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Synthesis and reactivity of the rhenium fulvene sandwich complex [Re(6-C₅H₄CH₂)(6-C₆H₆)]⁺

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Abstract: We present the synthesis of the first mixed-ring rhenium fulvene sandwich complex, [Re(6-C₅H₄CH₂)(6-C₆H₆)]⁺, from the respective carbinol precursor [Re(5-C₅H₄CH₂OH)(6-C₆H₆)]. The demanding preparation on the basis of the reactive cross-conjugated system of the fulvene ligand restricts the synthetic accessibility for such fulvene complexes, and the only pathways elaborated originate from the respective carbinols. In contrast to related systems, a suitable rhenium-containing precursor did not exist hitherto. Recently, we described the synthesis of the mixed-aromatic complex [Re(5-C₅H₄CHO)(6-C₆H₆)] which gave access to the carbinol complex [Re(5-C₅H₄CH₂OH)(6-C₆H₆)] and the title compound, both described herein. With [Re(6-C₅H₄CH₂)(6-C₆H₆)]⁺ in hand, the susceptibility of the exocyclic methylenidene group of the coordinated pentafulvene to nucleophilic attacks was investigated with a variety of Lewis bases (hydride, cyanide, amide, alkoxide, thiolate, and phosphine moieties). The characteristic NMR pattern and X-ray crystal structures of [Re(6-C₅H₄CH₂)(6-C₆H₆)]⁺ and postfunctionalized [Re(5-C₅H₄CH₂R)(6-C₆H₆)] complexes are presented to confirm their authenticities.

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Synthesis and Reactivity of the Rhenium Fulvene Sandwich Complex $[\text{Re}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)]^+$

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ABSTRACT: We present the synthesis of the first mixed-ring rhenium fulvene sandwich complex $[\text{Re}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)]^+$ from the respective carbinol $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH})(\eta^6\text{-C}_6\text{H}_6)]$ precursor. The demanding preparation on the basis of the reactive cross-conjugated π -system of the fulvene ligand restricts the synthetic accessibility for such fulvene complexes and the only pathways elaborated originate from the respective carbinols. In contrast to related systems, a suitable rhenium containing precursor did not exist hitherto. Recently, we described the synthesis of the mixed-aromatic complex $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{CHO})(\eta^6\text{-C}_6\text{H}_6)]$ which gave access to the carbinol complex $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{OH})(\eta^6\text{-C}_6\text{H}_6)]$ and the title compound, both described herein. With $[\text{Re}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)]^+$ in hand, the susceptibility of the exocyclic methylenide group of the coordinated pentafulvene to nucleophilic attacks was investigated with a variety of Lewis bases (hydride, cyanide, amide, alkoxide, thiolate and phosphine moieties). The characteristic NMR pattern and X-ray crystal structures of $[\text{Re}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)]^+$ and post-functionalized $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R})(\eta^6\text{-C}_6\text{H}_6)]$ complexes are presented to confirm their authenticities.

INTRODUCTION

Organometallic sandwich complexes emerged as key compounds in many applications such as homogenous catalysis, material science and medicinal-oriented chemistry, e.g., bioorganometallic pharmaceuticals.¹⁻⁴ For many years, arene sandwich complexes existed in the shadow of cyclopentadienyl complexes only, in particular of ferrocene.^{5,6} Through the reduction of CrCl_3 with Al/AlCl_3 , Fischer and Hafner⁷ synthesized the first metal bis-arene sandwich complex, $[\text{Cr}(\eta^6\text{-C}_6\text{H}_6)_2]$, in 1955. Two years later, the same group opened up the field for rhenium bis-arene complexes with $[\text{Re}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ from $\text{ReCl}_5/\text{Al}/\text{AlCl}_3$.⁸ Recently reported modifications by Trifonova et al.⁹ and by our group¹⁰ presented an improved pathway from $[\text{ReO}_4]^-$ to enhance the yield up to 50%.

The complex $[\text{Re}(\eta^6\text{-C}_6\text{H}_6)_2]^+$ turned out to be exceptionally stable against oxidation or hydrolysis, ideal properties for applications as building block in pharmaceuticals or eventually catalysis. This aim was targeted in our group over the past few years via post-functionalization of the arene rings through the introduction of various functionalities.^{10,11} In the course of these studies, we found an unprecedented ring-contraction reaction towards the novel mixed-aromatic ring sandwich complex $[\text{Re}(\eta^5\text{-C}_5\text{H}_4\text{CHO})(\eta^6\text{-C}_6\text{H}_6)]$.¹¹ This reaction was pivotal for the development of further mixed-ligand rhenium sandwich complexes. Herein, we describe in a first part the route to the rhenium fulvene complex $[\text{Re}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)]^+$,

which shows some analogies to a pathway described by Barlow et al. for the ruthenium congener.¹²

Fulvenes were discovered in 1900 as an interesting class of organic compounds that display a cyclic cross-conjugated π -system.¹³⁻¹⁵ In concord with the size of the ring system, they are classified as either tria-, penta-, hepta- or nonafulvenes.¹⁶ They attracted attention due to their exhibition of non-benzenoid aromaticity and high polarizability, leading to a position in-between the benzenoid isomers and the olefins.^{17,18} On the basis of the synthetic route, we focused on one specific fulvene, namely 5-methylenecyclopenta-1,3-diene (herein referred as pentafulvene or fulvene). In contrast to iron¹⁹ or ruthenium¹², rhenium complexes bearing pentafulvene moieties as ligands are poorly, if at all, described in literature. Most of the reported ones comprise a fully methylated fulvene, synthesized either by photolysis of $[\text{Re}(\eta^5\text{-C}_5(\text{CH}_3)_5)(\text{CO})_3]$ or via metal vapor synthesis (co-condensation).^{20,21} Besides, the early transition metals Ti, Zr, Nb, Mo and W are known to form complexes of fulvenes, typically di-substituted at the exocyclic carbon atom.²²⁻²⁶ Thereby the bulky substituents prevent C–C coupling to form ansa-metalloenes.²⁶ Apart from density functional theory (DFT) calculations published in 2009, complexes of the $[\text{Re}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\eta^6\text{-C}_6\text{H}_6)]^+$ type are not described so far.²⁷ Comparable complexes comprising an unsubstituted fulvene ligand were reported for Fe^{II} , Cr^0 and Ru^{II} ,^{12,19,28} whereof the neutral Cr complex contains three CO ligands instead of a second arene. $[\text{Cr}(\eta^6\text{-C}_5\text{H}_4\text{CH}_2)(\text{CO})_3]$ can be obtained by treatment of

[Cr(CH₃CN)₃(CO)₃] with fulvene in the non-coordinating solvent pentane.²⁸ The Fe¹⁹ and Ru¹² congeners of [Re(η⁶-C₅H₄CH₂)(η⁶-C₆H₆)]⁺ were synthesized from their respective carbinols, e.g., in acidic media.

The relatively high polarization of the exocyclic olefin and the resulting dipolar character of the double bond make pentafulvenes susceptible to nucleophilic attacks, as the resulting aromaticity of the five-membered ring is the driving force of such reactions.²⁹ An insight into the reactivity of the exocyclic double bond towards various nucleophiles was gained by investigating methylated fulvene, coordinated to rhenium or ruthenium.^{30,31} The addition of nucleophiles to the fulvene moiety resulted in functionalized, coordinated Cp-ligands. Similar behavior was mentioned by Jung et al.³² while treating RuCl₃ with 5-(propan-2-ylidene)cyclopenta-1,3-diene (6,6-dimethylfulvene) in a Fischer–Hafner type reaction. On account of the unforeseen nucleophilic attack by the solvent (amines, alcohols) on the exocyclic carbon atom of 6,6-dimethylfulvene, functionalized ruthenocenes were isolated instead of the attempted zero-valent Ru fulvene complexes. Similarly, we present the interactions of the [Re(η⁶-C₅H₄CH₂)(η⁶-C₆H₆)]⁺ cation with various nucleophiles (hydride, cyanide, amide, alkoxide, thiolate and phosphine moieties).

RESULTS AND DISCUSSION

Synthesis of [Re(η⁶-C₅H₄CH₂)(η⁶-C₆H₆)]⁺. The mixed-aromatic ring sandwich complex [Re(η⁵-C₅H₄CHO)(η⁶-C₆H₆)] (**1**) prepared by our group¹¹ is an excellent starting material for a variety of reactions, especially with respect to a more systematic study of mixed-ligand pentafulvene sandwich complexes of group VII elements. By reduction of the aldehyde group in **1** with NaBH₄, the corresponding alcohol [Re(η⁵-C₅H₄CH₂OH)(η⁶-C₆H₆)] (**2**) was obtained in >90% yield. Carbinol **2** is, on the basis of related systems with Fe¹⁹ and Ru¹², a suitable precursor to attain the novel mixed-ligand sandwich complex [Re(η⁶-C₅H₄CH₂)(η⁶-C₆H₆)]⁺ (**3**⁺), bearing a pentafulvene ligand. Besides the straight reduction of the aldehyde group in **1**, the complex is also highly reactive towards amines. A condensation reaction of the aldehyde **1** with benzylamine gave the secondary aldimine complex [Re(η⁵-C₅H₄CH=NCH₂C₆H₅)(η⁶-C₆H₆)] (**4**) in 93% yield, whose structure could be elucidated by single-crystal X-ray diffraction analysis (Scheme 1 and Figure 1 right).

Scheme 1. Reaction Pathways from [Re(η⁵-C₅H₄CHO)(η⁶-C₆H₆)] to the Mixed-Ring Sandwich Complex **2, Comprising a Carbinol Ligand, and to the Aldimine Complex **4**.^a**

^a i) NaBH₄, THF, 80 °C, overnight; ii) TMSOTf, Et₂O, 0 °C to r.t., 15 minutes; iii) benzylamine, THF, r.t., overnight.

The fulvene complex **3**⁺ was synthesized from **2**, either by the addition of a strong acid such as an aqueous solution of HPF₆ in tetrahydrofuran (THF) at r.t. within 20 minutes or with trimethylsilyl trifluoromethanesulfonate (TMSOTf) in diethyl ether (Et₂O) from 0 °C to r.t. within 15 minutes. The formation of **3**⁺ could easily be followed, since it precipitated as its yellow PF₆[−] or OTf[−] salt, respectively. The reaction with HPF₆ gave suitable single crystals for X-ray diffraction analysis but [3](PF₆) is poorly water soluble, therefore unfavorable for further functionalization and application. Uncoordinated pentafulvene polymerizes³³ and related complexes [M(η⁶-C₅H₄CH₂)(η⁵-C₅H₅)]⁺ (M = Fe¹⁹, Ru¹²) are dioxygen sensitive and the former dimerizes at r.t. In contrast, the mixed-ligand complex **3**⁺ is of high stability against oxidation as well as against hydrolysis. If present as the OTf[−] salt, it combines these properties with good water solubility. With respect to stability properties, it resembles very closely its isoelectronic [M(η⁶-C₆H₆)₂]⁺ pre-precursor. Complex **3**⁺ is thus a promising building block for combining an organometallic moiety with biological molecules, e.g., by interaction with their Lewis basic side chains in peptides or proteins.

To corroborate the authenticity of the structures of the fulvene **3**⁺ and the aldimine **4**, NMR spectroscopy (see supplementary information) and single-crystal X-ray diffraction analysis were performed (Figure 1).

Figure 1. Displacement ellipsoids of the **3**⁺ cation in the crystal structure of [3](PF₆) (left) and Schiff base complex **4** (right). Hydrogen atoms and anions have been omitted for clarity; thermal ellipsoids represent 50% probability. Selected bond lengths (Å) for **3**⁺: Re1–C1 2.267(8), Re1–C2 2.217(5), Re1–C3 2.229(5), Re1–C4 2.256(7), Re1–C5 2.281(6), Re1–C6 2.209(5), Re1–C7 2.105(7), Re1–C8 2.267(9), C5–C5 1.400(11), C5–C6 1.402(8), C6–C7 1.470(7), C7–C8 1.351(11). Selected bond lengths (Å) for **4**: Re1–C7 2.236(6), Re1–C8 2.231(5), Re1–C9 2.236(5), Re1–C10 2.247(6), Re1–C11 2.264(5), C7–C12 1.454(8), C12–N1 1.292(8), N1–C13 1.464(8).

The ¹H NMR of **3**⁺ revealed a strongly high-field shifted signal for the exocyclic methylenic group of coordinated pentafulvene at δ 3.95 ppm. This was unexpected since the uncoordinated pentafulvene (lit.³⁴ δ 5.89 ppm, CDCl₃), as well as the Fe (lit.¹⁹ δ 6.00 ppm, CDCl₃) and Ru (lit.¹² δ 5.07 ppm, CD₂Cl₂) congeners displayed the CH₂-protons at much lower field. A comparably substantial upfield shift was reported for [Cr(η⁶-C₅H₄CH₂)(CO)₃] (lit.²⁸ δ 3.97 ppm, CDCl₃) only. A possible explanation for this phenomenon involves the three different coordination modes of the pentafulvene ligand (Chart 1).

Chart 1. Three Possible Coordination Modes of the Pentafulvene Ligand to Different Metals (M).^b

^b Published characters for given metal centers: Mo (L = C₆H₆, n = 1, R = CH₃, **I**); Cr (L = CO, n = 3, R = H, **II**); Fe (L = C₅H₅, n = 1, R = H, **II**); Ru (L = C₅H₅, n = 1, R = H, **II**).

The more Cp-like ($\pi\text{-}\eta^5\text{:}\sigma\text{-}\eta^1$) binding mode (Chart 1, **I**), was observed only in early transition metal complexes for substituted fulvenes, such as [Mo($\eta^5\text{:}\eta^1\text{-C}_5\text{H}_4\text{CMe}_2$)($\eta^6\text{-C}_6\text{H}_6$)], in which the electron donating substituents stabilize the exocyclic carbocation.²² In contrast, the mentioned congeneric complexes were all described to exhibit tri-olefinic ($\eta^2\text{:}\eta^2\text{:}\eta^2$) coordination (Chart 1, **II**) and thus contain an exocyclic double bond. Although their coordination is identical, the chemical shifts vary by about 1–2 ppm. The differences between the complexes exhibiting low-field (Fe^{II}, Ru^{II}) and high-field (Cr⁰, Re^I) shifted signals are the charges on the metal centers, directly affecting the electron densities. Regarding the bond lengths in **3⁺**, it becomes apparent, that the pentafulvene moiety display three successive intra-ring double bonds with delocalized character, rather than the expected alternation, typical for the diene. In addition, the exocyclic double bond character was confirmed by a short bond length of 1.351(11) Å, almost identical to the one reported for uncoordinated fulvene (lit.²⁹ 1.348 Å). In conclusion, the fulvene ligand in **3⁺** is thus present in a third ($\pi\text{-}\eta^4\text{:}\pi\text{-}\eta^2$) coordination mode (Chart 1, **III**). We note that all those coordination modes have the non-planarity of the pentafulvene ligand in common. The degree of kinking is variable and depends mainly on the metal center. For **3⁺** a distortion angle between the exocyclic double bond and the plane of the five-membered ring was found to be 40.3°. In the case of the ruthenium analogue a comparable value of 42.6° was reported.¹²

Synthesis of [Re($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R}$)($\eta^6\text{-C}_6\text{H}_6$)]. Based on the susceptibility of pentafulvenes to nucleophilic attacks, we investigated the reactivity of the exocyclic methylenide group towards a variety of Lewis bases. In this process, the aromaticity of the five-membered ring is re-established and mixed-aromatic ring sandwich complexes of the general composition [Re($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R}$)($\eta^6\text{-C}_6\text{H}_6$)] are formed. Depending on the employed nucleophiles, the overall charge of the resulting complexes will vary between neutral, for anionic or acidic nucleophiles, and positively charged, for neutral Lewis bases. Accordingly, the reaction of **3⁺** in water or organic solvents at r.t. in a direct, one-step synthesis with nucleophiles gave [Re($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R}$)($\eta^6\text{-C}_6\text{H}_6$)] (R = H (**5**), -C≡N (**6**), -NEt₂ (**7**), -OMe (**8**), -SEt (**9**), -S(CH₂)₂OH (**10**) and PTA (**11⁺**)) complexes in good to very good yields (Scheme 2). The selection of nucleophiles was made for introducing functionalities as diverse as possible. Evidently, the exocyclic double bond in **3⁺** shows a nucleophilicity dependent selectivity. Accordingly, the reaction with 2-mercaptoethanol gave exclusively complex **10** in a fast and complete reaction. The X-ray structure of complex **10** was elucidated and is shown in the supplementary information.

Scheme 2. Schematic Representations of Mixed-Aromatic Ring Sandwich Complexes [Re($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R}$)($\eta^6\text{-C}_6\text{H}_6$)].

In contrast to the highly stable pentafulvene complex **3⁺**, all isolated compounds of type [Re($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R}$)($\eta^6\text{-C}_6\text{H}_6$)] are prone to oxidation by O₂. Thus, all syntheses and analyses had to be performed under inert atmosphere (N₂) and in degassed solvents. Due to the neutral or even positive charges of the complexes, they are insoluble in water, hence they could be isolated by extraction with organic solvents (Et₂O or pentane).

By virtue of the structural similarity of complexes **5–10**, the NMR data of their core sandwich structures display a high degree of similarity. The simplest representative of the series bearing an exocyclic methylene group, complex **6**, shows four signals at δ 5.23, 5.01, 4.73 and 3.51 ppm in the ¹H NMR spectrum. While the signal at δ 3.51 ppm was assigned to the exocyclic CH₂-group, the remaining three signals with integrals of two, two and six protons, respectively, were similar to the ones already detected in the spectrum of complex **2**. A nucleophilic attack will always lead to an exocyclic methylene (R ≠ H) or a methyl group, likewise donating. A characteristic pattern for the core structure of mixed-ring sandwich complexes of the type [Re($\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{R}$)($\eta^6\text{-C}_6\text{H}_6$)] is always present, with chemical shifts that differ only slightly depending on the nature of the donor attached to the exocyclic carbon atom. The two signals for the aromatic protons of the Cp-ring display pseudo-multiplicities of singlets or triplets. The effective coupling constants can therefore not be resolved fully and the pseudo-triplets were treated as multiplets. The purity and presence of the tertiary amine in **7** was additionally confirmed by ¹⁵N NMR analysis, where a singlet was detected at δ 7.71 ppm (for syntheses and full characterization of all complexes see experimental part in the supplementary information).

The authenticities of **6** and **8** were confirmed by single-crystal X-ray diffraction analysis. ORTEP representations are shown in Figures 2 and 3. The difference between the mixed-aromatic ring sandwich structures and the starting material **3⁺** is obviously the planarity of the aromatic five-membered Cp-ring (C1 to C5) with respect to the exocyclic C1–C6 bond. The expected single bond character is supported by the elongation of the bond length of C1–C6 from 1.351(11) Å (**3⁺**, C7–C8) to 1.509(5) and 1.479(7) Å for **6** and **8**, respectively.

Figure 2. ORTEP representation of complex **6**. Hydrogen atoms have been omitted for clarity; thermal ellipsoids represent 50% probability. Selected bond lengths (Å) for **6**: Re1–C1 2.238(4), Re1–C2 2.242(4), Re1–C3 2.246(4), Re1–C4 2.251(4), Re1–C5 2.241(4), Re1–C8 2.211(4), Re1–C9 2.206(4), Re1–C10 2.205(4), Re1–C11 2.197(4), Re1–C12 2.204(4), Re1–C13 2.208(4), C1–C2 1.429(5), C1–C5 1.419(5), C1–C6 1.509(5), C2–C3 1.427(5), C3–C4 1.421(6), C4–C5 1.418(6), C6–C7 1.466(6), C7–N1 1.136(6).

Figure 3. ORTEP representation of complex **8**. Hydrogen atoms and minor components of disorder have been omitted for clarity; thermal ellipsoids represent 50% probability. Selected bond lengths (Å) for **8**: Re1–C1 2.216(4), Re1–C2 2.233(4), Re1–C3 2.254(4), Re1–C4 2.250(4), Re1–C5 2.237(4), Re1–C8 2.213(4), Re1–C9 2.213(5), Re1–C10 2.219(4), Re1–C11 2.207(5), Re1–C12 2.209(4), Re1–C13 2.210(4), C1–C2 1.433(7), C1–C5 1.430(7), C1–C6 1.479(7), C2–C3 1.411(7), C3–C4 1.409(7), C4–C5 1.413(7), C6–O1 1.414(6), O1–C7B 1.460(9).

The synthesis of **11**⁺ differs from the previous ones by the employment of the neutral Lewis base 1,3,5-triaza-7-phosphaadamantane (PTA). This phosphine was chosen on the basis of its good water solubility and air stability, which minimize the amount of unreactive phosphine oxide. Additionally, the rigid structure of caged phosphines increases the accessibility of the lone pair in comparison to ones with three independently flexible substituents. Besides standard characterization methods, complex **11**⁺ was evaluated by ³¹P NMR. Thereby, not only the characteristic ¹H NMR pattern for mixed-aromatic ring sandwich complexes could be identified, but the direct covalent bonding of the methylene carbon in **11**⁺ to a phosphorus atom could be confirmed by a single peak at δ –45.79 ppm in the ³¹P NMR spectrum and a doublet for the CH₂-group in the ¹H NMR analysis from phosphorus coupling.

The stabilities of the mixed-aromatic ring sandwich complexes **5–11** were investigated by UHPLC-MS and NMR analysis in acidic environments. As soon as the complexes were exposed to acidic conditions, the reverse reactions towards the fulvene complex **3**⁺ took place as evident from dominant mass peaks of m/z 343.1 (**3**⁺) in the UHPLC-MS of, e.g., **7** and **10**. Furthermore, the ¹H NMR spectrum of **8** in CDCl₃ (containing some HCl) revealed a rising amount of fulvene **3**⁺ and methanol. The mixed-aromatic ring sandwich complexes [Re(η^5 -C₅H₄CH₂R)(η^6 -C₆H₆)] are sensitive towards O₂ and decomposed slowly confirmed by the appearance of free benzene in their ¹H NMR spectra.

CONCLUSION

Sandwich complexes bearing an unsubstituted pentafulvene moiety are comparably rare in literature, especially for rhenium. Since pentafulvene is a highly reactive cross-conjugated ligand, the only pathway to its complexes starts from the respective carbinol precursors. A related complex for rhenium was hitherto proposed by DFT calculations only.²⁷ In organometallic rhenium chemistry, [Re(η^5 -C₅H₄CHO)(η^6 -C₆H₆)] represents an excellent starting material for [Re(η^6 -C₅H₄CH₂)(η^6 -C₆H₆)]⁺, whose existence was confirmed in this study. The fulvene complex **3**⁺ is of unexpectedly high stability against oxidation and hydrolysis. The exocyclic methylenide group of the fulvene moiety is highly susceptible to nucleophilic attacks to form the described mixed-aromatic ring sandwich complexes [Re(η^5 -C₅H₄CH₂R)(η^6 -C₆H₆)] in excellent yields. The presented series of “R” groups (R = H, –C≡N, –NEt₂, –OMe, –SEt, –S(CH₂)₂OH and PTA) may well be extended to other, more complex nucleophiles, eventually attached to further functionalities. Considering the good water solubility of **3**⁺, interactions with peptides or proteins in living systems could make it a corresponding marker. The reactivity is furthermore dependent on the nucleophilicity of the Lewis bases, as shown with 2-mercaptoethanol, in which only the thiolate group binds to the exocyclic carbon. According investigations are ongoing.

EXPERIMENTAL SECTION

General Information. Experimental methods, synthetic procedures, and analytical data for all compounds are described in detail in the Supporting Information. We give here only the procedures for the key compounds **2**, [**3**](OTf), **6**, **8** and [**11**](OTf). Complex **1** was prepared according to literature procedures starting from Na[ReO₄].^{10,11}

[Re(η^5 -C₅H₄CH₂OH)(η^6 -C₆H₆)] (**2**). Aldehyde **1** (63 mg, 0.18 mmol, 1.0 eq.) and NaBH₄ (69 mg, 1.82 mmol, 10.3 eq.) were suspended in dry THF (7 mL). The orange reaction mixture was stirred overnight at 80 °C. The slightly yellowish, turbid mixture was concentrated and subsequently quenched with degassed H₂O (5 mL). THF was evaporated and the product was extracted from the aqueous solution with Et₂O (3 × 3 mL). After combining the organic phases, the solvent was evaporated to give **2** as analytically pure, colorless to yellowish solid. Yield: 59 mg (93%).

Analysis. ¹H NMR (500 MHz, C₄D₈O) δ [ppm]: 5.16 (s, 2H, α -CH_{Cp}); 4.98 (s, 2H, β -CH_{Cp}); 4.66 (s, 6H, CH_{arom}); 3.99 (d, J = 5.95 Hz, 2H, CH₂); 2.89 (t, J = 5.95 Hz, 1H, OH). ¹³C NMR (125 MHz, C₄D₈O) δ [ppm]: 96.02 (1C, C–CH₂); 73.49 (2C, α -CH_{Cp}); 71.92 (2C, β -CH_{Cp}); 61.48 (1C, CH₂); 60.98 (6C, CH_{arom}). IR (neat) ν [cm^{–1}]: 3357 (w), 3196 (br., w), 3086 (w), 2958 (w), 2921 (s), 2851 (m), 1658 (w), 1632 (w), 1467 (w), 1419 (m), 1376 (w), 1260 (s), 1235 (w), 1093 (m), 1037 (s), 1019 (s), 969 (w), 904 (s), 814 (s), 800 (s). HR-ESI-MS m/z : [M]⁺ calcd for C₁₂H₁₃ORe, 360.05184; found, 360.05136.

[Re(η^6 -C₅H₄CH₂)(η^6 -C₆H₆)](OTf) (**3**)(OTf). Carbinol **2** (32 mg, 0.09 mmol, 1.0 eq.) was dissolved in dry Et₂O (5 mL). The slightly yellowish clear solution was cooled to 0 °C and a solution of

trimethylsilyl trifluoromethanesulfonate (TMSOTf; 1% in Et₂O; 1.8 mL, 0.10 mmol, 1.1 eq.) was added dropwise. A precipitate formed instantaneously and the suspension was further stirred for 15 min at r.t. After decanting the supernatant, the solid residue was washed with Et₂O (3 × 3 mL) and dried *in vacuo* to afford [3](OTf) as analytically pure, yellow solid. Yield: 40 mg (91%).

Analysis. ¹H NMR (500 MHz, C₄D₈O) δ [ppm]: 6.32–6.30 (m, 2H, β-CH_{CP}); 5.66 (s, 6H, CH_{arom}); 5.58–5.57 (m, 2H, α-CH_{CP}); 4.00 (s, 2H, CH₂). ¹³C NMR (125 MHz, C₄D₈O) δ [ppm]: 97.08 (1C, C–CH₂); 90.41 (2C, β-CH_{CP}); 83.27 (2C, α-CH_{CP}); 80.75 (6C, CH_{arom}); 51.50 (1C, CH₂). IR (neat) ν [cm^{−1}]: 3094 (w), 1426 (w), 1408 (w), 1259 (s), 1222 (m), 1152 (s), 1029 (s), 970 (w), 895 (w), 839 (m), 754 (w). HR-ESI-MS *m/z*: [M]⁺ calcd for C₁₂H₁₂Re, 343.04911; found, 343.04940.

[Re(η⁵-C₅H₄CH₂CN)(η⁶-C₆H₆)] (6). Complex [3](OTf) (11 mg, 0.02 mmol, 1.0 eq.) and KCN (12 mg, 0.18 mmol, 8.4 eq.) were dissolved in degassed H₂O (0.8 mL). The yellow clear reaction mixture was stirred overnight at r.t. to form a colorless precipitate in a still slightly yellowish solution. The product was extracted with Et₂O (3 × 2 mL) from the aqueous solution, the Et₂O was evaporated and the yellowish solid was dried *in vacuo* to result in analytically pure **6** as colorless solid. The product was recrystallized from Et₂O, yielding single crystals of **6**, suitable for X-ray diffraction analysis. Yield: 7.0 mg (86%).

Analysis. ¹H NMR (500 MHz, C₄D₈O) δ [ppm]: 5.23 (s, 2H, α-CH_{CP}); 5.01 (s, 2H, β-CH_{CP}); 4.73 (s, 6H, CH_{arom}); 3.51 (s, 2H, CH₂). ¹³C NMR (125 MHz, C₄D₈O) δ [ppm]: 118.40 (1C, C≡N); 83.48 (1C, C–CH₂); 73.38 (2C, α-CH_{CP}); 72.05 (2C, β-CH_{CP}); 62.11 (6C, CH_{arom}); 20.06 (1C, CH₂). IR (neat) ν [cm^{−1}]: 3358 (w), 3185 (w), 3059 (w), 2961 (m), 2922 (m), 2852 (m), 2255 (w, C≡N), 1659 (w), 1632 (w), 1467 (m), 1414 (w), 1261 (s), 1094 (m), 1021 (s), 798 (s), 706 (m). HR-ESI-MS *m/z*: [M]⁺ calcd for C₁₃H₁₂NRe, 369.05218; found, 369.05276.

[Re(η⁵-C₅H₄CH₂OMe)(η⁶-C₆H₆)] (8). Compound [3](OTf) (6 mg, 0.01 mmol, 1.0 eq.) and NaOMe (6 mg, 0.11 mmol, 9.3 eq.) were dissolved in degassed MeOH (0.5 mL). The yellow turbid reaction mixture was stirred for 2 h at r.t. and turned colorless. The remaining MeOH was evaporated and the product was extracted from the colorless-yellowish solid residue with degassed pentane (3 × 1 mL) to give **8** as analytically pure, yellowish solid. The product was recrystallized from pentane, yielding single crystals of **8**, suitable for X-ray diffraction analysis. Yield: 4 mg (92%).

Analysis. ¹H NMR (500 MHz, C₄D₈O) δ [ppm]: 5.16–5.14 (m, 2H, α-CH_{CP}); 5.01–4.99 (m, 2H, β-CH_{CP}); 4.64 (s, 6H, CH_{arom}); 3.90 (s, 2H, CH₂); 3.20 (s, 3H, OCH₃). ¹³C NMR (125 MHz, C₄D₈O) δ [ppm]: 89.62 (1C, C–CH₂); 74.73 (2C, α-CH_{CP}); 72.65 (1C, CH₂); 72.44 (2C, β-CH_{CP}); 61.11 (6C, CH_{arom}); 57.14 (1C, OCH₃). IR (neat) ν [cm^{−1}]: 2954 (m), 2922 (s), 2852 (m), 1460 (w), 1376 (w), 1261 (m), 1093 (m), 1020 (m), 801 (m). HR-ESI-MS *m/z*: [M]⁺ calcd for C₁₃H₁₅ORe, 374.06749; found, 374.06754.

[Re(η⁵-C₅H₄CH₂PTA)(η⁶-C₆H₆)](OTf) ([11](OTf)). Fulvene [3](OTf) (10 mg, 0.02 mmol, 1.0 eq.) and 1,3,5-triaza-7-phosphaadamantane (PTA; 5 mg, 0.03 mmol, 1.6 eq.) were dissolved in degassed H₂O (1.5 mL). The clear yellow reaction mixture was stirred overnight at r.t. to form a brownish-colorless precipitate in a slightly yellowish solution. The supernatant was removed and the almost colorless solid residue was washed with H₂O (3 × 1 mL) and dried *in vacuo* to afford analytically pure [11](OTf) as colorless solid. Yield: 10 mg (75%).

Analysis. ¹H NMR (400 MHz, CD₃CN) δ [ppm]: 5.17–5.16 (m, 2H, α-CH_{CP}); 5.12–5.11 (m, 2H, β-CH_{CP}); 4.75 (s, 6H, CH_{arom}); 4.48–4.34 (m, 12H, PCH₂N, NCH₂N); 3.12 (d, *J* = 12.53 Hz, 2H, CH₂). ¹³C NMR (100 MHz, CD₃CN) δ [ppm]: 76.59 (d, *J* = 2.54 Hz, 1C, C–CH₂); 74.19 (d, *J* = 1.77 Hz, 2C, α-CH_{CP}); 73.46 (2C, β-CH_{CP}); 72.35 (d, *J* = 9.44 Hz, 3C, NCH₂N); 62.63 (6C, CH_{arom}); 47.71 (d, *J* = 29.75 Hz, 3C, PCH₂N); 24.25 (d, *J* = 16.38 Hz, 1C, CH₂). ³¹P NMR (162 MHz, CD₃CN) δ [ppm]: −45.79. IR (neat) ν [cm^{−1}]: 2974 (w), 2929 (w), 2891 (w), 1460 (w), 1423 (w), 1258 (s), 1241 (s), 1225 (s), 1157 (s), 1097 (w), 1028 (s), 1013 (m), 968 (s), 943 (m), 916 (m), 880 (w), 852 (w), 816 (m), 786 (m). HR-ESI-MS *m/z*: [M]⁺ calcd for C₁₈H₂₄N₃PRe, 500.12599; found, 500.12582.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details for the synthesis and full characterization, including crystallographic data, for all new complexes (PDF)

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Notes

The authors declare no competing financial interest.

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