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Abstract: The oxidation of [Re(6-C₁₀H₈)₂]⁺ with AgI in acetonitrile yields [Re(NCCH₃)₆]²⁺. This fully solvated ReII compound was characterized by spectroscopic methods and X-ray structure analyses. We show that [Re(NCCH₃)₆]²⁺ acts as a precursor complex for a variety of substitution reactions. Treatment with monodentate triphenylphosphine (PPh₃) and bidentate 1,2-bis(diphenylphosphino)ethane (dppe) yields the complexes [trans-Re(PPh₃)₂(NCCH₃)₄]²⁺ and [trans-Re(dppe)₂(NCCH₃)₂]⁺, respectively. [trans-Re(dppe)₂(NCCH₃)₂]⁺ is oxidized under mild conditions by AgI to its ReII analogue [trans-Re(dppe)₂(NCCH₃)₂]²⁺. Reactions of [Re(NCCH₃)₆]²⁺ with a halide mixture consisting of NaX and AgX (X = Cl, I) result in the formation of the corresponding ReIII complexes [trans-ReX₂(NCCH₃)₄]⁺. [trans-ReBr₂(NCCH₃)₄]⁺ can be obtained directly from [Re(6-C₁₀H₈)₂]⁺ by oxidation with FeBr₃ in acetonitrile. The title compound is thus a convenient starting material for ReII and ReIII complexes by simple solvent exchange, which are otherwise difficult to access.

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Fully Solvated, Monomeric Re^{II} Complexes: Insights into the Chemistry of [Re(NCCH₃)₆]²⁺

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Rhenium, Precursor, Coordination Chemistry, Acetonitrile Complexes, Bis-arene Complexes.

ABSTRACT: The oxidation of [Re(η⁶-C₁₀H₈)₂]⁺ with Ag^I in acetonitrile yields [Re(NCCH₃)₆]²⁺. This fully solvated Re^{II} compound was characterized by spectroscopic methods and X-ray structure analyses. We show that [Re(NCCH₃)₆]²⁺ acts as a precursor complex for a variety of substitution reactions. Treatment with monodentate triphenyl phosphine (PPh₃) and bidentate 1,2-bis(diphenylphosphino)ethane (dppe) yields the complexes [trans-Re(PPh₃)₂(NCCH₃)₄]²⁺ and [trans-Re(dppe)₂(NCCH₃)₂]⁺, respectively. [trans-Re(dppe)₂(NCCH₃)₂]⁺ is oxidized under mild conditions by Ag^I to its Re^{III} analogue [trans-Re(dppe)₂(NCCH₃)₂]³⁺. Reactions of [Re(NCCH₃)₆]²⁺ with a halide mixture consisting of NaX and AgX (X = Cl, I) results in the formation of the corresponding Re^{III} complexes [trans-ReX₂(NCCH₃)₄]⁺. [trans-ReBr₂(NCCH₃)₄]⁺ can be obtained directly from [Re(η⁶-C₁₀H₈)₂]⁺ by oxidation with FeBr₃ in acetonitrile. The title compound is thus a convenient starting material for Re^{II} and Re^{III} complexes by simple solvent exchange, which are otherwise difficult to access.

Introduction

Group 7 transition metals rhenium and technetium show a rich coordination chemistry, including all possible oxidation states. The most prominent oxidation state is +V, which is stabilized by π-donors such as oxo or nitrido ligands.^{1,2} Over the past years, the number of +I complexes increased significantly due to the development of suitable precursor complexes comprising the tricarbonyl cores (*fac*-M(CO)₃]⁺, M = Re, ⁹⁹Tc).^{3–5} A relatively rare oxidation state of Re and Tc is +II. Until today, the number of Re^{II} and Tc^{II} complexes is limited e.g. due to a lack of stable but reactive precursor complexes, e.g. fully solvated Re^{II} species. Re^{II} and ⁹⁹Tc^{II} complexes are generally formed by oxidation of a M^I or reduction of a higher valent complex (mostly M^{III}).^{6–10} A homoleptic M^{II} precursor would therefore significantly support the exploration of complexes with the metal center in the oxidation state +II, as found for the +I state with [*fac*-MX₃(CO)₃]²⁺ (M = Re, X = Br; M = ⁹⁹Tc, X = Cl).

Fully solvated metal centers are appropriate precursors. They consist of a metal core with one specific type of ligands, ideally solvent molecules. Solvent ligands are easily exchanged while still stabilizing a particular oxidation state. Hence, all coordination sites are accessible for substitution. The hexaqua-complexes of the first-row transition metals such as [Cr(H₂O)₆]³⁺ and [Fe(H₂O)₆]²⁺ are good examples but they do in general not exist for 4d and 5d elements. Some fully solvated Re^{II} or Tc^{II} complexes exist though with acetonitrile as ligand. Bernstein and Dunbar reported 1992 the solvolysis of the dimeric Re^{II} complex [Re₂Cl₄(PR₃)₄] (R = *n*-propyl) giving the dinuclear complex [Re₂(NCCH₃)₁₀]⁴⁺.¹¹ The homologous ⁹⁹Tc complex was reported three years later by Sattelberger *et al.*¹² They also showed that the metal-metal triple bond in [⁹⁹Tc₂(NCCH₃)₁₀]⁴⁺

is photochemically cleaved in acetonitrile, which yielded monomeric [⁹⁹Tc(NCCH₃)₆]²⁺ in nearly quantitative yield.¹³ This complex is a fully solvated and highly useful Tc^{II} species, however, any attempt to prepare the rhenium homologue along the same path failed.

We now present the synthesis and full characterization of [Re(NCCH₃)₆]²⁺, prepared from the Re^I sandwich complex [Re(η⁶-C₁₀H₈)₂]⁺. In addition we illustrate the first reactivity studies of [Re(NCCH₃)₆]²⁺ involving various substitution reactions, the products of which were fully characterized as well.

Results and Discussion

In the past few years, we developed synthetic strategies towards new [Re(η⁶-C₆R₆)₂]⁺ and [^{99(m)}Tc(η⁶-C₆R₆)₂]⁺ sandwich complexes (see SI Scheme S1).^{14–18} Similar to other [M(η⁶-C₁₀H₈)₂] bis-naphthalene complexes (M = Cr, Mo),^{19–21} coordination of the naphthalene ligands to the Re^I center is comparably weak in [Re(η⁶-C₁₀H₈)₂]⁺ ([1]⁺). Ligand substitution reactions are therefore possible with strong nucleophiles such as PR₃, P(OR)₃, CNR or arene metathesis.^{16,18} Complex [1]⁺ also shows useful redox reactivity; when [1]⁺ was heated at 70°C for 7h in acetonitrile in presence of AgPF₆ or AgOTf (OTf = SO₃CF₃), [Re(NCCH₃)₆]²⁺ ([2]²⁺) formed in 94 % yield besides the formation of elemental Ag and liberation of naphthalene (Scheme 1). The reaction can also be performed at room temperature but requires 4 days for completion. Mechanistically, this reaction is not trivial. According to their redox potentials, AgOTf in CH₃CN (E_{1/2} = – 0.60 V vs. Fc⁺/Fc⁰, see supporting information (SI)) cannot oxidize [1]⁺ (E_{1/2} = + 0.77 V vs. Fc⁺/Fc⁰, see SI) to give [2]²⁺ (for electrochemical details see Experimental Section). In addition, hypothetical [1]²⁺ does not

seem to be the precursor for $[2]^{2+}$ as cyclic voltammetry experiments in CH_3CN indicated no formation of $[2]^{2+}$ after the irreversible oxidation of $[1]^+$ (for details see SI Figure S13). Mechanistically, concerted ring slippage of one naphthalene to η^4 -coordination and coordination of L (e.g. CH_3CN) in a prior-equilibrium situation could lead to a complex that may be oxidized by Ag^I . Such an intermediate has already been proposed by Kündig *et al.* for substitution reactions with $[\text{Cr}(\eta^6\text{-C}_{10}\text{H}_8)_2]^+$.¹⁹ This mechanism is corroborated by the fact that the analogous reaction with $[\text{Re}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ does not yield $[2]^{2+}$ although its redox potential in CH_3CN ($E_{1/2} = +0.89$ V vs. $\text{Fc}^+/\text{Fc}^\circ$, see SI Figure S14) is in a similar range as for $[1]^+$. Ring slippage for benzene is more difficult than for naphthalene and does not occur easily.^{19,22}

Figure 1. Schematic depiction of the energy levels of the highest occupied molecular orbitals (HOMO) of $[1]^+$ and different CH_3CN adducts of $[1]^+$. HOMO energy levels were calculated by density functional theory (DFT). Structures from left to right: $[1]^+$, $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\eta^4\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)]^+$, $[\text{Re}(\eta^4\text{-C}_{10}\text{H}_8)_2(\text{NCCH}_3)_2]^+$, and $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)_3]^+$.

To further elucidate the mechanism for the formation of $[2]^{2+}$, computational studies by DFT of $[1]^+$ and different CH_3CN adducts of $[1]^+$ were conducted. These CH_3CN adducts have not yet been detected experimentally, but are potential intermediates for the Ag^I -mediated oxidation of $[1]^+$ in CH_3CN . Of special interest are the energy levels of the highest occupied molecular orbital (HOMO) of $[1]^+$, $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\eta^4\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)]^+$, $[\text{Re}(\eta^4\text{-C}_{10}\text{H}_8)_2(\text{NCCH}_3)_2]^+$, and $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)_3]^+$ as the to be transferred electron originates from one of those orbitals (Figure 1, results for additional CH_3CN adducts as well as a depiction of the potential energy surface of the CH_3CN addition reactions can be found in SI Figures S18 and S19). In case of $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\eta^4\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)]^+$ the perturbation of the bis-arene system results in the destabilization of the HOMO by +0.25 eV. Computation of $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\eta^2\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)_2]^+$ was not feasible as the structure always converted back to the CH_3CN monoadduct during geometry optimization. A computable CH_3CN diadduct was $[\text{Re}(\eta^4\text{-C}_{10}\text{H}_8)_2(\text{NCCH}_3)_2]^+$, whose HOMO was energetically more stable than the monoadduct albeit still destabilized by +0.12 eV as compared to the HOMO of $[1]^+$. The HOMO of the piano stool compound $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)(\text{NCCH}_3)_3]^+$ is the most destabilized of the series (+0.71 eV compared to $[1]^+$). The general trend of these findings suggests that perturbation of the bis-naphthalene system leads to a destabilization of the HOMO and thus increases the reducing power of the

CH_3CN adducts compared to $[1]^+$. These results corroborate our mechanistical proposal that the Ag^I -mediated oxidation does not directly occur from $[1]^+$ but instead from a more energetically destabilized CH_3CN adduct of $[1]^+$, which ultimately results in the formation of $[2]^{2+}$.

X-Ray diffraction analysis of $[2](\text{OTf})_2$ reveals a slightly distorted octahedral geometry around the Re^{II} center (Figure 2). This is indicated by the N-Re-N angles, which are in the range of $86.6(1)^\circ$ to $93.4(1)^\circ$. The Re-N mean bond distance (2.053(3) Å) is in a similar range as for the corresponding complex $[\text{}^{99}\text{Tc}(\text{NCCH}_3)_6]^{2+}$ (2.062(4) Å).¹³

Figure 2. Ellipsoid displacement representation of the cation in $[2](\text{OTf})_2$ (ellipsoids drawn at 50 % probability). Only half of the asymmetric unit is depicted. All structural features of both species in the asymmetric unit are similar. Hydrogen atoms and triflate anions were omitted for clarity. Selected bond lengths [Å]: Re(1)-N(1) 2.059(3), Re(1)-N(2) 2.054(4), Re(1)-N(3) 2.054(3), Re(1)-N(4) 2.056(3), Re(1)-N(5) 2.058(4), Re(1)-N(6) 2.046(3).

The ^1H NMR spectrum of $[2]^{2+}$ in d^3 -acetonitrile shows a broad signal at $\delta = 63.6$ ppm ($\Delta = 307$ Hz). The signal of the homologous $[\text{}^{99}\text{Tc}(\text{NCCH}_3)_6]^{2+}$ is reported at $\delta = 70.3$ ppm ($\Delta_{1/2} = 110$ Hz).¹³ The IR spectrum of $[2]^{2+}$ shows only one $\nu(\text{CN})$ absorption corresponding to the coordinated acetonitrile ligands at 2257 cm^{-1} . This is in contrast to $[\text{}^{99}\text{Tc}(\text{NCCH}_3)_6]^{2+}$ (2319 cm^{-1} and 2280 cm^{-1}) and various first row transition metal analogues, which have two absorptions.^{13,23} In cyclic voltammetry, $[2](\text{PF}_6)_2$ exhibits a reversible reduction at $E_{1/2} = -1.00$ V vs. $\text{Fc}^+/\text{Fc}^\circ$, which is assigned to the $\text{Re}^{\text{II}} / \text{Re}^{\text{I}}$ redox couple. A reversible oxidation wave at $E_{1/2} = +0.24$ V vs. $\text{Fc}^+/\text{Fc}^\circ$ belongs to the $\text{Re}^{\text{II}} / \text{Re}^{\text{III}}$ couple (Figure 3). The analogous redox couples for $[\text{}^{99}\text{Tc}(\text{NCCH}_3)_6]^{2+}$ were reported at $E_{1/2} = -0.81$ V ($\text{Tc}^{\text{II}} / \text{Tc}^{\text{I}}$) and at $E_{1/2} = +0.72$ V ($\text{Tc}^{\text{II}} / \text{Tc}^{\text{III}}$), both vs. $\text{Fc}^+/\text{Fc}^\circ$.¹³ Following general trends in triads, the rhenium is more difficult to reduce but easier to oxidize than its higher homologue Tc.

Figure 3. Cyclic voltammogram of $[2](PF_6)_2$ depicting its reduction (a) and its oxidation (b). Conditions: CH_3CN ($NBu_4(PF_6)$ (0.1 M) as electrolyte). Concentration of $[2]^{2+} = 1.0$ mM.

As a solid $[2](OTf)_2$ is stable at ambient conditions. For storage over longer periods of time requires exclusion of O_2 . While $[2](PF_6)_2$ is only soluble in CH_3CN , $[2](OTf)_2$ can be dissolved in various solvents such as CH_3CN , MeOH, DMSO, and acetone. In solution, $[2]^{2+}$ is very prone to decomposition when exposed to oxygen. A 1H NMR experiment of $[2](OTf)_2$ in d^3 -acetonitrile and under air showed that decomposition is a rather slow process with $k \approx 3.2 \cdot 10^{-4} s^{-1} \pm 4.8 \cdot 10^{-5} s^{-1}$ for its disappearance (SI Figure S2). The actual acetonitrile self-exchange of $[2]^{2+}$ (monitored by 1H NMR spectroscopy in d^3 -acetonitrile under N_2) is an even slower process, which is still under investigation.

Scheme 1. Formation of $[2]^{2+}$ by Ag^I -mediated oxidation of $[1]^+$. Substitution reactions of $[2]^{2+}$ with the phosphines PPh_3 and dppe yield the complexes $[3]^{2+}$ and $[4]^+$.

Substitution reactions of $[2](OTf)_2$ in CH_3CN are generally very slow at room temperature. A reaction with 10eq. of triphenylphosphine (PPh_3) at $130^\circ C$ gave $[trans-Re(PPh_3)_2(CH_3CN)_4](OTf)_2$ ($[3](OTf)_2$) in 64 % yield (Scheme 1). The analogous ^{99}Tc complex $[trans-^{99}Tc(PPh_3)_2(CH_3CN)_4](PF_6)_2$ has been synthesized by Freiberg *et al.* in 2002 along another route, namely by reduction of $[TcCl_4(PPh_3)]$ with elemental Zn in CH_3CN .²⁴ Besides the up-field shifted signal for the remaining CH_3CN ligands ($\delta = -0.57$ ppm for $[3](OTf)_2$ vs. $\delta = +3.76$ ppm for the ^{99}Tc analogue), the 1H NMR spectra of the two compounds are very similar. Furthermore, X-ray diffraction analysis (Figure 4) displays similar structural features of these two homologues. The Re-N bond lengths are between 2.0453(16) Å – 2.0504(16) Å, in the same range as found for the ^{99}Tc analogue (2.0439(5) Å –

2.0478(5) Å). The same applies for the Re-P and ^{99}Tc -P bond lengths (Re-P: 2.4287(5) Å and 2.4294(5)) which are comparable for both homologues (^{99}Tc -P: 2.4414(14) Å).

Figure 4. Ellipsoid displacement representation of a) the cation in $[3](OTf)_2$ and b) the cation in the structure $[4](OTf)$ (ellipsoids drawn at 50 % probability). For a) only half of the asymmetric unit is depicted. All structural features of both species in the asymmetric unit are similar. Hydrogen atoms and triflate anions were omitted for clarity. Selected bond lengths [Å]: a) Re(1)-P(1) 2.4294(5), Re(1)-N(1) 2.0504(16), Re(1)-N(2) 2.0453(16); b) Re(1)-P(1) 2.3916(5), Re(1)-P(2) 2.4015(5), Re(1)-N(1) 2.0529(18).

The substitution reaction with 10eq. of 1,2-bis(diphenylphosphino)ethane (dppe) resulted in the formation of the highly oxygen and moisture sensitive $[trans-Re^I(dppe)_2(CH_3CN)_2](OTf)$ ($[4](OTf)$) in 64 % yield (Scheme 1). The metal center is reduced to the oxidation state +I. Avoiding the reduction by reacting $[2](OTf)_2$ with only two equivalents of dppe resulted again in the formation of $[4](OTf)$. A synthesis for $[4]^+$ had already been reported in literature by Walton *et al.* in 1986. Deprotonation and phosphine exchange of the Re^{III} hydride species $[ReH(NCCH_3)_4(PPh_3)_2](BF_4)_2$ with dppe gave $[4]BF_4$.²⁵ X-Ray diffraction analysis of the so far unreported structure of the cation $[4]^+$ (Figure 4) displays similar structural features as found with the nitrile containing cation in the complex double salt $[trans-Re(dppe)_2(NCC_6H_4Me-4)_2][trans-Re(dppe)_2F_2](BF_4)_2$. The Re-N bond of $[4]OTf$ has a length of 2.0529(18) Å, which is slightly shorter than the one reported for the cation $[trans-Re(dppe)_2(NCC_6H_4Me-4)_2]^+$ (2.063(7) Å).²⁶

Scheme 2. Formation of the Re^{II} complex $[4](OTf)_2$ by $AgOTf$ -mediated oxidation of the Re^I complex $[4]OTf$ in CH_3CN .

Besides the expected m/z signals, HR-ESI-MS of pure samples of $[4]OTf$ always contain m/z signals belonging to its Re^{II} -analogue $[4]^{2+}$. Accordingly, $[4]OTf$ was treated with $AgOTf$ and oxidized rapidly at $25^\circ C$ in CH_3CN to give its Re^{II} analogue $[trans-Re(dppe)_2(CH_3CN)_2](OTf)_2$ ($[4](OTf)_2$) in 98 % yield (Scheme 2). X-Ray diffraction analysis showed that the oxidation led to an elongation of the Re-P bonds (2.4429(9) Å and 2.4602(8) Å for $[4](OTf)_2$ vs. 2.3916(5) Å and 2.4015(5) Å for $[4]OTf$) and a shortening of the Re-N bonds (2.045(3) Å for

[4](OTf)₂ vs. 2.0529(18) Å for [4]OTf). In contrast to [4]OTf, the ¹H NMR spectrum of [4](OTf)₂ only displays two distinct signals for the aromatic protons. The signal for the methyl groups of the CH₃CN ligands are strongly upfield shifted (δ = −0.99 ppm for [4](OTf)₂ vs. δ = +1.92 ppm for [4]OTf, see SI Figures S4 and S9). It should be mentioned that the combined integrals of the aromatic ¹H signals compared to the methylene and acetonitrile ¹H signals are about 50 % smaller than expected. This discrepancy is likely due to the special parameters used for the paramagnetic ¹H NMR experiment (see Experimental Section). Due to different T₁-relaxation times of chemically different ¹H nuclei, the areas below the paramagnetic NMR signals are not necessarily depicting the complex's inherent proton ratios correctly.²⁷

The reaction of [2](OTf)₂ with two eq. of alkyl ammonium halides (NR₄X: X = Cl, R₄ = Et₃Bz; X = Br, R = C₁₂H₂₅; X = I, R = Bu) in CH₃CN led to the formation of the Re^{III} complexes [*trans*-ReX₂(NCCH₃)₄]⁺ ([5]⁺ for X = Cl; [6]⁺ for X = Br; [7]⁺ for X = I). Residual oxygen from air might be responsible for the oxidation. Based on cyclic voltammetry the in situ formed Re^{II} dihalides are strong reductants. The cyclic voltammogram of [6]PF₆ shows a reversible reduction at E_{1/2} = −0.85 V vs. Fc⁺/Fc⁰ (SI Figure S17). Making use of this electrochemical information, improvement of the Re^{III} dihalide syntheses was achieved by exchanging the organic ammonium halides with a mixture of AgX (1 eq.; oxidizing agent and halide source) and NaX (3–6 eq.; X = Cl, Br, I). Heating of [2](OTf)₂ in CH₃CN with the correct halide mixture, anion exchange with sodium tetraphenylborate (NaBPh₄), and washing with H₂O led to the formation of the complexes [5]BPh₄ and [7]BPh₄ in 87 % and 48 % yield, respectively (Scheme 3). The reaction with AgBr and NaBr was less successful and only gave [6]⁺ in minor amounts (based on ¹H NMR and MS analysis).

Scheme 3. Synthetic pathways for the synthesis of Re^{III} halides of the [*trans*-ReX₂(NCCH₃)₄]⁺ type (X = Cl, Br, and I).

An improved synthesis for [6]⁺ was found when oxidizing [1]⁺ with FeBr₃. Heating a mixture of [1]⁺ and two eq. of FeBr₃ in acetonitrile for 2 h at 80 °C leads to product formation in 55 % yield (Scheme 3). An intermediate Re^{II} species was not observed even with one eq. of FeBr₃ only. In that case, only incomplete consumption of [1]⁺ and formation of [6]⁺ was detected. If the mechanism consists of two consecutive one electron transfer processes, this observation indicates that the second electron transfer from a potential Re^{II} intermediate occurs at a much faster rate than the first oxidation. Similar to the for-

mation of [2]²⁺, the redox potential of FeBr₃ is too low for directly oxidizing [1]⁺ (Fe^{III}/Fe^{II} at E_{1/2} = −0.16 V vs. Fc⁺/Fc⁰ in CH₃CN, see SI). In contrast to oxidations with AgX (X = OTf or PF₆), [Re(η⁶-C₆H₆)₂]⁺ can be oxidized to [6]⁺ with FeBr₃, although not in quantitative yields. This is a striking difference to the reaction of [Re(η⁶-C₆H₆)₂]⁺ with Ag^I, which showed no formation of [2]²⁺ at all. Hence, it can be concluded that the formations of [2]²⁺ and [6]⁺ might follow different reaction mechanisms. In case of the FeBr₃ induced oxidation, an internal electron-transfer via a Fe-Br-Re bridge cannot be excluded. The analogous reaction of [1]⁺ in CH₃CN with FeCl₃ gave [5]⁺ though in much poorer yield (17 %, Scheme 3).

¹H NMR spectra assess the trans-arrangements of the halides in all three complexes. The spectra consist of only one narrow singlet for the coordinated acetonitrile ligands (δ = 65.5 ppm [5]⁺; δ = 60.0 ppm [6]⁺; δ = 54.7 ppm [7]⁺). The crystal structure of [5](ReCl₆)_{1/2} is known in literature but further spectroscopic analyses have not been reported.²⁸ The reported crystal structure aligns very well with the values found for [5]BPh₄. As expected X-ray diffraction analysis of [5]BPh₄, [6]PF₆, and [7]BPh₄ (Figure 5) showed that the structures of all three complexes are very similar. The Re-N bonds are nearly identical (2.0611(16) Å and 2.0612(16) Å for [5]BPh₄; 2.062(2) Å for [6]PF₆; 2.057(3) Å and 2.058(3) Å for [7]BPh₄), while the Re-X bonds (X = Cl, Br, I) elongate in accordance to the respective halogen atom sizes (2.3339(5) Å for [5]BPh₄; 2.4729(4) Å for [6]PF₆; 2.6643(2) Å for [7]BPh₄).

Figure 5. Ellipsoid displacement representation of a) the cation in [6]PF₆ and b) the cation in the structure [7]BPh₄ (ellipsoids drawn at 50 % probability level). Hydrogen atoms and a) hexafluorophosphate and b) tetraphenylborate counter-ion are omitted for clarity. Selected bond lengths [Å]: a) Re(1)-Br(1) 2.4729(4), Re(1)-N(1) 2.062(2); b) Re(1)-I(1) 2.6643(2), Re(1)-N(1) 2.057(3), Re(1)-N(2) 2.058(3).

Conclusions

Fully solvated Re^{II} complexes such as the title compound are very suitable precursors. Coordinated solvent exchange reactions on Re^{II} allow for directed syntheses of new complexes in the +II or neighboring oxidations states. [Re(NCCH₃)₆]²⁺ is a prototypical and exclusive example.

First insights into stabilities and reactivities of this complex disclosed though an unexpected stability and inertness against substitution reactions. The substitution products presented in here are prone to oxidation and controlling the redox chemistry of this reactions is challenging. However, this stable [Re(NCCH₃)₆]²⁺ complex is a first example of a new group of complexes, which will path the way for the synthesis of novel Re^{II} complexes in the future. Handling of and substitution reactions with [Re(NCCH₃)₆]²⁺ can be performed with standard Schlenk techniques and do not necessarily require gloveboxes.

Experimental Section

General: All reactions were performed under N₂ atmosphere using standard Schlenk techniques. NMR sample preparations and crystallizations (unless otherwise stated) were performed under N₂ atmosphere in a MBRAUN Labmaster DP glovebox. Reagent grade chemicals from Sigma Aldrich Chemie GmbH, Fluka Chemie AG, and Merck KGaA were used without further purification. NMR solvents (CD₃CN and CD₂Cl₂) were purchased from Cambridge Isotopes Laboratories, Inc. NMR solvents were used without further purification except for the NMR measurements of [4](OTf) and [4](OTf)₂ for which the solvents were additionally dried by molecular sieves (4 Å, 20 wt%). Dry diethyl ether (Et₂O) was obtained from distillation over sodium. Dry toluene and dry CH₃CN were obtained by chromatographical separation on a MB SPS system from MBRAUN. Microwave reactions were carried out in a Biotage Initiator microwave. Freeze-drying carried out with a Christ Alpha 2-4 LD plus lyophilizer. [1]⁺ was produced following a literature procedure.¹⁶ ¹H and ³¹P{¹H} NMR spectra were recorded on a Bruker AV-400 400 MHz spectrometer. ¹³C NMR spectra were proton decoupled recorded and measured on a Bruker DRX-500 500 MHz spectrometer. ¹H and ¹³C chemical shifts are reported relative to residual protio solvent resonances.²⁹ ³¹P chemical shifts are reported relative to an 85 % H₃PO₄ external standard (δ 0). Special parameters for paramagnetic ¹H NMR measurements: time of delay = 0.1 s, acquisition time = 0.1 s. FT-IR spectra were measured as neat samples on a Perkin Elmer Spectrum Two spectrophotometer. High-resolution electrospray mass spectra (HR-ESI-MS) were recorded on a maXis QTOF-MS instrument (Bruker Daltonics GmbH, Bremen, Germany). The samples were dissolved in CH₃CN at a concentration of ca. 50 µg/mL and analyzed via continuous flow injection (2 µL/min). The mass spectrometer was operated in the positive (and negative) electrospray ionization mode at 4'000 V (-4'000 V) capillary voltage, -500 V (500 V) endplate offset, with a N₂ nebulizer pressure of 0.8 bar and dry gas flow of 4 l min⁻¹ at 180°C. Mass spectra were acquired in the mass range from m/z 50 to 2'000 at 20'000 resolution (full width at half maximum) and 1.0 Hz rate. The mass analyzer was calibrated between m/z 118 and 2721 using an Agilent ESI-L low concentration tuning mix solution (Agilent, USA) at a resolution of 20'000 and a mass accuracy below 2 ppm. All solvent used were purchased in best LC-MS qualities. Elemental analysis performed with a LECO Truespec CHNS(O)-microanalyser. Electrochemical measurements were carried out with a standard three-electrode setup of glassy carbon working electrode (i.d. = 3 mm), platinum auxiliary electrode and Ag/AgCl reference electrode. Measurements were done in acetonitrile containing NBu₄(PF₆) (0.1 M) as a conducting electrolyte. The measurements were performed first by measuring the compound alone and in a second step a small amount of [Fe(η⁵-C₅H₅)₂] was added as an internal reference. The combined sample was then remeasured under the same condition. All potentials are given vs. Fc⁺/Fc. Sweep rate = 0.1 V/s. The crystal structures of [2](OTf)₂, [3](OTf)₂, [4](OTf), [4](OTf)₂ and [6](PF₆) were obtained by single crystal X-ray diffraction analyses on a Rigaku OD Synergy (Pilatus 200K detector) instrument equipped with an Oxford liquid-nitrogen Cryostream cooler and using a single wavelength X-ray source from a micro-focus sealed X-ray tube (Cu K_α radiation, λ = 1.54184 Å). The X-ray diffraction data for the crystal structures of [5](BPh₄) and [7](BPh₄) were collected on a Rigaku OD SuperNova (Atlas area-detector) diffrac-

tometer using the Mo K_α radiation (λ = 0.71073 Å) from a micro-focus X-ray source and an Oxford Instruments Cryojet XL cooler. All experiments were carried out at low temperature (160 K). Pre-experiment, data collection, data reduction and analytical absorption correction³⁰ were performed with the program suite *CrysAlisPro*.³¹ Using *Olex2*,³² the structure was solved with the SHELXT³³ small molecule structure solution program and refined with the *SHELXL2018/3* program package³⁴ by full-matrix least-squares minimization on F². The data collections and structure refinement parameters are summarized in Tables S1 – S4. CCDC 2032159 for [2](OTf)₂, 2032158 for [3](OTf)₂, 2032160 for [4](OTf), 2032157 for [4](OTf)₂, 2032162 for [5](BPh₄), 2032163 for [6](PF₆) and 2032161 for [7](BPh₄) contain the supplementary crystallographic data for these compounds, and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[Re(NCCH₃)₆](OTf)₂ ([2](OTf)₂). In a microwave tube [1](OTf) (110 mg, 0.19 mmol) and AgOTf (49.2 mg, 0.19 mmol) were flushed with N₂ before dry CH₃CN (7 mL) was added giving in a red solution. The tube was heated in a microwave oven for 7 h at 70°C resulting in orange solution and grey precipitate. The suspension was filtered through a syringe filter into a second microwave tube, which had already been flushed with N₂. Solid residuals were extracted with dry CH₃CN (1.5 mL) and filtered into the new vial. Solvent was reduced with a stream of N₂ to approx. 0.5 mL which caused some precipitation. Dry toluene (4 mL) was added and the suspension centrifuged. The yellowish supernatant was decanted, the grey reddish precipitate was washed with additional dry toluene (2.5 mL), and dried with a stream of N₂, giving [2](OTf)₂ (127 mg, 0.17 mmol) in 94 % yield as a pinkish-grey solid. Crystals suitable for X-Ray diffraction analysis were obtained from vapor diffusion CH₃CN / Et₂O.

¹H NMR (d³-acetonitrile, 400 MHz): 63.8 (br, Δ = 307 Hz). HR-ESI-MS: C₁₃H₁₈O₃N₆F₃ReS⁺ [2](OTf)⁺: calculated 582.06652, found 582.06651. IR: 2989w, 2929w, 2257m, 1420w, 1369w, 1261s, 1224s, 1141s, 1028s, 943m. Anal. calc. for C₁₄H₁₈F₆N₆O₆ReS₂: C 23.01, H 2.48, N 11.50; found: C 22.70, H 2.18, N 11.53.

[trans-Re(PPh₃)₂(CH₃CN)₄](OTf)₂ ([3](OTf)₂). In a 5 mL microwave tube [2](OTf)₂ (4.8 mg, 6.6 µmol) and PPh₃ (18.6 mg, 71 µmol) were flushed with N₂. Dry CH₃CN (1.5 mL) was added and the slightly yellowish solution was heated in a microwave oven to 130°C for 3.5 h (2 h + 1.5 h) leading to an intensely yellow solution. Solvent was concentrated with a stream of N₂ to approx. 0.2 mL and dry Et₂O (4 mL) was added, leading to a pink precipitate. The yellow supernatant was decanted after centrifugation and the precipitate was washed with additional dry Et₂O (2 mL) and dried with a stream of N₂, giving [3](OTf)₂ (4.9 mg, 4.2 µmol) as a light brownish solid in 64 % yield. Crystals suitable for X-Ray diffraction analysis were obtained from vapor diffusion experiments (CH₃CN / Et₂O).

¹H NMR (d³-acetonitrile, 400 MHz): 6.61 (s, 10 H), 5.19 (s, 20 H), -0.57 (br, Δ_{1/2} = 119 Hz, 12 H, 4 x CH₃CN). HR-ESI-MS: C₄₄H₄₂N₄P₂Re²⁺ [3]²⁺: calculated 437.62156, found 437.62181; C₄₅H₄₂F₃N₄O₃P₂ReS⁺ [3]OTf⁺: calculated 1024.19570, found 1024.19549. IR: 3063w, 2977w, 2919w, 2257w, 1573w, 1482w, 1435m, 1367w, 1264s, 1224m, 1188w, 1140s, 1092m, 1029s, 999w, 949w.

[*trans*-Re(CH₃CN)₂(dppe)₂](OTf) ([4](OTf)). In a 5 mL microwave tube [2](OTf)₂ (29.2 mg, 40.0 μmol) and 1,2-bis(diphenylphosphino)ethane (dppe, 163 mg, 409 μmol) were flushed with N₂ and suspended in dry CH₃CN (4.5 mL). The suspension was heated to 130 °C for 3.5 h resulting in a violet suspension, which was concentrated with a stream of N₂ to approx. 0.5 mL. Dry Et₂O (6 mL) was added resulting in a purple precipitate. The supernatant was decanted after centrifugation and the precipitate was washed with additional dry Et₂O (4 mL). The same procedure (addition of dry Et₂O (4 mL) to a CH₃CN (0.5 mL) solution of the crude product, centrifugation and decanting of supernatant, and washing of the precipitate with dry Et₂O (2 mL)) was repeated twice to give a green solid. Finally, the green solid was dissolved in dry CH₂Cl₂ (0.5 mL) and dry Et₂O (4 mL) was added, leading to a green precipitate, which was separated from the colorless supernatant by centrifugation. This process was repeated three times, before the green solid was dried with a stream of N₂ to afford [4]OTf (31.0 mg, 25.5 μmol) in 64 % yield. Crystals suitable for X-Ray diffraction analysis were obtained from vapor diffusion experiments (CH₃CN / Et₂O).

¹H NMR (d²-dichloromethane, 500 MHz): 7.32 (t, *J* = 7.3 Hz, 8 arom. H), 7.15 (t, *J* = 7.6 Hz, 16 arom. H), 6.93 (d, *J* = 7.3 Hz, 16 arom. H), 2.43 (s, 4 x CH₂); 1.92 (br, 2 x CH₃). ¹³C NMR (d²-dichloromethane, 126 MHz): 135.7 (br, *ipso*-C), 132.6 (arom. C-H), 129.8 (arom. C-H), 128.7 (arom. C-H), 121.5 (*q*, *J* = 69.3 Hz, F₃CSO₃), 127.4 (NC), 30.7 (CH₂), 5.1 (CH₃). ³¹P NMR (d²-dichloromethane, 202 MHz): 30.1. HR-ESI-MS: C₅₆H₅₄N₂P₄Re⁺ [4]⁺: calculated, 1065.27895, found 1065.27816. IR: 3057w, 2216m, 1586w, 1483m, 1432s, 1262s, 1222m, 1147s, 1095m, 1030s, 999w, 943w, 866w, 803m.

[*trans*-Re(CH₃CN)₂(dppe)₂](OTf)₂ ([4](OTf)₂). AgOTf (2.6 mg, 10.3 μmol) dissolved in CH₃CN (1.5 mL) was added to a 2 mL microwave tube containing [4](OTf) (5.0 mg, 4.1 μmol) resulting in a pink-violet solution and grey precipitate. After stirring at 25 °C for 2 h, the suspension was filtered through a syringe filter into a second microwave tube, which had already been flushed with N₂. Solid residuals were extracted with dry CH₃CN (1 mL) and filtered into the new vial. Solvent was reduced with a stream of N₂ to approx. 0.3 mL and dry Et₂O (4 mL) was added giving a magenta suspension. After centrifugation the colorless supernatant was decanted, the precipitate was washed with additional dry Et₂O (2 mL), and dried with a stream of N₂ to give [4](OTf)₂ (5.5 mg, 4.0 μmol) in 98 % yield. Crystals suitable for X-Ray diffraction analysis were obtained from vapor diffusion experiments (CH₃CN / Et₂O).

¹H NMR (d³-acetonitrile, 400 MHz): 6.88 (s, 15 arom. H), 6.49 (s, 7 arom. H), 2.34 (br, Δ = 239 Hz, 4 x CH₂); 1.92 (br, Δ = 174 Hz, 2 x CH₃). HR-ESI-MS: C₅₆H₅₄N₂P₄Re²⁺ [4]²⁺: calculated 532.63920, found 532.63872. IR: 3061w, 2973w, 2911w, 1486w, 1435m, 1257s, 1223m, 1150m, 1097m, 1030s, 999w, 869w, 811w.

[*trans*-ReCl₂(CH₃CN)₄]⁺ ([5]⁺). *Method A:* In a 2 mL microwave tube [2](OTf)₂ (5.1 mg, 7.0 μmol), NaCl (2.6 mg, 44 μmol), and AgCl (1.2 mg, 8.4 μmol) were flushed with N₂ and dissolved in dry CH₃CN (1.5 mL). The slightly yellowish suspension was heated to 100 °C for 77 h. The yellowish solution was separated from the grey precipitate by filtration through a syringe filter into a second N₂-flushed 2 mL microwave tube containing NaBPh₄ (4.4 mg, 12.9 μmol). Solid residues were extracted with dry CH₃CN (1 mL) and filtered into the new vial.

The solution was concentrated in volume with a N₂-stream to approximately 0.3 mL and degassed H₂O (4 mL) was added. The formed yellowish precipitate was separated from the yellowish supernatant by centrifugation, washed with additional degassed H₂O (3 x 2 mL), and freeze-dried to yield [5]BPh₄ (4.5 mg, 6.1 μmol, 87 %).

Method B: In a 2 mL microwave tube [1](OTf) (20.0 mg, 33.8 μmol) and FeCl₃ (13.6 mg, 83.8 μmol) were flushed with N₂ and dissolved in dry CH₃CN (2 mL). The orange solution was heated for 3 h at 80 °C and subsequently for 1 h at 70 °C giving a brownish suspension. The solution was separated from the precipitate by filtration through a syringe filter into a second N₂-flushed microwave tube. Solid residues were extracted with dry CH₃CN (1 mL) and filtered into the new vial. The filtrate was concentrated to approx. 0.3 mL with a stream of N₂, before dry toluene (4 mL) was added. The brown precipitate was separated from the orange supernatant by centrifugation and washed with dry THF (2 mL) and degassed H₂O (1 mL). The yellow solid was freeze-dried to give [5](OTf) (2.4 mg, 4.3 μmol, 12 %). Additional [5]⁺ was obtained by addition of NaBPh₄ (9.3 mg, 27.2 μmol in 0.5 mL H₂O) to the aqueous washings, which led to a yellowish brown precipitate. The precipitate was isolated by centrifugation, washed with degassed H₂O (1 mL), and freeze-dried to yield [5](BPh₄) (1.3 mg, 1.8 μmol, 5 %). Crystals suitable for X-Ray diffraction analysis for [5](BPh₄) were obtained from vapor diffusion experiments (CH₃CN / Et₂O) under ambient conditions.

¹H NMR (d³-acetonitrile, 400 MHz): 65.5 (s, 4 x NCCH₃). HR-ESI-MS: C₈H₁₂N₄Cl₂Re⁺ [5]⁺: calculated 420.99910, found 420.99953. IR (measured for [5]BPh₄): 3051m, 2997m, 2982m, 2915m, 2277w, 1710w, 1578m, 1477s, 1427s, 1356m, 1264m, 1179m, 1150m, 1066m, 1026s, 848m.

[*trans*-ReBr₂(CH₃CN)₄](PF₆) ([6]PF₆). In a 5 mL microwave tube [1]PF₆ (50.2 mg, 0.085 mmol) and FeBr₃ (52.3 mg, 0.177 mmol) were flushed with N₂ and dissolved in dry CH₃CN (5 mL) giving a red solution. The solution was heated to 80 °C for 2.5 h before it was stirred at 20 °C for additional 16 h. The red-orange solution was concentrated in volume with N₂ to approximately 0.4 mL, before dry toluene (4.5 mL) was added. The formed precipitate was separated from the supernatant by centrifugation and washed with additional dry toluene (3 mL). The precipitate was washed in the same manner twice with dry THF (3 mL and 2 mL, respectively) and with degassed H₂O (1.5 mL). Drying with N₂ led to the isolation of the red solid [6]PF₆ (30.8 mg, 0.047 mmol) in 55 % yield. Crystals suitable for X-Ray diffraction analysis were obtained directly after a slightly changed work-up procedure. Instead of washing the crude with degassed H₂O, the crude was washed with CH₂Br₂ (1.5 mL) and dry Et₂O (1 mL).

¹H NMR (d³-acetonitrile, 400 MHz): 60.1 (s, 4 x NCCH₃). HR-ESI-MS: C₈H₁₂N₄Br₂Re⁺ [6]⁺: calculated 508.89807, found 508.89604. IR: 2998w, 2934w, 2282w, 1638w, 1413w, 1363w, 1098w, 1059w, 1025w, 947w, 914w, 881w, 827s, 757w.

[*trans*-ReI₂(CH₃CN)₄](BPh₄) ([7](BPh₄)). In a 2 mL microwave tube [2](OTf)₂ (4.9 mg, 6.7 μmol), NaI (2.5 mg, 17 μmol), and AgI (1.9 mg, 7.8 μmol) were flushed with N₂ and dissolved in dry CH₃CN (1.5 mL). The yellow suspension was stirred at 25 °C for 1 h, which led to a decolorization of the supernatant. Upon heating to 80 °C for 21 h the supernatant became orange and a grey precipitate was observed. The supernatant was separated from the grey precipitate by filtration through a syringe

filter into a second N₂-flushed 2 mL microwave tube containing NaBPh₄ (3.5 mg, 10 μmol). Solid residues were extracted with dry CH₃CN (2 x 1 mL) and filtered into the new vial. The solution was concentrated in volume with a N₂-stream to approximately 0.3 mL, which caused some precipitation, and degassed H₂O (3 mL) was added. The formed red precipitate was separated from the orange supernatant by centrifugation, washed with additional degassed H₂O (2 mL), and freeze-dried to yield [7]BPh₄ (3.0 mg, 3.2 μmol, 48 %). Single crystals suitable for X-Ray diffraction analysis were obtained from vapor diffusion experiments (CH₃CN / Et₂O).

¹H NMR (d³-acetonitrile, 400 MHz): 54.7 (s, 4 x NCCCH₃). HR-ESI-MS: C₈H₁₂N₄I₂Re⁺ [7]⁺: calculated 604.87033, found 604.87067. IR: 3218w, 3051s, 2978s, 2910s, 2272w, 1579m, 1479s, 1428s, 1404s, 1363m, 1268m, 1181w, 1151m, 1066w, 1023s, 977w, 915w, 864w, 849m.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at [link](#).
NMR data of new compounds, electrochemistry data, computational and crystallographic details.

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Notes

The authors declare no competing financial interest. A preprint version of the manuscript is available on *ChemRxiv*.³⁵

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$[\text{Re}(\text{NCCH}_3)_6]^{2+}$ is obtained from a Ag^{I} mediated oxidation of $[\text{Re}(\eta^6\text{-C}_{10}\text{H}_8)_2]^+$ in CH_3CN . This fully solvated Re-core in the rare oxidation state +II was fully characterized. Its potential as a rhenium precursor complex was assessed with different substitution reactions with phosphines and halides. The products of these substitution reactions are fully characterized by various spectroscopic methods and X-Ray diffraction analysis. The title compound is a convenient starting material for a wide variety of Re^{II} chemistry.