Electronic communication in phosphine substituted bridged dirhenium complexes – clarifying ambiguities raised by the redox non-innocence of the C4H2- and C4-bridges†

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The mononuclear rhenium carbonyl complex trans-[Re(C==CSiMe3)(C==CH)(PMe3)4][PF6] (2) was prepared in 90% yield by heating a mixture of the dinitrogen complex trans-[ReCl(N2)(PMe3)4] (1), TipPF6, and an excess of HC==CSiMe3. 2 could be deprotonated with KOTBu to the vinylidene complex trans-[Re(C==CSiMe3)(C==CH)(PMe3)4][PF6] (3) in 98% yield. Oxidation of 3 with 1.2 equiv. of [Cp2Fe][PF6] at −78 °C gave the C=C coupled dinuclear rhenium biscarbonyl complex trans-[[Me3SiC==C][PMe3]2Re==C==CH2−CH2−C==Re(PMe3)4][PF6] (5) in 92% yield. Deprotonation of 5 with an excess of KOTBu in THF produced the diamagnetic trans-[[Me3SiC==C][PMe3]2Re==C==CH-CH==C==Re(PMe3)4][PF6] (6(S)) complex (E-6(S)) in 87% yield with an E-butadienediylidene bridge. Density functional theory (DFT) calculations of E-6(S) confirmed its siglelet ground state. The Z-form of 6 (Z-6(S)) could not be observed, which is in accord with its DFT calculated 17.8 kJ mol⁻¹ higher energy. Oxidation of E-6 with 2 equiv. of [Cp2Fe][PF6] resulted in the stable diamagnetic dicarbonyl trans-[[Me3SiC==C][PMe3]2Re==C==CH⁻CH==C==Re(PMe3)4][PF6] (E-6[PF6]2) with an ethylenidyldiene dicarbonyl structure of the bridge. The paramagnetic mixed-valence (MV) complex E-6[PF6] was obtained by comproportionation of E-6(S) and E-6[PF6]2 or by oxidation of E-6(S) with 1 equiv. of [Cp2Fe][PF6]. The dicarbonyl trans-[[Me3SiC==C][PMe3]2Re==C==CH⁻CH==C==Re(PMe3)4][PF6] (7[PF6]2) complex, attributed a butytedi(triyl) bridge structure, was obtained by deprotonation of E-6[PF6]2 with KOTBu followed by oxidation with 2 equiv. of [Cp2Fe][PF6]. The neutral complex 7 could be accessed best by reduction of 7[PF6]2 with KH in the presence of 18-crown-6. According to DFT calculations 7 possesses two equilibrating electronic states: diamagnetic 7(S) and triplet 7(T) with ferromagnetically coupled spins. The latter is calculated to be 5.2 kcal mol⁻¹ lower in energy than 7(S). There is experimental evidence that 7(S) prevails in solution. 7 could not be isolated in the crystalline state and is unstable transforming mainly by H-abstraction to give E-6(S). UV-Vis-NIR spectroscopy for the dinuclear rhenium complexes E-6(S), E-6[PF6] and E-6[PF6]2 as well as EPR spectroscopic and variable-temperature magnetization measurements for the MV complex E-6[PF6] were also conducted. Spectro-electrochemical reduction studies on 7[PF6]2 allowed the characterization of the mono- and direduced forms of 7(T) and 7 by means of IR- and UV-Vis-NIR-spectroscopy and revealed the chemical fate of the higher reduced form.

I. Introduction

Organometallic rigid-rod dinuclear complexes consisting of a rigid π-conjugated organic carbonyl or hydrocarbyl bridge C4H2 with redox-active metal end groups of the type [LmMC4H2MLn] (M = metal; L = ligand) have recently received considerable attention due to their potential function in molecular electronic devices. In this paper we will address the tetracarbonyl (C4) and butadiene-1,4-di(ylidene) (C4H2) units as rigid π-conjugated bridging moieties of rhenium based complexes. Rigid molecules of these kinds are denoted as molecular wires...
potentially providing molecular conductance between the remote ends.\textsuperscript{1,2} For instance, Gladysz and co-workers reported a series of dinuclear rhenium complexes with \( \mu^{-}\text{C} \) carbyl chains \((x \leq 20)\) composed of up to ten alkynyl units.\textsuperscript{3} Voltammetric studies revealed that with increasing chain lengths, the potential difference \( \Delta E_{1/2} \) between the two main metal derived redox processes decreases and the oxidation becomes increasingly irreversible. In other words, the longer the chain length, the smaller is the electronic interaction between the remote redox sites and the higher is the reactivity of the \((\text{hydro})\text{carbyl} \) chain. The HOMO and LUMO of bridged polycarbonyl systems \([\text{L}_n\text{MC}_n\text{ML}_n]\), \(x = \text{even number}\) are in most cases \(\pi\)-type molecular orbitals with only limited \(\pi\)-delocalization, large HOMO–LUMO gaps, and quite low polarizabilities of the bridges also preventing strong metal–bridge–metal interactions. Furthermore, for molecules serving as junctions in single-molecule conductivity devices the energetic alignment of the HOMO or the LUMO with the Fermi level in single-molecule conductivity devices the energetic alignments for, for instance, their hook up to electrodes, which allow spontaneous removal of the tin groups upon contact with the gold surface.\textsuperscript{2b,c,1b}

The \( \text{C}_2\text{H}_4 \) and \( \text{C}_4 \) bridges belong to the class of redox non-innocent ligands\textsuperscript{5} and are by this property expected to enable the terminal binding of metal centers by various canonical forms (Scheme 1). These bridges are prone to electronic flexibility in their \(\sigma\)–\(\pi\)-bonding adjusting electronically via varying electron counts at the bridges’ termini. It would be natural to assume that in the case of metal attachment the \( \text{C}_2\text{H}_4 \) or \( \text{C}_4 \) bridging systems adopt to the electron demands of electron-precise metal centers. The bridges’ \(\pi\) electrons are variably distributed between CC \(\pi\) bonding electrons and electrons \(\pi\) donated to the metal centers. The \(\pi\) electrons donated to a metal center account for varying strengths of the metal–carbon bonds and the \(\pi\) electrons of the bridge account for different \(\pi\) stabilizations within the bridges (Scheme 1).

For instance, the butadiyne-1,4-diydyl bridging unit is expected to have the lowest \(\pi\)-delocalization between the metal centers,\textsuperscript{1a,18} of all possible forms of the \( \text{C}_4 \) bridge, since the number of \(\pi\) electrons donated to the metal centers is zero and the \(\pi\)-delocalization of diynes is quite low.\textsuperscript{19,20}

In special cases, when the M–C bond is strongly covalent, the bridging ligands will sometimes not adjust to the electron demand of the metal centers. This in turn might lead to ligand-dominated redox-processes and the so-called “non-innocent” behaviour.\textsuperscript{17,21} It maybe interesting to note that the isomeric forms of the \( \text{C}_4\text{H}_2 \) and the \( \text{C}_4 \) bridge are expected to be related by bond-stretch isomerism revealing different carbon–carbon bond lengths as free molecules and as ligands in complexes.\textsuperscript{22}

For the development of dinuclear complexes with conjugated \( \text{C}_2\text{H}_4 \) and \( \text{C}_4 \) bridges we selected the 16e\textsuperscript{th} rhenium fragment \([\text{RC=C}]\text{(diphosphine)}\text{]_W} \text{Re} \), which is bifunctional in the sense that it allows for hooking up to electrodes via the \(\text{RC=C} \) group and can act at the same time as one terminus of bridging systems. The targeted dinuclear rhenium complexes were anticipated to be analogous to manganese-based ones reported by our group earlier and to be related to systems with \([\text{X(diphosphine)}]\text{]_W} \) end groups possessing one electron less per metal site. Both types of systems should therefore differ in the preferred canonical form of the bridge and in their electronic properties.\textsuperscript{8,13c,23} Rhenium as a heavier transition element was expected to render structurally stable complexes and to form

\[
\begin{align*}
\text{butadiyne-1,4-diyl} & \quad \text{butadiyne-1,4-diyl} \\
\text{butadiyne-1,4-diyl} & \quad \text{butadiyne-1,4-diyl}
\end{align*}
\]

Scheme 1 Different canonical forms of the \( \text{C}_2\text{H}_4 \) and the \( \text{C}_4 \) ligand bridges.
strong ligand bonds concomitant with higher barriers for ligand exchange. To avoid difficulties in the synthetic access to \( \text{[L}_4\text{ReC}_2\text{H}_3\text{ReL}_4] \) and \( \text{[L}_4\text{ReC}_2\text{ReL}_4] \) complexes, we tried to circumvent the direct introduction of the \( \text{C}_4\text{H}_2 \) and \( \text{C}_4 \) bridges by ligand exchange by the alternative construction of \( \mu\text{-C}_2\text{H}_2 \) (n = 0, 2 or 4) dinuclear complexes by oxidative C–C coupling processes, i.e. by ‘dimerizing’ mononuclear \( \text{C}_4\text{H}_2 \) (n = 0, 1 or 2) complex units. Our work on manganese coupling chemistry\(^{8,9,21a,22,23a,24} \) and related work on niobium,\(^{15a} \) tungsten,\(^{13a} \) molybdenum,\(^{1,3a,26} \) manganese,\(^{28a,27} \) rhenium,\(^{30} \) iron,\(^{9,29,34} \) and ruthenium\(^{10} \) complexes demonstrated the synthetic utility of the oxidative coupling of metal alkynyls or of oxidative dehydro-dimerizations of metal vinylidens.\(^{18b,31} \)

A key point of our rhenium based endeavors to access mononuclear \( \text{C}_2\text{H}_2 \) and \( \text{C}_4 \) bridges by successive oxidative dehydrogenations.

II. Results and discussion

IIa. Synthesis and characterization of mononuclear rhenium complexes

The synthesis of the dinuclear rhenium complex trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}==\text{C}\text{-CH}_2\text{-CH}_2==\text{C-Re}(\text{PMe}_3)_4(\text{C}==\text{SiMe}_3)]\) \([\text{PF}_6]_2\) (1) from the mononuclear rhenium carbonyl complex trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}(\text{C}==\text{SiMe}_3)]\) \([\text{PF}_6]_2\) (2) was formed in 90% yield by heating in a 1:1 mixture with TIPF\(_6\) and by the addition of excess HC=CSiMe\(_3\) in N,N-disopropylethylamine (DIPEA)/THF at 95 °C (Scheme 2).

The mononuclear rhenium carbonyl complex 2 readily underwent deprotonation using excess KOBu in THF to form the corresponding mononuclear rhenium vinylidene complex trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{C}==\text{CH}_2)(\text{PMe}_3)_4]\) (3) in 98% yield\(^{18b,31c} \) (Scheme 2). Re-protonation of 3 could be accomplished using HCl to recover the carbonyl complex trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}(\text{C}==\text{SiMe}_3)]\) \([\text{PF}_6]_2\) (4) as a chloride salt, which in turn could be deprotonated with KOBu to regenerate 3.

The mononuclear rhenium complexes 2, 3 and 4 were characterized by NMR, IR, elemental analyses and mass spectroscopy. The \(^1\text{H} NMR\) spectrum of trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{C}==\text{SiMe}_3)]\) \([\text{PF}_6]_2\) (3) displayed a characteristic quintet for the vinylidene protons at 1.35 ppm (\(\nu\text{PH} = 3.5 \text{ Hz}\)). In the \(^1\text{C} NMR\) spectrum two resonances were found at 301.6 ppm (\(\nu\text{PC} = 11.9 \text{ Hz}\)) and 87.8 ppm that could be assigned to the \(\text{C}_a\) and \(\text{C}_b\) atoms of the vinylidene group. The other two resonances at 150.1 ppm and 67.8 ppm were attributed to the \(\text{C}_a\) and \(\text{C}_b\) atoms of the acetylide moiety\(^{9a,18b,21a,22,27,28} \) presumably reflecting an extraordinary electron-richness. The IR spectrum of 3 showed strong \(\nu(C==C)\) and \(\nu(C==C)\) bands at 1558 and 1982 cm\(^{-1}\), respectively.

The carbyne complexes trans-[\(\text{Re}(\text{C}==\text{SiMe}_3)](\text{C}==\text{Me})(\text{PMe}_3)_4]\) \([\text{PF}_6]_2\) (2) and trans-[\(\text{Re}(\text{C}==\text{SiMe}_3)](\text{C}==\text{Me})(\text{PMe}_3)_4]\) \([\text{Cl}]_2\) (4) exhibited in the \(^1\text{H} NMR\) spectra a characteristic quintet for \(\nu\text{PH} = 4.0 \text{ Hz}\), respectively, while the \(^1\text{C} NMR\) spectra of 2 and 4 displayed respective resonances for the \(\text{C}_a\) atoms at 284.5 or 284.9 ppm. Their intensity was, however, too low to allow extraction of the apparently small \(\nu\text{PC}\) values. Two additional \(^1\text{C} NMR\) resonances at 134.7 and 125.7 ppm or at 135.0 ppm and 125.8 ppm for 2 and 4 confirmed the presence of the acetylide groups. In the IR spectra \(\nu(C==C)\) bands for 2 and 4 were observed at 2929 cm\(^{-1}\) or 2025 cm\(^{-1}\), respectively. A singlet resonance in the \(^{31}\text{P} NMR\) spectra complied with the trans-arrangements of the alkynyl and carbyne ligands in 2, 3 and 4.

IIb. Synthesis and characterization of \(\text{C}_4\text{H}_2\) bridged dirhenium complexes

Oxidative C–C coupling was demonstrated to be an effective method for the build-up of the bridges of dinuclear \(\mu\text{-C}_2\text{H}_2\) and \(\mu\text{-C}_4\) complexes.\(^{18b,21a,22,27,28,30} \) To adjust this method to dinuclear rhenium complexes with \(\text{C}_4\text{H}_2\) bridges, we initially tried a variation of the oxidative coupling of 3 with electron and proton removal in the presence of a base. However, the reaction of 3 with \([\text{Cp}_2\text{Fe}]\) \([\text{PF}_6]_2\) in the presence of quinuclidine, DBU, or KOBu inevitably resulted in a mixture of complexes: the mononuclear rhenium carbonyl complex trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}(\text{C}==\text{SiMe}_3)]\) \([\text{PF}_6]_2\) (5), and the dicaticonic bisvinylidene complex trans-\([\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}(\text{C}==\text{CH}\text{-CH}==\text{C}(\text{PMe}_3)_4]\) \([\text{Cl}]_2\) \([\text{PF}_6]_2\) (6). This complex reaction behavior was partly attributed to the highly basic nature of 3, which competed with the base added to deprotonate the oxidatively formed radical cation \([3^+]\) giving 2 and the acetylide complex trans-[\(\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}(\text{C}==\text{Me})(\text{PMe}_3)_4]\) \([\text{PF}_6]_2\) and, by subsequent oxidation, the trans-[\(\text{Me}_3\text{SiC}==\text{C}](\text{PMe}_3)_4\text{Re}(\text{C}==\text{Me})(\text{PMe}_3)_4]\) \([\text{Cl}]_2\) \([\text{PF}_6]_2\) cation, which dimerized by C–C coupling to give 6. We anticipated that a better control of the resulting products could be achieved by performing the reaction in the absence of a base at low temperatures\(^{27} \) to accumulate \([3^+]\) at higher concentrations, thus promoting the second order recombination reaction to 5. Oxidation of 3 was carried out at


Scheme 3

-78 °C by adding a THF solution of 3 dropwise to an excess of [Cp₂Fe][PF₆]

The ¹H NMR spectrum of 5 displayed three signals. A resonance at 1.56 ppm was ascribed to the CH₂ protons of the bridge and two other signals at 1.75 ppm and 0.05 ppm were attributed to the terminal acetylide groups; additionally a signal at 42.2 ppm, while the [PF₆]⁻ anion gave rise to a septet at -146.6 ppm. The composition of 5 was confirmed by a correct elemental analysis.

5 could be deprotonated by applying an excess of KOtBu yielding the brownish-green bisvinylidene complex E-[{Me₂SiC≡C}(PMe₅)₄]₂Re=C=CH-CH=C=Re(PMe₅)₄(=C≡CSiMe₃)]⁻ (E-6(S)) in 87% yield (Scheme 4). The use of lithium diisopropylamide (LDA) as a base at room temperature in THF furnished a somewhat lower yield (83%), but the work-up procedure to E-6(S) was found to be more facile in this case. It is quite remarkable that the Z-isomer Z-6(S) could not be traced at any stage of the reaction to 5. Z-6(S) might indeed form in these reactions. Kohn–Sham density functional theory (DFT) calculations indicate that Z-6(S) is at a high energy of 17.8 kcal mol⁻¹ above E-6(S) and transforms quickly into E-6(S) (see section III). An alternative deactivation pathway of Z-6(S) could be its dehydrogenation (Z-6(S) → 7(S) + H₂) assuming a low activation barrier for this process (Scheme 6). The latter process was calculated by DFT to be energetically downhill by -7.8 kcal mol⁻¹. In this context it should be mentioned that the dehydrogenation reaction of E-6(S) (E-6(S) → 7(F) + H₂) was calculated to be energetically uphill by 10.0 kcal mol⁻¹ and is therefore anticipated not to occur. The Z-6(S) dehydrogenation process to 7(F) could make up for the 13 or 17% of the missing yield of E-6(S) in its formation process along Scheme 4. It should be mentioned at this point that the open-shell structure E-6(F) with ferromagnetically coupled electrons is an excited state of E-6(S) at a too high electronic energy to be reached by thermal activation and is therefore expected to be non-existing at room temperature in solution.

The ¹H NMR spectrum of E-6(S) in THF-d₈ at room temperature revealed a 'normal' H_vinylidene chemical shift of 2.50 ppm; but its doublet structure (J = 4 Hz) was unexpected and indicated a peculiar phenomenon. The solid state structure of E-6(S) (Fig. 1a) possesses an approximate planarity of the [Re] moiety. On this basis, the mentioned coupling can be interpreted as ²J_vin coupling originating from the trans-isocyclic arrangement of the closest H_vinylidene atom (plane (H_vinylidene, C₂, C₁)) to the strongly 'bent-back' P₃ atom (plane (P₃, Re, C₁) of Fig. 1a and Scheme 5). The coupling effect would be strongest, if the ReP₃ fragment is subject
to hindered rotation, which prevents averaging on the NMR time scale with the other three non-coupled P atoms ($J_{PH} = 0$).

The $^{13}$C, $^{31}$P and $^{29}$Si NMR signals of E-6(S) are in agreement with the presence of a diamagnetic compound. In the $^{13}$C ($^{1}$H) NMR spectrum of E-6(S) in THF-d$_8$ at 10 °C two characteristic signals appeared, which were assigned to the C$_α$ and C$_β$ vinylidene atoms at 309.4 ppm (quint, $J_{PC} = 12.8$ Hz) and 96.7 ppm. Two additional resonances at 152.8 ppm ($J_{PC} = 16.0$ Hz) and 127.8 ppm were attributed to the C$_α$ and C$_β$ atoms of the acetylide groups. The $^{31}$P and the $^{29}$Si NMR spectra showed singlet resonances of E-6(S) at $\delta = -40.5$ ppm ($^{31}$P NMR) and at $\delta = -31.8$ ppm ($^{29}$Si NMR).

The solid state IR and Raman spectra displayed a strong $\nu$(C=CH) band at 1975 cm$^{-1}$ (IR) or 1973 cm$^{-1}$ (Raman) for the terminal acetylide moieties. Bands at 1543 cm$^{-1}$ (IR) and 1581 cm$^{-1}$ (Raman) were attributed to the $\nu(CHCHCH)$ vibration of the bridge (IR) and to the corresponding $\nu(CHCHCH)$ vibration (Raman). The molecular structure of E-6(S) obtained by single crystal X-ray diffraction (vide infra) also demonstrated the E-configuration for this molecule and, moreover, the bond distances in the bridge reflected the singlet state of the butadiene-1,4-diyldiene(bisvinylidene) canonical form (Scheme 1).

As shown in Scheme 6 E-6(S) could be oxidized by two equiv. of [Cp$_2$Fe][PF$_6$] to yield the diamagnetic dicaticion complex $E[[\{Me_3SiC=C\}](PMMe_3)_3]$Re$_{14}C\equiv CH\equiv CHC\equiv CH\equiv CRe(PMe_3)_4\{C\equiv CSiMe_3\}][PF$_6$]$_3$ and E-6[PF$_6$]$_3$ preserving the E-configuration, but adopting an ethylenylidene dicarbide canonical structure of the bridge (see also X-ray diffraction study of E-6[PF$_6$]$_3$ summarized in Table 1 and displayed in the ES†). The $^1$H NMR spectrum of E-6[PF$_6$]$_3$ showed a unique resonance for both vinylidene protons at 5.82 ppm in the typical chemical shift range of olefinic protons, but in a shift range distinct from the corresponding resonances of E-6(S) indicating a significantly different electronic structure. E-6[PF$_6$]$_3$ revealed resonances for the C$_α$ and C$_β$ nuclei at 265.3 ppm and 145.8 ppm, again appearing in a chemical shift range distinct from that of E-6(S). Due to their low intensities we could not extract the $J_{PC}$ values. Additional $^{13}$C NMR resonances at 135.5 ppm and 130.9 ppm were attributed to the acetylide groups. In the $^{31}$P NMR spectrum a resonance at -43.8 ppm was ascribed to the P nuclei of the PMe$_3$ ligands. The characteristic signal for the [PF$_6$]$^-$ anion appeared as a septet at -143.9 ppm. Although reduction of E-6[PF$_6$]$_3$ to E-6(S) could be carried out with an excess of Na/benzophenone, this reaction was achieved with better control using lithium diisopropylamide (LDA) acting initially as a hydride transfer agent leading to dimethylisopropyl imine$_3$ and the hydride added putative intermediate species E$^-$[PF$_6$]$_3$, which becomes subsequently deprotonated by LDA to form E-6(S) (Scheme 6).

The comproportionation reaction of E-6(S) with E-6[PF$_6$]$_3$ or the oxidation of E-6(S) with one equiv. of [Cp$_2$Fe][PF$_6$] produced the stable mixed valence complex E-6[PF$_6$]$_2$ (Scheme 5). Only broad signals were observed in the $^1$H NMR spectra for E-6[PF$_6$]$_2$ indicating paramagnetic behavior. For E-6[PF$_6$]$_2$ and the dicaticion species E-6[PF$_6$]$_3$, the IR spectra showed weak acetylenic bands at 1987 cm$^{-1}$ and 2221 cm$^{-1}$, respectively. In the Raman spectra the corresponding bands were assigned at 2001 cm$^{-1}$ and 2017 cm$^{-1}$. $\nu$(C$_α$) bands of the C$_β$H$_2$ bridge could not be observed for E-6[PF$_6$]$_2$ and E-6[PF$_6$]$_3$ in the IR. In the case of E-6[PF$_6$]$_3$, this can be viewed as an indication of strong electron delocalization on the IR time scale (10$^{-13}$ s).$^{13}$c The diamagnetic dicaticion ethylenylidene bisscarbyne complex E-6[PF$_6$]$_3$ showed good solubility and stability in polar solvents, such as CH$_2$Cl$_2$ and MeCN. In contrast, neutral E-6(S) complexes and monocaticion E-6[PF$_6$]$_2$ decomposed quickly in CH$_2$Cl$_2$, and over longer period of times also in MeCN, and they underwent facile oxidation in the solid state and in solution. E-6(S) is stable for several months under an inert atmosphere, but should be stored as a solid at -30 °C.

IIC. Characterization of C$_3$ bridged dirhenium complexes

The dicaticion trans-[Me$_3$SiC=C](PMMe$_3$)$_3$Re$_{14}$Re$_{14}$(C=CSiMe$_3$)][PF$_6$]$_3$ complex (7[PF$_6$]$_3$) could be obtained by repetitive cycles of deprotonations and oxidations starting from E-6[PF$_6$]$_3$, or from 2 following method a or method b as depicted in Scheme 7.

In the $^1$H NMR spectrum the dicaticion complex 7[PF$_6$]$_3$ showed singlet resonances for the PMe$_3$ ligands at 1.82 ppm and for the trimethylsilyle groups at 0.26 ppm. The $^{13}$C ($^{1}$H) NMR spectrum revealed characteristic resonances for C$_α$ and C$_β$ at 235.0 and 95.8 ppm, but the intensities of these signals were too low to extract $J_{PC}$ couplings. The resonances of the acetylide groups appeared at 135.5 ppm and 128.4 ppm. In the $^{31}$P NMR spectrum a singlet resonance at -43.6 ppm was ascribed to the PMe$_3$ ligands. The characteristic signal for the [PF$_6$]$^-$ counterion appeared as a septet at -143.9 ppm. The
IR spectrum of $[\text{PF}_6]_2^-$ revealed a weak band at 2013 cm$^{-1}$ attributed to a vibrational band of the acetylenic substituents. Vibrational bands for the C$_4$ moiety could not be found, which supports the notion of a highly symmetric bridging unit of $[\text{PF}_6]_2^-$. The reduction of the dicatonic species $[\text{PF}_6]_2^-$ was attempted by treatment with Na/Hg or Na/benzophenone, but these reactions resulted in a mixture of many components. Using KH in the presence of 18-crown-6 in THF the neutral trans-[[Me$_2$SiC$_{\mu}$=C(PMe$_3$)$_3$]ReC$_{\mu}$Re(PMe$_3$)$_3$]$_2$(C$_{\mu}$=C(SiMe$_3$)$_3$) complex 7 was formed. As depicted in Scheme 7 and according to DFT calculations (section III), two different electronic structures have to be considered for 7: diradical $[\text{PF}_6]^-_2$ with a but-2-ynediyldiene bridge and with ferromagnetically coupled electrons and diamagnetic $[\text{PF}_6]^-_2$ with a butatrienediyldiene bridge. The unpaired spins of $[\text{PF}_6]^-_2$ would be delocalized over the entire ReC$_{\mu}$Re moiety and occupy two degenerate perpendicular $\pi$ orbitals, which according to Hund’s rule should lead to a ferromagnetic electronic state. $[\text{PF}_6]^-_2$ possesses a cumulenic structure (Scheme 1) providing 2-electrons to each electron-precise Re(0) center, thus establishing a diamagnetic molecule. The MO description of the cumulenic structure is particularly complex, since it is based on different occupancies of the two $\pi$ planes of the bridge. The inequality of these $\pi$ planes becomes further amplified in the complex $[\text{PF}_6]^-_2$ by interaction with the unequal $\pi$ planes of the rhenium centers strongly distinguished in their binding capacity via dislocation of the PMe$_3$ ligands from planarity (section IIId). These electronic states of 7 are expected to co-exist at room temperature in solution. However, experimentally it was not possible to distinguish these isomers or to determine the ratio at which these isomers equilibrate.

It should be mentioned at this point that another conceivable isomeric form of 7 is based on a dicataylenic canonical form of the bridge (Schemes 1 and 8). The dicataylenic bridge would need to formally accept one $\sigma$ electron from each rhenium center to form a diaetylide ligand bridging two low-spin d$^5$ Re(II) fragments with different occupancies of the two $\pi$ planes of the bridge. The inequity of these $\pi$ planes and the different binding capacity of the PMe$_3$ ligands from planarity (section IIId). These electronic states of 7 are expected to co-exist at room temperature in solution. However, experimentally it was not possible to distinguish these isomers or to determine the ratio at which these isomers equilibrate.

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H-abstraction from the solvent by any form of 7 (Scheme 7). Formally this reaction could be envisaged to occur preferably with 7(F) in a resonance structure with radical centers at C\(_\beta\) and C\(_\gamma\). H-abstraction of 7 to form E\(E\)-6(S) could further be substantiated by spectro-electrochemical studies (vide infra) identifying E\(E\)-6(S) as a subsequent product of 7 by IR and UV-Vis spectroscopy (section IVc). Nuclei in close vicinity to radical centers are excluded from NMR identification due to paramagnetic broadening and shifting of the signals. Therefore, in 7(F) only NMR signals of atoms distant to the radical centers may be observable as broadened or somewhat broadened resonances. In solutions of 7 slightly broadened \(^1\)H NMR resonances could be detected at 1.10 and 0.53 ppm, which were assigned to the protons of the Me\(_p\) and Me\(_{Si}\) groups, respectively, but the \(^{29}\)Si spectrum showed only a very broad signal and \(^{13}\)C NMR and \(^{31}\)P NMR signals could not be observed at all. The \(^1\)H NMR signal broadening of the methyl resonances of 7 was, however, rather low. From these observations we conclude that, in solution, 7(S) is the prevalent species, coexisting with 7(F), rapidly equilibrating at room temperature on the NMR time scale. Additional evidence for the prevalence of 7(S) as the main solution component of 7 was derived from the spectro-electrochemical studies (vide infra) in THF. For instance, the appearance and position of a cumulenic type \(\nu(C=C)\) IR band at 1758 cm\(^{-1}\) speaks for the existence of 7(S) in solutions of 7. We note here that for the related complex \([(\eta^5-MeC_5H_4)\{dpme\}MnC\equivCMn(dpme)\{\eta^5-MeC_5H_4\}]\) diamagnetic and paramagnetic states have also been postulated to equilibrate in solution.\(^{23c}\)

It should be mentioned at this point that in particular the spectro-electrochemical studies (section IVc) provided clear evidence that the mono-oxidized species 7\(\text{[PF}_6\text{]}\) is existent in solution.

**IId. Structural features of the [P\(_2\)Re\]C\(_2\)H\(_2\)[ReP\(_4\)] and [P\(_2\)Re\]C\(_4\)[ReP\(_4\)] units of 5, E\(E\)-6(S), E\(E\)-6[PF\(_6\)], E\(E\)-6[PF\(_6\)]\(_2\) and 7[PF\(_6\)]\(_2\)**

The dinuclear rhenium compounds 5, E\(E\)-6(S), E\(E\)-6[PF\(_6\)], E\(E\)-6[PF\(_6\)]\(_2\) and 7[PF\(_6\)]\(_2\) could be structurally characterized. The structures of 5, E\(E\)-6(S), E\(E\)-6[PF\(_6\)], E\(E\)-6[PF\(_6\)]\(_2\), and 7[PF\(_6\)]\(_2\) are described in the ESL\(\dagger\) ORTEP like drawings of E\(E\)-6(S) and 7[PF\(_6\)]\(_2\) are displayed in Fig. 1 and selected bond lengths and angles of 5, E\(E\)-6(S), E\(E\)-6[PF\(_6\)], E\(E\)-6[PF\(_6\)]\(_2\) and 7[PF\(_6\)]\(_2\) are summarized in Table 1.

The Re1--C1 bond of \(\text{trans-}[\{\text{Me}_2\text{SiC}==\text{C}(\text{PMe}_3)\}_2\text{Re}==\text{C}-\text{CH}_2-\text{C}==\text{Re}(\text{PMe}_3)\}_2(\text{C}==\text{C}==\text{SiMe}_3)\text{[PF}_6\text{]}\) 5 (see the ESL\(\dagger\)) showed a Re==C distance of 1.7834(19) Å, slightly longer than the expected range (1.75–1.72 Å) of the sum of covalent radii of the Re==C(sp) unit. The C1--C2 and C2--C2' bond lengths of 1.491(3) Å and 1.513(4) Å fall into the range of C(sp)-C(sp\(^3\)) and C(sp\(^3\))-C(sp\(^3\)) single bonds.

The structures of E\(E\)-6(S), E\(E\)-6[PF\(_6\)] and E\(E\)-6[PF\(_6\)]\(_2\) all revealed E-configurations of the bridging units. The C\(_2\)H\(_2\) bridges of E\(E\)-6(S), E\(E\)-6[PF\(_6\)] and E\(E\)-6[PF\(_6\)]\(_2\) show features of delocalized systems, for instance the Re1--C1 bond distance of 1.904(2) Å is significantly shorter than the Re==C distance of 2.046(8) Å of the vinylidine complex \(\text{trans-}[\text{ReCl}==\text{C}(==\text{CHPh})\{\text{dppe}\}]_2\)\(^{14}\) Upon stepwise oxidation to E\(E\)-6[PF\(_6\)] and E\(E\)-6[PF\(_6\)]\(_2\) the Re--C1 bonds shorten to 1.851(6) Å and to 1.805(5) Å, respectively, indicating gradual adoption of a triple bond character. The C1--C2 bond length 1.337(3) Å of E\(E\)-6(S) lies within the C==C double bond range 1.33–1.38 Å, while the same bonds of E\(E\)-6[PF\(_6\)] and E\(E\)-6[PF\(_6\)]\(_2\) with 1.414(7) Å and 1.375(8) Å, respectively, elongate and move closer in distance toward C(sp)-C(sp\(^2\)) single bonds averaging at 1.43 Å.\(^{15}\) The C2--C2' distance of 1.469(4) Å of E\(E\)-6(S) is in agreement with a single bond between two sp\(^3\) hybridized carbon atoms,\(^{15}\) while the same bonds in E\(E\)-6[PF\(_6\)] and E\(E\)-6[PF\(_6\)]\(_2\) are 1.388(10) Å and 1.331(10) Å, respectively, within the range of C==C double bonds 1.33–1.38 Å. In conclusion, according to Table 1, upon oxidation of the neutral complex E\(E\)-6(S) to the dicaticionic complex E\(E\)-6[PF\(_6\)]\(_2\), the Re1--C1 distances gradually shorten coinciding with a change in the bond order from Re==C to Re==C. The C1--C2 distances gradually lengthen from a C==C double to a C--C single bond, while the C2--C2' distances shorten from a C--C single bond to a C==C double bond. The Re...Re distances gradually decrease from the neutral complex E\(E\)-6(S) to the corresponding dicaticionic complex E\(E\)-6[PF\(_6\)]\(_2\). All these observations clearly indicate that the oxidation of E\(E\)-6(S) causes the sp\(^3\) C\(_3\)H\(_2\) linkage to transform to a bisvinylene bond of a ethylenylidine biscarbonye structure (Scheme 1). These data coincide with the results of the NMR experiments that upon oxidation of E\(E\)-6(S) to E\(E\)-6[PF\(_6\)]\(_2\), the resonances of C\(_3\) showed an up-field shift, while those of C\(_\beta\) and H moved downfield.

The Re1--C1 bond distance of 7[PF\(_6\)]\(_2\) of 1.814(4) Å is close to the corresponding bond length of E\(E\)-6[PF\(_6\)]\(_2\) of 1.805(4) Å. Taken together with the short C2--C2' bond of 1.197(8) Å, this provides clear evidence for an alkyndiyld biscarbonye canonical form of the bridge in 7[PF\(_6\)]\(_2\).

The phosphine ligands of the Re\(_4\) subunits of all complexes 5, E\(E\)-6(S), E\(E\)-6[PF\(_6\)], E\(E\)-6[PF\(_6\)]\(_2\), and 7[PF\(_6\)]\(_2\) may not just play the role of ancillary ligands being ‘innocent’ bystanders, but, in most cases, seem to actively contribute to stabilize the respective valence structure of the C\(_3\)H\(_2\) bridge (see section III). We first note that the Re\(_4\) ‘equatorial’ arrangements as subunits of pseudo-octahedral complexes are not planar, but are significantly distorted towards C\(_3\)v symmetry with one trans P–Re–P angle significantly smaller than 180° (about 156°) and bent back toward the acetylide ligands and with the other trans P–Re–P angle being between 166° and 170° and bent towards the C\(_2\)H\(_2\) or C\(_3\) bridge as schematically sketched in Scheme 9.
As was already discussed, the structural and compositional changes of the bridges of 5, E-6[SF6], E-6[PF6]2, and 7[PF6]3 are also reflected in the 13C(1H) NMR spectra. This lets us conclude that the carbon framework in the alkyn biscarbyne complex 7[PF6]3 is more electron-rich than that in the ethylenylidene biscarbyne complex 6[PF6]2. The C1–C2 bond length in 7[PF6]3 of 1.363(5) Å is slightly shorter than a typical C(sp)–C(sp) single bond (1.377 Å), but close to the corresponding C1–C2 bond distance in the tungsten complex \([\text{W(dppe)}]_2\) with a bond length of 1.34(1) Å.33c The C2–C2’ distance of 1.197(8) Å is within the C=C triple bond range (1.18–1.20 Å). Therefore the structure of 7[PF6]3 consists of two symmetrically arranged [trans-X(PMe3)3Re] fragments linked by a C4 system resembling a canonical alkenylidene biscarbyne structure. Owing to the practically linear structure of the Re–C4H7–Re entity, the Re····Re distance in 7[PF6]3 of 7.536 Å is longer than the corresponding distance in E-6[PF6]3. The alkenylidene biscarbyne structure of the C4 chain in 7[PF6]3 differs from the all-cumulene butatrienilydene one in the dicatonic dinuclear rhenium complex \([\text{(Cp})_2\text{Re}C_4\text{Re}(\text{NO})(\text{PPh}_3)]\) reported by Gladysz and coworkers. The results clearly reflect the influence of the different electron counts and redox properties of the terminal metal entities and of the ancillary ligand frameworks eliciting different valence structures of the [Re]–C4[Re] linkages.

III. DFT calculations on the electronic states of E-6 and 7 revealing redox non-innocent structures

A closer insight into the electronic structures of the complexes E-6 and 7 was expected from a thorough DFT analysis based on an appropriate methodological approach to enable the description and proper evaluation of open and closed shell electronic configurations (for details, see the ESI†).

IIIa. Qualitative orbital representation of the pseudo-octahedral \([(\text{acetylide})\text{(PMe3)}_3\text{Re}(\text{bridge})]\) complex unit

The ligand field picture of the pseudo-octahedral \([(\text{acetylide})\text{(PMe3)}_3\text{Re}(\text{bridge})]\) complex is expected to reveal three non-bonding \(\pi\) orbitals at the rhenium center. According to their parent octahedral coordination geometries (Oh symmetry) these occupied orbitals are denoted as “\(t_{2g}\)”. Due to the observed apparently sterically induced lowering of the symmetry of the ReP4 units to \(C_{2v}\) splitting of the “\(t_{2g}\)” orbitals into two \(\pi\)-type d/p hybridized donor orbitals and one \(\delta\)-type orbital occurs (Scheme 10).

In the small P angle plane \((\pi_p)\) the extent of the d/p hybridization is larger and the larger side of the hybrid lobes is directed toward the bridge. The extent of d/p hybridization in the large P angle plane \((\pi_s)\) is smaller and the larger side of the hybrid lobes is directed away from the bridge. The \(C_{2v}\) distortion thus makes the \(\pi\) plane of the smaller P angle plane \((\pi_s)\) more electron donating to the side of the bridge and the \(\pi\) plane of the larger P angle plane \((\pi_s)\) less electron donating toward the bridge. The \(\pi\) interactions are thus anisotropic to the bridge side with the consequence that the strongest \(\pi\) orbital interaction results in \(\pi\) anisotropic orbitals of a bridge possessing for instance a \(\pi_s\) acceptor orbital and a \(\pi_s\) donor orbital.33 This mechanism of an optimum electronic fit seems to be in operation for the complexes E-6(S), E-6[PF6]2, E-6[PF6]3, and 7(S) supporting the binding in certain ReC4H7Re and ReC4Re moieties. For the carbony complex 5 and for 7[PF6]3 involving a conical Re=CC interaction the \(C_{2v}\) distortion of the ReP4 fragment is anticipated to be primarily of steric origin without additional support from the rhenium-bridge interaction.

IIIb. DFT calculations on trans-[[Me3SiC≡C]X(PMe3)3ReC4H7Re(PMe3)](C≡CSiMe3)] (E-6(S)) and trans-[[Me3SiC≡C]X(PMe3)3ReC4H7Re(PMe3)](C≡CSiMe3)] (E-6(A))

We carried out structure optimizations for trans-[[Me3SiC≡C]X(PMe3)3ReC4H7Re(PMe3)](C≡CSiMe3)] (E-6(S)) and trans-[[Me3SiC≡C]X(PMe3)3ReC4H7Re(PMe3)](C≡CSiMe3)] (E-6(A)) by means of Kohn–Sham DFT (for details, see Computational methodology). If not mentioned otherwise, the B3LYP hybrid functional with 50% Hartree–Fock exchange was employed.36 As shown for organic mixed-valence compounds,37 it is important to include a proper amount of the exact exchange, since standard non-hybrid and hybrid exchange–correlation functionals give a too delocalized description.38

trans-[[Me3SiC≡C]X(PMe3)3ReC4H7Re(PMe3)](C≡CSiMe3)] (E-6) The possible isomers of the neutral molecule E-6 are the diamagnetic geometric isomers E-6(S) and Z-6(S) and the open-shell, diradical alternatives E-6(F) and E-6(A) (Scheme 1) possessing SOMOs with either anti- or ferromagnetically coupled electrons. Isomers Z-6(F) and Z-6(A) were not considered due to the expected very high electronic energies for these molecules and the fact that none of them was experimentally observed.

E-6(S) was calculated to have the lowest electronic energy constituting the ground state of E-6 (Scheme 10). The calculations for the singlet diradical structure E-6(A) did not converge (the same was found, if the PBE039 or B3LYP density
functions, were used) indicating that this state is possibly also not of practical relevance. The $E$-6(F) state could be optimized with different density functionals (BLYLYP/B2LYP) leading to slightly different electronic energies, but all of these energies were at levels much higher (34.1/35.3/28.4 kcal mol$^{-1}$) than that of $E$-6(S) (Scheme 11). Given the large energy difference $E$-6(F) can be considered an electronic excited state of $E$-6(S).

The potential energy surface of $E$-6(S) was theoretically explored further by a thermodynamic evaluation calculating first the geometric Z isomer $Z$-6(S), which could not be detected in solution. By structural optimizations $Z$-6(S) turned out to be 17.8 kcal mol$^{-1}$ higher energy than $E$-6(S). This makes its existence in solution at room temperature very unlikely. One can safely assume that, if formed, it will spontaneously convert to $E$-6(S) with a very low barrier. Another possible deactivation pathway is dehydrogenation to 7. For the thermally stable $E$-6(S) the dehydrogenation process is uphill in energy (Scheme 12).

In the following section the electronic structures of $E$-6(S) and $E$-6(F) are discussed, which will be accomplished by a fragmental view of the molecules dividing the molecules up into the [(acetylide)(PMe$_3$)$_4$Re] fragment with the π type large and small P angle plane d$_{Re}$ orbitals combined with π orbitals of the different bridge states.

The frontier orbitals of $E$-6(S). The DFT calculations of $E$-6(S) as the ground state of $E$-6, gave proof of the butadiene-1,4-diylidine canonical form (Scheme 1) as the prevailing MO picture of the bridge. The π orbital system of a butadiene-1,4-diylidene is qualitatively described in Scheme 12.

The qualitative MO picture of the C$_4$H$_2$ bridge (Scheme 12) shows two perpendicular π systems denoted as π$_x$ and π$_y$, which have different electron occupancies for the closed shell or open shell electronic configurations of butadiene-1,4-diylidine and butenyl-1-triy-4-ylidene. Scheme 11 will be used to identify the bridge contributions of prominent MOs of $E$-6(S) and $E$-6(F) as they are obtained from the DFT calculations.

The butadiene-1,4-diylidine bridge of $E$-6(S) possesses two main components for π-type orbital interactions with the rhenium fragments. First there is a net weak π donor interaction in the π$_x$ plane originating from the interaction with the filled π$_z$ orbital, which is complemented by the π acceptor interaction with the empty π$_z$ orbital. Second in the π$_y$ plane the bridge behaves as a strong π acceptor due to the interactions with the empty carbene π orbitals and the d$_z$ orbitals at each rhenium center. The main destabilizing component of the π donor interaction is found in the HOMO of $E$-6(S) and can be viewed as the antibonding component $d_{Re}(π_z)−π_z$, where π$_z$ is out-of-phase with the $d_{Re}(π_z)$ orbitals (Fig. 2, bottom left). The antibonding $d_{Re}(π_z)−π_z$ orbital has as a bonding counterpart $d_{Re}(π_z)+π_z$ lying at a quite low energy. Of further significance for the overall orbital description of $E$-6(S) is the HOMO−1 (Fig. 2, bottom right), which is composed of the bonding combination of π$_z$ with the in-phase-combination of $d_{Re}(π_z)$ orbitals in the small P angle plane $d_{Re}(π_z)+π_z$. The HOMO−1 thus has the effect of a π acceptor interaction counteracting and attenuating partly the effect of π electron donation. The overlay of the electron densities of these π interactions with the mentioned main contributions of the [Re]CC(H)C(H)C[Re] fragment describes well the bridge’s C1−C2 and C2−C2’ full and partial double bond characters. The minor influence of HOMO−1 can be recognized by (a slight) elongation...
tion of the C1–C2 and C1′–C2′ bonds of E-6(S) and a greater influence on the shortening of the C2–C2′ toward a double bond (cf. Table 1). Selected calculated structural parameters of E-6(S) are compiled in Table 1 in comparison with the data obtained from the X-ray diffraction study demonstrating very good agreement in distances and angles.

The frontier orbitals of E-6(F). The diradical non-innocent isomer E-6(F) turns out to be an excited state of E-6(S). This excitation of one electron is reflected in the orbitals of the bridge: one electron of $\pi_7$ of the butadiene-1,4-diylidene was promoted to a $\pi_x$ orbital of the butenyl-1-triy-4-yliylene (Scheme 12). The butenyl-1-triyl-4-yliylene moiety has thus two energetically different SOMOs. The SOMO at the highest energy is localized on one of the carbenic p orbitals. Upon interaction with the (acetylide)Re(PMe$_3$)$_4$ fragment this electron resides at one rhenium center in a strongly antibonding orbital via the interaction of $\pi_x$ of the bridge and the d$_{xy}$(Re) orbital in the small P angle plane (d$_{xy}$(Re)–$\pi_x$) (Fig. 2, top left) weakening the (rhenium–carbon) bridge bond and forming the high energy SOMO of E-6(F). Together with the bonding orbital d$_{xy}$(Re)+$\pi_x$, the counterpart of d$_{xy}$(Re)–$\pi_x$, a three-electron $\pi$ bond with a $\pi$ bond order of 1/3 results. The other SOMO of E-6(F) at a lower energy (Fig. 2, top right) is mainly localized over one [Re]CCHCHC unit and is composed of an out-of-phase combination of the d$_{xy}$(Re) orbital (Scheme 11) and the singly occupied $\pi_x$ orbital of the butenyl-1-triyl-4-yliylene system d$_{xy}$(Re)–$\pi_x$. This antibonding (d$_{xy}$(Re)–$\pi_x$)–$\pi_x$ orbital has a bonding counterpart 2(d$_{xy}$(Re)+$\pi_x$) summing up to a rhenium–carbon three-electron $\pi$ bond and a total $\pi$ bond order of 1/2. The bonding balance of each of the SOMOs is thus based on two three-electron-interactions of the bond order 1/3 each at one rhenium center. It may be worth mentioning that none of the SOMOs of E-6(F) provides full ‘through-bridge’ electronic interaction between the rhenium centers (Fig. 2, top). Actually removing the two antibonding SOMO electrons from the E-6(F) molecule makes the rhenium centers electron precise allowing for a strong carbynic ethylenylidene-1,4-diyld bridge structure (Re)≡C–CH=CH–C≡(Re).

trans-[\{Me$_3$SiC≡C\}(PMe$_3$)$_3$]ReC=CRe(PMe$_3$)$_3$(C≡CSiMe$_3$)] (7).

In contrast to complex E-6, where the diradical structure E-6(F) is energetically too high to be considered as a ground state or close to it, DFT calculations on 7 suggest that the diradical structure of 7(F) is slightly lower in energy by 5.3/0.9 kcal mol$^{-1}$ than the singlet state 7(S) using the BHYLP/B3LYP density functional (Scheme 11). Given the relatively high confidence intervals for the electronic energies of the hybrid type DFT calculations, we have to consider both configurations energetically close so that they may co-exist at room temperature in solution. It is also possible that 7(S) is even of a lower energy than 7(F). The calculated main structural parameters of 7(S) and 7(F) are compiled in Table 1 and according to these both have very similar structures. The slightly longer Re–C bond lengths of 7(F) may reflect a somewhat higher degree of the antibonding character of the metal–carbon bonds. Despite these small structural differences, these molecules may constitute examples of bond length isomerism.$^{21c,42}$

Orbital and electronic states of the non-innocent isomers 7(F) and 7(S). The qualitative MO picture of the C$_4$ bridge reveals that terminal $\sigma$ orbitals and two mutually perpendicular and degenerate $\pi$ systems, $\pi_x$ and $\pi_y$, may exhibit two different electron occupancies (Scheme 13), namely the closed or open shell configurations of butatriene-1,4-diylidene and butyne-1,4-di(triyl), respectively. The $\pi_x$ and $\pi_y$ orbitals of the C$_4$ system are occupied by a total of 6 electrons (Scheme 13). Arranging these 6 electrons in pairs as in the spin-paired butatriene-1,4-diylidene configuration an asymmetric distribution of the $\pi$ planes results with 4 and 2 electrons for $\pi_x$ and $\pi_y$. For the butyne-1,4-di(triyl) moiety Scheme 13 describes the equal distribution of six $\pi$ electrons of the bridge generating two singly occupied SOMOs corresponding to the degenerate, bonding $\pi_x$ orbitals in the orthogonal $\pi_x$ and $\pi_y$ orbital planes.

Given these basic orbital descriptions of the bridge we continue to first analyze the compositions of the 7(F) orbitals by attachment of (acetylide)Re(PMe$_3$)$_4$ fragments on both sides of the butyne-1,4-di(triyl) bridge. The two $\pi_x$ SOMO orbitals interact with the filled $\pi_x$ and $\pi_y$ orbitals of the rhenium centers and get transformed into SOMOs of 7(F) forming two half-filled $\pi$ donor interactions antibonding with respect to the rhenium–carbon interactions of the d$_{xy}$(Re)–$\pi_x$ orbital character. Fig. 3 (top) shows the orbital drawing of one of the – on the DFT basis – nearly degenerate SOMOs. The bonding orbital counterparts of the SOMOs are the d$_{xy}$(Re)–$\pi_x$ orbitals, occupied by two electrons, which are located at quite low electronic energies. These two 3-electron $\pi$ donor interactions amount to a total binding balance of the rhenium–carbon $\pi$ bond order of 1/3 each. In each $\pi$ plane ($\pi_x$ and $\pi_y$) there is however an additional $\pi$ acceptor interaction involving $\pi_x$ and $\pi_y$ (d$_{xy}$(Re)–$\pi_x$)+$\pi_y$), which could in the best case reach a maximum bond order of 1 at each rhenium center. Counting in addition the two $\sigma$ electron pairs of the bridge contributing a bond order of 1 to the (Re–carbon)bridge bond a total bond order of 2 3/2 would result. Since the SOMOs of 7(F) bear the bonding character of $\pi_x$ of the bridge, these lie at lower electronic energies than the SOMOs of E-6(F), which have more antibonding character. The relatively low energy and the extensive delocalization of the SOMOs of 7(F) is also the cause for
the competitive total electronic energies of isomeric 7(F) and 7(S) (vide infra).

In line with the overlaid shapes of the SOMOs of 7(F), the spin density (spin-down (β) electronic densities) in Fig. 3 is conical along the main axis of the molecule and to a large extent positive on the rhenium centers, the carbon atoms of the bridge, and the acetylenic β atoms. A significant excess of the β spin density is also obtained on the acetylenic α atoms presumably via a spin polarization mechanism.43

As shown in Scheme 12 the butatriene-1,4-di(ylidene) electron occupancy of six π electrons of a C4 bridge would be unequal with respect to the πx and πy planes, which in the case of 7(S), causes anisotropy in the π interactions with the rhenium centers. Since the πx and πy planes of the rhenium centers are different in p,d hybridization and energy, they are anisotropic in character (Schemes 8 and 9). This leads to cooperativity in the interactions with the likewise anisotropic π orbitals of the bridge (the stronger π donor plane of the rhenium center interacts with the stronger π acceptor plane of the bridge and vice versa). The HOMO (πz plane), HOMO−1 (πx plane) and the second π acceptor interaction (πy plane) of 7(S) (Fig. 4, bottom) indeed reflect the highly anisotropic character of the ReC=Re π interactions consisting thus mainly of one π donor and two π acceptor interactions with the rhenium center.

The HOMO represents an antibonding interaction between the dπ(πz) orbital of the large P angle plane (Scheme 9) with π2 of the bridge. Due to the small bending toward the bridge orbital overlap is reduced on the bridge side, thus decreasing the repulsive character of the 4-electron interaction of dπ(πz) with π2 of the bridge (HOMO, Fig. 4, top).13 The πy MOs of the bridge – coplanar with the stronger πy donor orbitals of the rhenium fragment – are prone to very strong π acceptor interactions engaging even two dπ(πz)+(π2,π1) π-type interactions. The dπ(πy) orbitals at each rhenium center of 7(S) form an in-phase and an out-of-phase orbital combination, which at one time each interacts in a bonding fashion with πz (HOMO−1, middle of Fig. 4) or with π2 of the bridge to establish the second π acceptor orbital lying at low electronic energies (Fig. 4, bottom). In a localized bonding picture these two π bonding orbitals would account for one π bond at each rhenium center and together with the σ bonds the Re=C double bond character results.

IV. Electrochemical and spectroscopic studies of E-6(S) and 7

IVa. Cyclic voltammetry (CV) studies of the dinuclear rhenium complexes E-6(S), E-6[PF6]2 and 7[PF6]2

Voltammograms of E-6[PF6]2 (Fig. 2a) recorded in THF displayed two reversible waves at E1/2 = −1.292 V and E1/2 = −1.749 V. The electrochemical and structural data in concert support a stepwise reduction of E-6[PF6]2. This is accompanied by an electronic re-adjustment of the C2H2 linkage from an ethylene biscarbonyl to a bis(ylidene) structure revealing that the
Redox processes are to a great extent bridge-centered as is also mandated by the HOMO of E-6[PF₆]₄ as shown in Fig. 2. The potential difference \( \Delta E_{1/2} \) between the two redox waves of 0.457 V results in a \( K_c \) value of \( 7.1 \times 10^7 \). Cyclic voltammetry measurements of E-6(S) gave identical results apart from the fact that the forward peaks were now anodic instead of cathodic. In comparison with the manganese analog [(Me₅C₅)(dmpe)Mn[PF₆]₂, the values of the two redox couples of E-6[PF₆]₄ are more negative and the \( K_c \) value is smaller (Table 2). In accordance with the CV study, neutral E-6 is very easy to oxidize (Fig. 5).

The CV of trans-[Me₅SiC≡C][PF₆]₄Re≡C≡CH≡C≡Re[PMe₃][Me₅SiC≡C][PF₆]₂ (7[PF₆]₂) in THF showed four separate waves with high degrees of chemical reversibility corresponding to four consecutive reductions from [7]²⁺ → [7]⁻ → [7]⁻ → [7]⁰. The potential difference \( \Delta E_{1/2} \) between the first redox waves of 7[PF₆]₂ is 0.504 V resulting in a \( K_c \) value of \( 4.7 \times 10^8 \) with 7[PF₆]₂ as an in principle isolable intermediate redox state as also revealed in the spectro-electrochemical studies. However, attempts to prepare 7[PF₆]₂ were unsuccessful. The third and fourth redox processes have very negative potentials, which make the corresponding reduced species [7]⁻ and [7]⁻⁻ difficult to prepare by chemical methods. For [7]⁻ and [7]⁻⁻ we have to assume bridge-centered reduction steps. The \( \Delta E_{1/2} \) values of the complexes 6[PF₆]₄ (0.475 V) and 7[PF₆]₂ (0.504 V) are very close. The only difference in these complexes are the bridges, therefore one might conclude that the strengths of electronic communication through the C₄H₂ and the C₄ bridges are very similar.

### Table 2: Electrochemical data for 6, 6[PF₆]₄ and 7[PF₆]₂ and for some dinuclear manganese and rhenium complexes, E vs. Fc⁰/⁺

<table>
<thead>
<tr>
<th>Complexes</th>
<th>Couple 1</th>
<th>Couple 2</th>
<th>( \Delta E ) (V)</th>
<th>( K_c ) (M⁻¹ cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Me}_5\text{SiC≡C}][\text{PF}_6]_4\text{Re≡C≡CH≡C≡Re[PMe}_3][\text{Me}_5\text{SiC≡C}][\text{PF}_6]_2) (E-6[PF₆]₄)</td>
<td>−1.292</td>
<td>−1.749</td>
<td>0.457</td>
<td>( 7.1 \times 10^7 )</td>
<td>Present work</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7Bdepe%7D">\text{MeC}_5\text{H}_4</a>\text{Mn≡C≡CH≡C≡Mn}(\text{depe})[\text{MeC}_5\text{H}_4][\text{PF}_6]_2)</td>
<td>−0.820</td>
<td>−1.386</td>
<td>0.576</td>
<td>( 6.6 \times 10^9 )</td>
<td>23d</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7Bdmpe%7D">\text{MeC}_5\text{H}_4</a>\text{Mn≡C≡Mn(dmpe)}[\text{MeC}_5\text{H}_4][\text{PF}_6]_2)</td>
<td>−0.847</td>
<td>−1.835</td>
<td>0.988</td>
<td>( 8.6 \times 10^{16} )</td>
<td>23d</td>
</tr>
<tr>
<td>([\text{Me}_5\text{SiC≡C}][\text{PF}_6]_4\text{Re≡C≡C≡C≡Re[PMe}_3][\text{Me}_5\text{SiC≡C}][\text{PF}_6]_2) (7[PF₆]₂)</td>
<td>−1.164</td>
<td>−1.668</td>
<td>0.504</td>
<td>( 4.7 \times 10^8 )</td>
<td>Present work</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D">\text{Cp}^*</a>\text{Re≡C≡C≡C≡Re[PPh}_3]<a href="%5Ctext%7BCp%7D%5E*">\text{NO}</a>]</td>
<td>0.06</td>
<td>0.59</td>
<td>0.53</td>
<td>( 1.1 \times 10^8 )</td>
<td>10a</td>
</tr>
</tbody>
</table>

**IVb. NIR evidence for through-bridge electronic interaction in E-6(S), E-6[PF₆]₄ and E-6[PF₆]₂**

To further assess the extent of the electronic interaction between the two redox-active rhenium centers of E-6(S), E-6[PF₆]₄ and E-6[PF₆]₂, the UV-vis spectra of E-6(S), E-6[PF₆]₄ and E-6[PF₆]₂ were examined (Fig. 6). Due to limited solubility and stability in other solvents, the neutral complexes could be studied in THF only and the examination of a solvent effect of the MV complexes could not be performed. The UV-vis spectral data and IVCT absorption data for the MV complexes are listed in Tables 2 and S3.

The UV-vis spectra of all complexes E-6(S), E-6[PF₆]₄, and E-6[PF₆]₂ show intense absorption bands in the visible and ultraviolet region, which can be attributed to a metal-to-ligand charge transfer (MLCT) transition (Fig. 6 and Table S3 in the ESI†). In the visible and near-infrared region an additional absorption band is observed at approximately 897 nm (\( \epsilon \) is about \( 1.90 \times 10^4 \) M⁻¹ cm⁻¹) with a noticeable shoulder at \( \sim 800 \) nm for the MV complex E-6[PF₆]₂. There are no counterparts in the spectra of the corresponding neutral complex E-6(S) and the dicationic complex E-6[PF₆]₂, so that they may be identified as intervalence charge transfer (IVCT) bands. Observations of multiple IVCT bands have been reported previously for the MV complexes [(C₅Me₅)(dmpe)Mn(≡CPh≡CPh≡C≡C)]⁺, [(η⁵-C₅Me₅)(NO)(PPh₃)Re]₂[μ-C≡C=C≡C≡C]⁺, and [(C₅Me₅)(dpmm)Fe]₂[μ-C≡C=C≡C≡C]⁺. An explanation considered is spin–orbit coupling, which is of particular relevance in third-row transition metals. An alternative assignment is that one absorption is a LMCT transition, which is part of a MLCT transition, and the other a MLCT transition. Considering the strongly metal–ligand delocalized nature of the frontier MOs, the underlying transitions may be best viewed as \( π \rightarrow π^* \) type transitions within a conjugated open-shell metal–organic \( π \)-system with only a limited amount of charge transfer between the individual constituents. On the premise that the observed absorptions can be viewed as IVCT transitions, a Gaussian analysis of the IVCT absorption band of the MV complex was performed in order to calculate the electronic coupling energy \( H_{ab} \). The spectrum of the mixed valence complex E-6[PF₆]₄ can be deconvoluted into three Gaussian bands A, B, and C (ESI†), where band B is the major component, and with a tail of the MLCT band observed in the visible and ultraviolet regions. Spectral data extracted from the IVCT band shape analyses are summarized in Table S3 (ESI†).
The observed bandwidths of the three bands at half height \((\Delta \nu/2)\) are narrower than those predicted from the equation \(\Delta \nu = (2310 \nu_{\text{max}})^{1/2}\), which is in agreement with a class III character for the MV complex. In addition, the delocalization parameters \(I\) as calculated from the equation \(I = 1 - \Delta \nu/2(2310 \nu_{\text{max}})^{1/2}\), are larger than \((A, B)\) or close to \((C)\) 0.5 for all bands. Based on the CV and NIR spectroscopic data, the MV complex \(E-6[PF_6]\) can be described as a class III MV compound with the odd electron fully delocalized over the ReC4 core. Based on the values of Table 3 electronic coupling energies \(H_{ab}\) for band A, band B, and band C of \(E-6[PF_6]\) are 5.43 \times 10^{-1} \text{ cm}^{-1}, 6.10 \times 10^{-1} \text{ cm}^{-1}, and 7.24 \times 10^{-1} \text{ cm}^{-1}, respectively.

### Table 3 UV-vis-NIR spectral data for complexes \(E-6(S)\), \(E-6[PF_6]\), and \(E-6[PF_6]_2\)

<table>
<thead>
<tr>
<th>Complex</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\nu_{\text{max}}) (cm(^{-1}))</th>
<th>(\varepsilon_{\text{max}}) (M(^{-1})cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E-6(S))</td>
<td>390</td>
<td>(2.56 \times 10^{4})</td>
<td>(4.04 \times 10^{4})</td>
</tr>
<tr>
<td>(E-6[PF_6])</td>
<td>457</td>
<td>(2.19 \times 10^{4})</td>
<td>(5.02 \times 10^{4})</td>
</tr>
<tr>
<td>(E-6[PF_6]_2)</td>
<td>897</td>
<td>(1.14 \times 10^{4})</td>
<td>(1.90 \times 10^{4})</td>
</tr>
<tr>
<td></td>
<td>460</td>
<td>(2.17 \times 10^{4})</td>
<td>(3.30 \times 10^{4})</td>
</tr>
</tbody>
</table>

Variable-temperature magnetic susceptibility measurements were carried out in the temperature range from 5 K to 300 K. The magnetic properties are presented in the form of \(\chi_m\) and \(\chi_mT\) vs. \(T\) plots in Fig. 6b. The MV complex \(E-6[PF_6]\) showed typical paramagnetic behavior with the magnetic susceptibility \(\chi_m\) dropping abruptly from 5 K to 50 K then gradually and the \(\chi_mT\) value decreasing from 5 K to 300 K. This is a manifestation of the paramagnetism expected from the odd electron in this molecule.

**IVc. Spectro-electrochemical studies on \([7[PF_6]\)**

The high chemical reactivity of the reduced forms \(7[PF_6]\) prevented their isolation as pure compounds. In order to characterize them by IR- and UV-Vis-NIR-spectroscopy we resorted to their generation in situ by means of spectro-electrochemistry. Inside an OTTLE (optically transparent thin layer electrolysis) cell three consecutive reductions of \([7[PF_6]\] could be followed. Just like in the solid state, \([7[PF_6]\] only showed a weak \(\nu(C==C)\) stretching vibration at 1818 cm\(^{-1}\) in the THF/NBu4PF6 electrolyte. Upon reduction to \([7]^-\) species the original \(\nu(C==C)\) band was replaced by a much stronger absorption at 1992 cm\(^{-1}\) and a much weaker one at 1612 cm\(^{-1}\). During the second reduction to the neutral complex \(7\) the former \(\nu(C==C)\) band gave way to an even stronger absorption at 1597 cm\(^{-1}\), while the band at 1612 cm\(^{-1}\) was replaced by a stronger one at 1738 cm\(^{-1}\) (Fig. 8). Both these processes were fully reversible as ascertained by the presence of clean isosbestic points and

**Table 3**

UV-vis-NIR spectral data for complexes \(E-6(S)\), \(E-6[PF_6]\), and \(E-6[PF_6]_2\)

<table>
<thead>
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<th>Complex</th>
<th>(\lambda_{\text{max}}) (nm)</th>
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<td>(2.19 \times 10^{4})</td>
<td>(5.02 \times 10^{4})</td>
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<tr>
<td>(E-6[PF_6]_2)</td>
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<td>(1.14 \times 10^{4})</td>
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</tr>
<tr>
<td></td>
<td>460</td>
<td>(2.17 \times 10^{4})</td>
<td>(3.30 \times 10^{4})</td>
</tr>
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</table>
full recovery of the original spectrum of $[7\text{PF}_6]_2$ upon exhaustive back electrolysis at a potential sufficiently positive of the $[7^+\text{PF}_6]_2$ and $[7^2+\text{PF}_6]_2$ redox waves. Identical results were obtained using the 1,2-C$_2$H$_4$Cl$_2$/NBu$_4$PF$_6$ electrolyte ([7]$^+$): $\nu$(C≡C) = 2016 cm$^{-1}$; [7]$^+$: $\nu$(C≡C) = 1991 cm$^{-1}$, $\nu$(C≡C) = 1615 cm$^{-1}$; 7: $\nu$(C≡C) = 1958 cm$^{-1}$, $\nu$(C≡C) = 1738 cm$^{-1}$). Low energies of $\nu$(CC) stretching bands are not without precedence in C$_4$-bridged dimetal complexes and are indicative of the cumulenic character of the all-carbon bridge as in 7(S) (Scheme 6).$^{11,23}$ Of note is the rather strong shift of the $\nu$(C≡C) bands assigned to the terminal alkynyl ligands upon stepwise reduction. It is much stronger than in comparable C$_4$-bridged dimanganese complexes (2026 → 2010 cm$^{-1}$).$^{23,24}$ This points to significant contributions of the terminal alkynyl ligands to the HOMO of [7]$^+$ and the SOMO of [7]$^-$ and hence an enhanced delocalization of the charge onto the terminal alkynyl ligands for the heavier congener.

Attempts to further reduce 7 to [7]$^-$ resulted in a sequence of two consecutive electron transfers and subsequent protonation steps to ultimately yield complex E-6. This is clearly seen from the growth of $\nu$(C≡C) and $\nu$(C≡C) bands at 1972 and 1545 cm$^{-1}$ during this process. These bands are virtually identical to those of pristine solid E-6. Furthermore, stepwise re-oxidation of the exhaustively reduced solution first gave a $\nu$(C≡C) band at 1999 cm$^{-1}$ and, after the final re-oxidation step, a band at 2022 cm$^{-1}$ in agreement with the ATR data of complexes E-6[PF$_6$]$_2$ and E-6[PF$_6$]$_3$. When solutions of [7][PF$_6$]$_2$ were on partially electrolyzed at potentials negative of the 7/[7]$^-$ wave the spectroscopic features of species 6 and 7 were detected without any detectable intermediate [7]$^-$ (Fig. 9a). Stepwise reoxidation of such incompletely reduced solutions first produced mixtures of complexes 7[PF$_6$]$_2$ and E-6[PF$_6$]$_2$ and then of E-6[PF$_6$]$_2$ and 7[PF$_6$]$_2$ (Fig. 9b and c).

In situ reduction of [7][PF$_6$]$_2$ under UV/Vis/NIR monitoring also occurred in two well-resolved steps to first produce the radical cation [7]$^+$ and then neutral 7, again with clean isosbestic points for each individual step (Fig. 10). During the first reduction, the prominent near UV band of [7]$^+$ peaking at 376 nm sharpened and red-shifted into the visible range to produce an intense peak at 409 nm, while a plateau-like absorption of [7]$^2+$ with peak positions at 510 and 570 nm develops into a considerably more richly structured absorption...
with individual peaks at 498, 533, 588, and 696 nm. In the NIR a much weaker and likewise structured absorption is seen in the 900 to 1500 nm range (see the inset of Fig. 10a). This band is also seen in IR-spectroelectrochemistry as a rising baseline near the high-energy limit of the detector. None of these bands readily qualifies for an IVCT transition of a mixed-valent system. On the other hand structured absorptions of ligand centered radicals, they could not be fully characterized due to the instability of these species, thus defying its classification as a classical mixed-valent species. Further studies are ongoing in our group for functionalization of the terminal group of E-6 and 7 with the appropriate end groups sticking to gold electrodes suitable for single molecule conductance measurements.

Acknowledgements

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