12%; H, 2.41%; N, 0%. Found: C, 19.22%; H, 2.69%; N, 0%. IR (solid state, KBr, cm^{-1}): $\nu_{C\equiv O}$ 1921, 1856. Single crystals suitable for X-ray diffraction were grown by the slow evaporation of a DMF solution of the compound.

Results and Discussion

A precursor for rhenium complexes with a mixed carbonyl−halide coordination sphere is $(Et_4N)[Re^{III}Br_4(CO)_2]$ (**1**), the chemistry of which is not yet well explored.[28] The reduction of **1** by the two-electron reductant TDAE to Re^I complexes comprising the *cis*-$[Re^I(CO)_2]^+$ core has recently been introduced.[33,34] The straightforward two-electron reduction lead to *cis−trans*-$(NEt_4)[Re^IBr_2(NCCH_3)_2(CO)_2]$ (Scheme 1). Since direct two-electron transfer reactions are rare, it was likely that a Re^{II} complex would form as an intermediate. Accordingly, the reduction of **1** by 0.5 equiv of TDAE in acetonitrile immediately resulted in a clear orange solution. In the presence of excess (> 10 equiv) $[NEt_4]Br$, analytically pure $(Et_4N)_2[Re^{II}Br_4(CO)_2]$ (**2**) precipitated and was obtained in 92% yield (Scheme 1). The IR spectra showed a typical *cis*-$[M(CO)_2]$ pattern with the ν_{CO} stretching frequencies significantly red-shifted to 1972 and 1796 cm^{-1}, respectively, as compared to **1**.

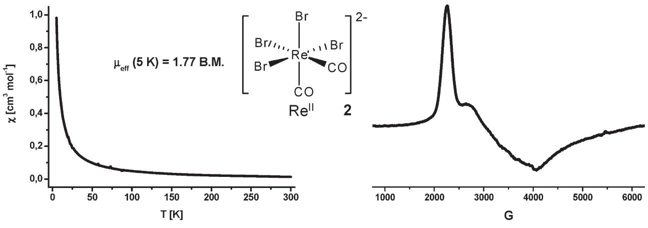


Figure 1. (Left) Temperature-dependent magnetic susceptibility data for **2**, recorded in the range 5−300 K showing a μ_{eff} = 1.77 μ_B. (Right) EPR spectrum of a methanol solution of **2** recorded at 5 K.

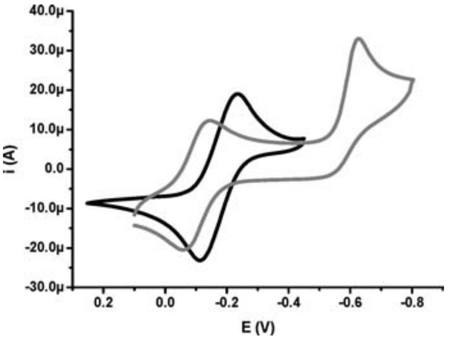


Figure 2. Cyclic voltammogram of **2** (black) and **4** (gray) in CH_3OH.

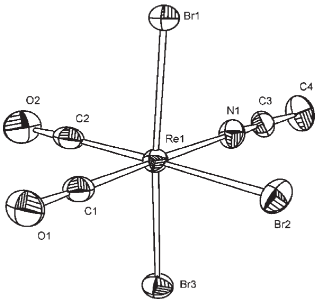


Figure 3. ORTEP plot of complex $\mathbf{3}^-$ (ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity).

Owing to the rapid exchange of at least one Br^- by coordinating solvent molecules (vide infra), crystals of **2** could not be collected. Elemental analysis supported the authenticity of **2**, and the low wavenumbers found in the IR spectrum indicated the presence of a "*cis*-$[Re(CO)_2]$" moiety in a negatively charged complex. The mononuclearity

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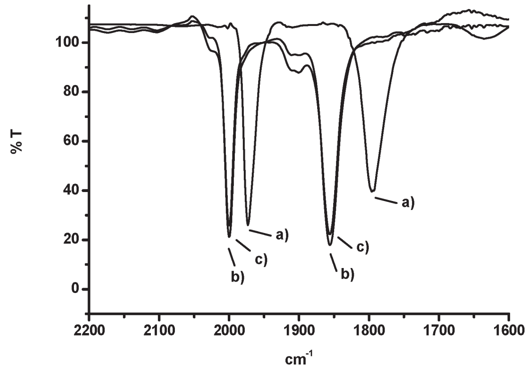

Figure 4. IR spectra of $[Re^{II}Br_4(CO)_2]^{2-}$: (a) solid (KBr), (b) methanol solution, and (c) methanol solution + 4 equiv of $TlPF_6$.

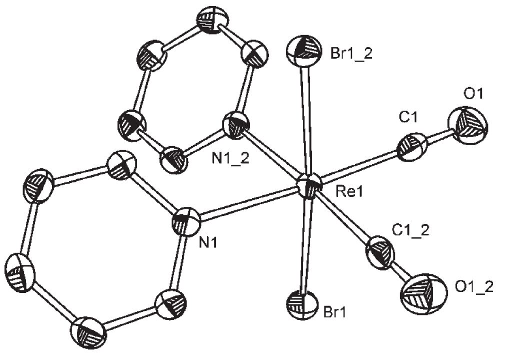

Figure 5. ORTEP plot of the Re^{II} complex **4** (ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity).

of **2** was assessed by magnetic measurements. The low-spin d^5 electronic configuration could be confirmed in the range between 5 and 300 K (Figure 1). At a low temperature (5 K), compound **2** exhibited a $\mu_{eff} = 1.77\ \mu_B$, as expected for a d^5 system with one single unpaired electron ($\mu = 1.73\ \mu_B$). At 5 K, an electron paramagnetic resonance (EPR) signal of **2** could also be detected. The spectrum (Figure 1) was strongly anisotropic, with *g* values between 3 and 1.7.

Complex **2** is air-stable, and solid samples, exposed to normal aerobic conditions for days, showed an identical elemental composition to that of freshly prepared samples. It is very soluble in polar coordinating solvents such as acetonitrile, methanol, or water but only slightly in CH_2Cl_2, acetone, or tetrahydrofuran. The dissolved complex does not decompose if kept anaerobic. The redox chemistry of **2** is of particular interest. In methanol, complex **2** showed a fully reversible one-electron reduction wave at −120 mV (vs Ag/AgCl, Figure 2). As discussed below, **2** converts to the fully solvated species $[Re^{II}(CO)_2(HOCH_3)_4]^{2+}$ in methanol; thus, the voltammogram in fact represents this species. The voltammogram did not change over an extended period of time, confirming the stability of **2** in solution.

As in $[Re^{I}Br_3(CO)_3]^{2-}$, the Br^- ligands in **2** are labile and can be exchanged for other ligands or coordinating solvents, as indicated by, for example, the high solubility of **2** in acetonitrile. Evaporation of an acetonitrile solution of **2** gave single crystals of $(Et_4N)[Re^{II}Br_3(NCCH_3)(CO)_2]$ (**3**). Complex **3** cocrystallized with 1 equiv of $[NEt_4]Br$. An ORTEP presentation of the complex anion $\mathbf{3}^-$ is given in Figure 3. For comparison with the other structurally characterized complexes, important bond lengths and angles are listed in Table 3.

Interestingly, **3** also crystallized from an acetonitrile solution presaturated with $[NEt_4]Br$, indicating that at least one coordinated Br^- is very efficiently exchanged for a solvent molecule. Compared to **2**, the IR spectrum of **3** showed blue-shifted ν_{CO} stretching frequencies at 1991, 1866, and 1850 cm^{-1}, respectively, and ν_{CN} at 2287 cm^{-1}.

When **2** was dissolved in methanol, the bromides readily exchanged for solvent molecules, forming $[Re^{II}(CO)_2(HOCH_3)_4]^{2+}$ (methanol may be partially deprotonated), as evident from IR spectroscopy (Figure 4). The IR spectrum of solid **2** in KBr shows two CO stretching frequencies at 1972 and 1796 cm^{-1} (a). A solution of **2** in MeOH exhibits the same ν_{CO} pattern but substantially blue-shifted to 2000 and 1856 cm^{-1} (b). The spectrum remains unchanged when the bromides are precipitated with 4 equiv of $TlPF_6$ (c), confirming the identity of the two complexes present in methanol prior to and after the precipitation of Br^-. This behavior parallels that of $[Re^{I}Br_3(CO)_3]^{2-}$ and underlines the presence of a fully solvated species in methanol as a synthon for subsequent Re^{II} chemistry.

As outlined in the introduction, Re^{II} complexes are generally prepared by redox reactions from either of the corresponding Re^{I} or Re^{III} complexes. This is especially true for coordination compounds,[8−10,12,35] but studies with organometallic complexes are rare. To probe whether the reduction of $Re^{III} \rightarrow Re^{II}$ and substitution occurred concertedly or stepwise, **1** was reduced with TDAE in the presence of 20 equiv of pyridine. When **1** was dissolved in DME and pyridine, no significant color change was observed. Upon the addition of 0.5 equiv of TDAE, *trans−cis*-$[Re^{II}Br_2(CO)_2(py)_2]$ (**4**) together with $[TDAE]Br_2$ precipitated immediately from the solution but in relatively poor yield. Concerted reduction/coordination thus did occur with pyridine, but a similar reactivity for other amines such as bipy or phen was not observed. This synthetic strategy was thus very limited with respect to ligand types, and a direct substitution with a Re^{II} synthon would be more convenient and flexible.

Compound **4** depicted two ν_{CO} stretching frequencies at 1990 and 1825 cm^{-1}, respectively. Its electrochemical behavior was different from that of **2**. Cyclic voltammetry in CH_3OH with 0.1 M $TBA[PF_6]$ as an electrolyte showed one reversible one-electron reduction at −76 mV (vs Ag/AgCl, Figure 2) attributed to the $Re^{II} \rightarrow Re^{I}$ couple and a second, irreversible wave at −565 mV. The low potential for the $Re^{II} \rightarrow Re^{I}$ reduction underlines the substantial oxidation properties of most of the Re^{II} complexes prepared so far. X-ray-quality red needles of **4** were obtained from CH_2Cl_2/pentane. The structure of the neutral complex molecule is shown in Figure 5.

The difficulties and limitations in the reduction/substitution process described above for **4** can immediately be eliminated by starting from the synthon **2**. The direct reaction of **2** with pyridine gave **4** in a short time and in 80% isolated yield with no byproducts. In a similar way, the corresponding imidazole $[Re^{II}Br_2(Im)_2(CO)_2]$ (**5**), 2,2′-bipyridine $[Re^{II}Br_2(bipy)(CO)_2]$ (**6**), and phenanthroline $[Re^{II}Br_2(phen)(CO)_2]$ (**7**) complexes could be obtained by the reaction of **2** with 2.5−5 equiv of the corresponding ligand in DME. Isolated yields were >80% for the monodentate ligands and quantitative for bipy and phen (Scheme 2). All reactions

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(35) Orth, S. D.; Barrera, J.; Sabat, M.; Harman, W. D. *Inorg. Chem.* **1993**, *32*, 594–601.

Scheme 2. Substitution Reactions of a Selection of Ligands with the *cis*-$[ReBr_4(CO)_2]^{2-}$ Synthon

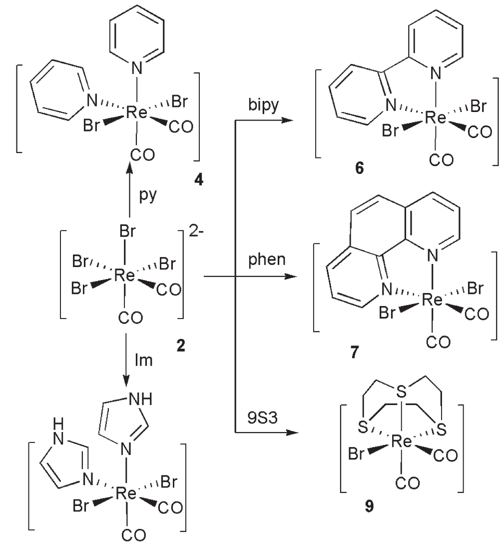

Table 1. Spectroscopic and Electrochemical Properties of Complexes **2**−**9**

complex	ν_{CO} (cm^{-1})^a	$E_{1/2}$ (mV)^b	λ_{max} (nm)^c
2^d	1972, 1796	−120^d	412 ^{d}
3	1991, 1866, 1850	−120	430
4	1990, 1825	−76	425
5	1988, 1826	dec.	418
5$^-$	1870, 1775		
6	1989, 1837	−80	424
7	1993, 1862	−74	426
8b	1883, 1770	+200	
9	1921, 1856	+750	

^{a} KBr. ^{b} Potentials are reported vs Ag/AgCl reference electrode in CH_3OH for **2**−**7** and in DMF for **8b** and **9** with 0.1 M $TBAPF_6$ as an electrolyte. All processes are one-electron and refer to the $Re^{II} \rightarrow Re^{I}$ reduction for **2**−**7** and to $Re^{I} \rightarrow Re^{II}$ oxidation for **8b** and **9**. ^{c} In CH_3OH for **2**, in CH_3CN for **3**, in CH_2Cl_2 for all others. ^{d} In methanol, **2** forms the $[Re^{II}(CO)_2(HOCH_3)_4]^{2+}$ cation, thus $E_{1/2}$ and λ_{max} refer to this species.

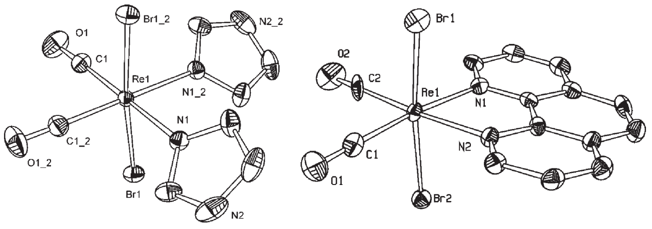

Figure 6. ORTEP plots of the Re^{II} complexes **5** and **7** (ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity).

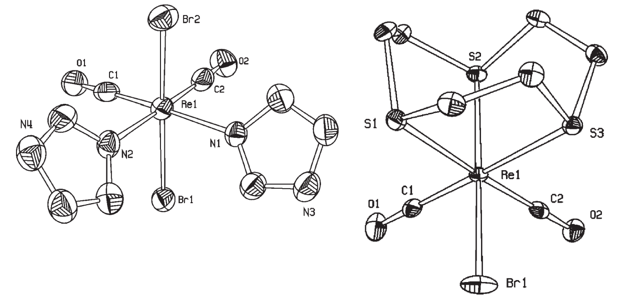

Figure 7. ORTEP plots of the Re^{I} complexes **5a**$^-$ (left) and **9** (right) (ellipsoids are drawn at 50% probability; hydrogen atoms are omitted for clarity).

with mono- and bidentate ligands have the *trans*−*cis*−*cis* arrangement of the ligands in common. Since the *cis* arrangement of the two COs is the only structural compulsion, other isomers are expected as well but were not observed. We propose the *trans*-labilizing effect of the CO ligands to be the reason for this selectivity but further mechanistic studies have to corroborate this assumption.

The reaction of **2** with 1,4,7-triazacyclononane (tacn) in acetonitrile is an example for direct Br^- substitution with a tridentate ligand. At RT and within 30 min, the Re^{II} complex $[Re^{II}Br(CO)_2(tacn)]^+$ (**8**) formed but was rapidly reduced to the corresponding Re^I complex $[Re^IBr(CO)_2(tacn)]$ (**8a**). Similarly, substitution of **2** with 1,4,7-trithiacyclononane (9S3) in acetonitrile led rapidly to the formation of a colorless precipitate in ca. 50% yield. An X-ray analysis of crystals grown from DMF confirmed the neutral Re^I complex $[Re^IBr(CO)_2(9S3)]$ (**9**; Figure 7). In **9**, the Re−S(2) bond length is 0.1 Å shorter than the Re−S(1)/S(3) bond. The weaker trans-influence Br^- ligand trans to S(2) rationalizes this observation as compared to the electron-accepting CO ligands trans to S(1)/S(3). In comparison to **8a** (1883 and 1770 cm^{-1}), the carbonyl stretching frequencies of **9** at 1921 and 1856 cm^{-1} are strongly blue-shifted but are clearly in agreement with those of Re^I. These IR shifts are coincidental with the donating properties of the two ligands, and the redox potentials confirm these trends with +200 mV (**8a**) and +750 mV for **9** versus Ag/AgCl (Table 1).

Given the relevance of a synthon for systematic Re^{II} chemistry, these few examples indicate the power of complex **2** as a convenient starting material. Reactions of **2** are not limited by aromatic amine ligands or cyclic thioethers but may extend to a wide variety of complexes with other ligand types of interest in, for example, catalysis. Table 1 summarizes some relevant analytical data for all complexes presented herein. The X-ray structures for the Re^{II} complexes **5** and **7** could be elucidated, and ORTEP presentations are given in Figure 6. Crystallographic information is given in the Supporting Information, while Tables 2 and 3 list crystallographic details.

In order to compare spectroscopic and structural data of the *cis*-$[Re^{II}(CO)_2]^{2+}$ and the *cis*-$[Re^{I}CO)_2]^+$ cores of two identical complexes, the Re^I analogue of **5**, (Et_4N)-$[Re^IBr_2(Im)_2(CO)_2]$ (**5a**), was synthesized by the reduction of **1** with an excess of TDAE and in the presence of large amounts of imidazole. The X-ray structure of **5a** is given in Figure 7. The higher oxidation state of **5** as compared to **5a** depletes the electron density at the metal center, thereby inducing substantially shorter bond lengths to the metal center for both the imidazole and the bromide ligands (by 0.05 and 0.08 Å, respectively). Since π-backbonding weakens, Re−C bond lengths to the CO ligand become longer in **5** (by 0.06 Å), and ν_{CO} in the IR spectra are shifted to higher wavenumbers (Table 1).

With the exception of **3**, all complexes derived from **2** are stable in solution under aerobic conditions. Compounds **4**, **6**, and **7** showed similar electronic spectra with a λ_{max} centered at 425 nm, while **5** showed an electronic absorption at 418 nm.

Table 2. Crystallographic Data for Compounds **3**−**9**

compound	**3**	**4**	**5**	**5a**	**7**	**9**
formula	$C_{20}H_{43}Br_4N_3O_2Re$	$C_{12}H_{10}Br_2N_2O_2Re$	$C_8H_8Br_2N_4O_2Re$	$C_{16}H_{28}Br_2N_5O_2Re$	$C_{14}H_8Br_2N_2O_2Re$	$C_8H_{12}BrO_2ReS_3$
fw	863.41	560.24	538.20	668.45	582.24	502.47
T, K	183(2)	183(2)	183(2)	183(2)	183(2)	183(2)
space group	$P2_1/n$	$C2/c$	$C2/c$	$P2_1/n$	$P\overline{1}$	$P2_1/n$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic	monoclinic
Z	4	4	4	4	2	4
a, Å	8.90790(10)	7.5498(1)	7.33620(10)	8.0465(5)	6.66422(18)	7.61890(10)
b, Å	13.8634(2)	14.6102(2)	14.13710(10)	18.4213(10)	9.3217(3)	12.5358(2)
c, Å	23.8045(3	12.9991(2)	12.7196(2)	14.7645(11)	12.6849(3)	13.4804(2)
α, deg	90	90	90	90	108.991(3)	90
β, deg	95.3090(12)	91.924(1)	90.1415(12)	99.161(8)	98.681(2)	104.7232(16)
γ, deg	90	90	90	90	93.262(2)	90
V, Å^3	2927.10(6)	1433.05(4)	1319.18(3)	2160.6(2)	731.83(3)	1245.22(3)
d_{calcd}, g/cm^3	1.959	2.597	2.710	2.055	2.642	2.680
R1^a, (wR2)^a	0.0470, 0.1236	0.0252, 0.0603	0.0161, 0.0372	0.0501, 0.1330	0.0340, 0.0835	0.0184, 0.0535
largest diff. peak/hole (e Å^{-3})	3.337 and −2.863	2.786 and −1.410	0.612 and −0.954	1.943 and −1.551	1.917 and −1.776	0.528 and −0.869

[a] $[I > 2\sigma(I)]$.

Table 3. Selected Bond Lengths [Å] and Bond Angles [deg] for Compounds **3**−**9**

bonds	**3**	**4**	**5**	**5a**	**7**	**9**
Re(1)−C(1)	1.904(8)	1.971(5)	1.929(3)	1.849(8)	1.971(7)	1.918(5)
Re(1)−C(2)	1.970(11)			1.891(9)	2.009(9)	1.892(5)
Re(1)−Br(1)	2.5365(9)	2.5187(4)	2.5258(3)	2.6054(8)	2.4961(8)	2.6147(5)
Re(1)−Br(2)	2.5866(9)			2.6129(8)	2.5339(7)	
Re(1)−Br(3)	2.5300(9)					
C(1)−O(1)	1.145(10)	1.074(6)	1.131(3)	1.185(10)	1.106(8)	1.143(5)
C(2)−O(2)	1.065(12)			1.157(10)	0.993(9)	1.164(5)
Re(1)−N(1)^a	2.168(7)	2.208(3)	2.1764(19)	2.231(5)	2.169(5)	2.4667(11)
Re(1)−N(2)^a				2.226(6)	2.173(5)	2.3517(10)
Re(1)−N(3)^a						2.4515(11)
angles	**3**	**4**^{b}	**5**^{b}	**5a**	**7**	**9**
C(1)−Re(1)−C(2)	84.0(4)	86.2(2)	83.89(16)	86.9(3)	87.1(3)	88.81(18)
C(1)−Re(1)−Br(1)	94.7(2)	89.21(12)	91.52(8)	90.1(2)	92.18(19)	94.86(12)
C(1)−Re(1)−Br(2)	90.7(3)	94.12(12)	92.96(8)	98.5(2)	88.96(19)	
Br(1)−Re(1)−Br(2)	90.23(3)	175.44(2)	173.97(1)	167.71(3)	173.05(2)	
Br(1)−Re(1)−Br(3)	171.03(3)					
C(1)−Re(1)−N(1)^a	179.1(3)	176.07(15)	177.96(10)	177.1(3)	174.7(2)	95.10(13)
C(1)−Re(1)−N(2)^a		94.74(15)	94.83(10)	93.5(3)	100.4(2)	93.28(13)
N(1)−Re(1)−N(2)^a		84.60(18)	86.50(10)	87.0(2)	75.64(19)	85.07(4)
Br(1)−Re(1)−N(1)^a	85.88(19)	89.71(9)	86.95(6)	87.02(15)	90.95(13)	84.57(3)
Br(1)−Re(1)−N(2)^a		86.92(9)	88.65(6)	86.77(16)	85.97(14)	167.36(3)

[a] For structure **9**, N(1), N(2), and N(3) refer to S(1), S(2), and S(3), respectively. [b] C(2), N(2), and Br(2) refer to symmetry-generated atoms.

If exposed to O_2, the UV/vis spectra of **4**−**7** did not change over a period of 2 days. Spectroscopic data of **4**, **6**, and **7** correlated well with electrochemical data, which all showed a fully reversible one-electron process between −74 and −80 mV referring to the $Re^{II} \rightarrow Re^{I}$ reduction. Under similar conditions, **5** decomposed and showed no appreciable signal.

Conclusion

The synthesis, properties, and ligand substitution reactions with the new, paramagnetic mononuclear 17-electron Re^{II} complex $[Re^{II}Br_4(CO)_2]^{2-}$ are described. The complex $[Re^{II}Br_4(CO)_2]^{2-}$ is convenient as a substitution labile synthon for the preparation of a wide variety of compounds comprising the *cis*-$[Re^{II}(CO)_2]^{2+}$ or *cis*-$[Re^{I}(CO)_2]^{2+}$ core. In its relevance, this synthon stimulates Re^{II} chemistry, which is largely underdeveloped in comparison to complexes of the other oxidation states with this element. The unexpected aerobic stability and well-behaved chemistry of complexes derived from **2** implies reactions leading to novel complexes relevant for applications in medicinal chemistry. Complex **2** may also be useful as a building block for paramagnetic clusters for, for example, SMM. Further fundamental aspects of the chemistry of **2** in water are currently being explored.

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Supporting Information Available: The CIF files are included. This material is available free of charge via the Internet at http://pubs.acs.org.