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Facile Synthetic Access to Rhenium(II) Complexes: Activation of Carbon–Bromine Bonds by Single-Electron Transfer

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Abstract: The five-coordinated Re^{I} hydride complexes $[Re(Br)(H)(NO)(PR_3)_2]$ (R = Cy **1a**, *i*Pr **1b**) were reacted with benzylbromide, thereby affording the 17-electron mononuclear Re^{II} hydride complexes $[Re(Br)_2(H)(NO)(PR_3)_2]$ (R = Cy **3a**, *i*Pr **3b**), which were characterized by EPR, cyclic voltammetry, and magnetic susceptibility measurements. In the case of dibromomethane or bromoform, the reaction of **1** afforded Re^{II} hydrides **3** in addition to Re^{I} carbene hydrides $[Re(=CHR^1)(Br)(H)(NO)(PR_3)_2]$ (R^1 = H **4**, Br **5**; R = Cy **a**, *i*Pr **b**) in which the hydride ligand is positioned *cis* to the carbene ligand. For comparison, the dihydrogen Re^{I} dibromide complexes $[Re(Br)_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$ (R = Cy **2a**, *i*Pr **2b**) were reacted with allyl- or benzylbromide, thereby affording the monophosphine Re^{II} complex salts $[R_3PCH_2R'][Re(Br)_4(NO)(PR_3)]$ (R′ = −CH=CH_2 **6**, Ph **7**). The reduction of Re^{II} complexes has also been examined. Complex **3a** or **3b** can be reduced by zinc to afford **1a** or **1b** in high yield. Under catalytic conditions, this reaction enables homocoupling of benzylbromide (turnover frequency (TOF): **3a** 150, **3b** 134 h^{-1}) or allylbromide (TOF: **3a** 575, **3b** 562 h^{-1}). The reaction of **6a** and **6b** with zinc in acetonitrile affords in good yields the monophosphine Re^{I} complexes $[Re(Br)_2(NO)(MeCN)_2(PR_3)]$ (R = Cy **8a**, *i*Pr **8b**), which showed high catalytic activity toward highly selective dehydrogenative silylation of styrenes (maximum TOF of 61 h^{-1}). Single-electron transfer (SET) mechanisms were proposed for all these transformations. The molecular structures of **3a**, **6a**, **6b**, **7a**, **7b**, and **8a** were established by single-crystal X-ray diffraction studies.

Keywords: carbenes · electron transfer · hydrides · phosphanes · rhenium

Introduction

Rhenium is an extraordinarily redox-active element spanning a wide range of oxidation states from −III to VII.[1] Among these redox states, the 17-electron Re^{II} chemistry is particularly interesting due to its potential application in inorganic medicinal chemistry, and other studies have demonstrated its potential application in molecular magnetism.[2] However, Re^{II} chemistry is surprisingly scarce with just a few mononuclear Re^{II} compounds reported; these were mainly accessed by the following approaches: 1) homolytic scission of Re–Re bonds of dinuclear Re^{II} units such as $[Re_2(NCCH_3)_{10}]^{4+}$;[3] 2) selective reduction of higher oxidation-state complexes such as the Re^{III} compound $[Re(OPPh_3)Cl_3(L)]$;[4] and 3) selective oxidation of lower oxidation-state complexes such as $[NBu_4]$*trans*-$[Re(CN)_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane),[5] *fac*-$[Re(PPh_3)(PF_3)(dien)(N_2)]^+$ (dien = diethylenetriamine),[6] and those with *fac*-$[Re(CO)_3]^+$ units.[7] In contrast to the manganese congeners, organometallic Re^{II} compounds possess inherent stability, which greatly depends on the ligand environment. Pseudo-octahedral, d^7 complexes, such as Re^{II} species, could in principle take over an important role in redox catalysis and homogeneous catalysis.[8] To be able to exploit Re^{II} chemistry for catalysis, we also needed to know about its prevalent radical character: σ or π type. Therefore we sought to explore organometallic Re^{II} chemistry and perhaps get an idea about the stability criteria for organometallic Re^{II} complexes. In addition, such knowledge was required to develop appropriate synthetic access.

In recent years, our group has focused on the exploration of low-valent rhenium hydride chemistry.[9] Lately, it was found that five-coordinate, 16-electron Re^{I} hydride complexes $[Re(Br)(H)(NO)(PR_3)_2]$ (R = Cy **1a**, *i*Pr **1b**),[10] de-

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rived from easily accessible Re^{I} dihydrogen dibromides $[Re(Br)_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$ (R = Cy **2a**, *i*Pr **2b**), exhibited a versatile reactivity toward H_2, olefins, *n*BuLi, N-heterocyclic carbenes (NHCs), carbenes, and terminal alkynes.[11] In an extension of this work and to account for the aspects of organometallic radical chemistry just discussed, we report here the reactions of **1** and **2** toward the alkyl bromides including allyl-, benzylbromide, dibromomethane and bromoform, which are often seen as radical initiators.

Results and Discussion

Reaction of $[Re(Br)(H)(NO)(PR_3)_2]$ (1) with benzylbromide, CH_2Br_2, and $CHBr_3$: Alkyl halides are known as single-electron acceptors in reductive electron-transfer processes.[12,8g,h] The C–X bonds next to π-conjugate groups such as benzyl are particularly weak.[13] Treatment of a violet solution of **1a** or **1b** in benzene with benzylbromide (1.1 equiv) at room temperature immediately afforded a brown solution, from which the mononuclear bisphosphine Re^{II} hydride complexes $[Re(Br)_2(H)(NO)(PR_3)_2]$ (R = Cy **3a**, *i*Pr **3b**) were isolated in 88 (**3a**) or 80% (**3b**) yield (Scheme 1). The presence of 1,2-diphenylethane in the reaction mixture was confirmed by both ^1H NMR spectroscopy and GC–MS analyses. In the IR spectra of **3a** and **3b**, strong ν(NO) absorptions were observed at 1703 (**3a**) or 1694 cm^{-1} (**3b**), thus indicating the presence of a single mononitrosyl species; despite the radical character of the species and expected thermal lability, satisfactory elemental analyses were also obtained. Single crystals of **3a** were obtained by means of slow diffusion of pentane into a solution of **3a** in benzene, and the molecular structure of **3a** was established by an X-ray diffraction study, as depicted in Figure 1.[14] The molecule adopted a pseudo-octahedral geometry around the rhenium center with the hydride being *trans* to one bromide ligand (Br2-Re1-H angle of 172.0(11)°). The NO group is linear with the *trans*-bromide ligand with a N1A-Re1-Br1A angle of 178.87(16)°. The two *trans*-phosphine ligands are bent strongly toward the rhenium hydride ligand with a P2-Re1-P1 angle of 147.94(2)°, presumably mainly due to the presence of the π-donating bromide ligand *trans* to the hydride ligand.[15] The asymmetry in the different angles of Br2-Re1-P2 (105.45(2)°) and P1-Re1-Br1A (90.00(2)°) indicates a distortion from a pseudo-octahedral towards a "pentagonal bipyramidal" geometry. The "pentagonal" equatorial plane would be defined by P1, P2, Br2, and H, and a sterically demanding σ-type radical. The P1-Re1-H (74.6(11)°) and P2-Re1-H (73.4(11)°) angles are indeed close to the angle of 72° expected for this pseudogeometry. This may point to a soft energy surface for the movement of Br_{eq} toward P1 or P2 reaching the extreme position of Br_{eq} with a P-Re(1)-Br(2) angle of 72° and a small activation barrier for the conversion of a π-type (Br_{eq} in symmetric pseudo-octahedral position) to a σ-type radical.

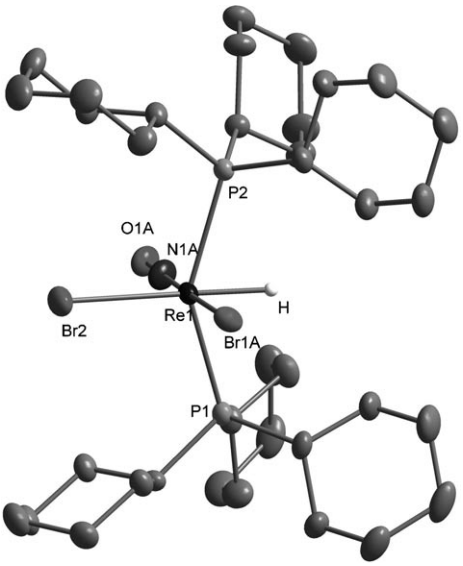
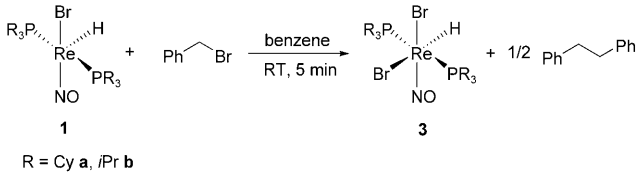


Figure 1. Molecular structure of $[Re(H)(Br)_2(NO)(PCy_3)_2]$ (**3a**) at 30% probability ellipsoids (selected hydrogen atoms and the *trans*-NO/Br positional disorder have been omitted for clarity). Selected bond lengths [Å]: P1–Re1 2.4709(7), P2–Re1 2.4732(8), Br1A–Re1 2.5213(6), N1A–O1A 1.229(6), Br2–Re1 2.5809(4). Selected bond angles [°]: P1-Re1-P2 147.94(2), O1A-N1A-Re1 179.0(4), N1A-Re1-Br1A 178.87(16), P1-Re1-H 74.6(11), P2-Re1-H 73.4(11), P1-Re1-Br2 106.486(18), P2-Re1-Br2 105.45(2), P1-Re1-Br1A 90.00(2), Br2-Re1-H 172.0(11).



Scheme 1.

EPR measurements were carried out on **3b** in toluene at 293 and 98 K. The spectra are shown in Figure 2. At room temperature, a well-resolved sextet was observed due to the hyperfine coupling of the unpaired electron with the magnetic nuclei of rhenium (^{185}Re, 37.4%, spin (I) = 5/2, μ_N(nuclear magnetic moment) = 3.187; ^{187}Re, 62.6%, I = 5/2, μ_N = 3.220). The hyperfine coupling constants a_i are unequal and increase from low-field to high-field spanning in the range of 22.0–29.1 mT (average: 25.5 mT) due to second-order effects (hyperfine splitting non-negligible versus external field).[16] Such a pattern resembles closely those of reported Re^{VI} compounds.[17] The observed center field g value of 2.0018 is surprisingly but only coincidentally close to the free-electron value of 2.00232. The magnitude of a_i indicates that the spin density is mainly concentrated on the metal center, which speaks more to a σ-type radical. The EPR measurement in toluene glass at 98 K showed a complex spectrum with overlapping signals, which was caused by

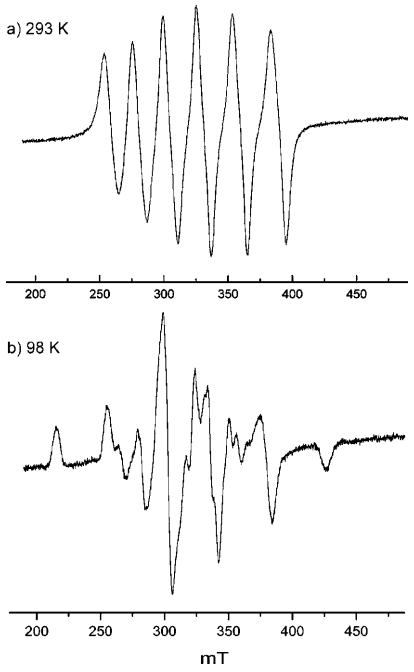


Figure 2. a) X-band EPR spectra of a solution of **3b** in toluene at 293 K (top). b) Low-temperature glass spectrum of **3b** at 98 K (bottom).

g anisotropy rather than by hyperfine coupling with the hydride (^{1}H, $I=^{1}/_{2}$), phosphine (^{31}P, $I=^{1}/_{2}$), bromide (^{79,81}Br, $I=^{3}/_{2}$), or nitrosyl ligand (^{14}N, $I=1$). The extracted values are $g_1=1.98$, $g_2=2.05$, $g_3=1.98$, and $a_1=43$, $a_2=18$, $a_3=15$ mT for the ^{185,187}Re coupling. These results further stress that spin density is mainly localized on the rhenium center and not to a significant extent on the ligands.

Magnetic susceptibility data of **3a**,**b** were measured in the temperature range of 5–300 K and are shown in Figure 3. At low temperature, the effective magnetic moment (μ_{eff}) values of 1.61 μ_B for **3a** and of 1.64 μ_B for **3b** (μ_B Bohr magneton) were determined in accordance with a d^5 system bearing an unpaired electron. The electrochemical behavior of **3b** has also been investigated by cyclic voltammetry. However, both oxidation and reduction are irreversible in

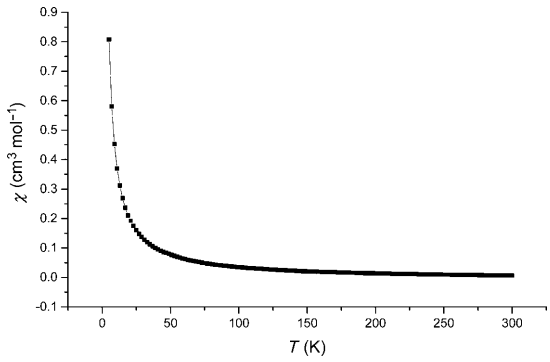
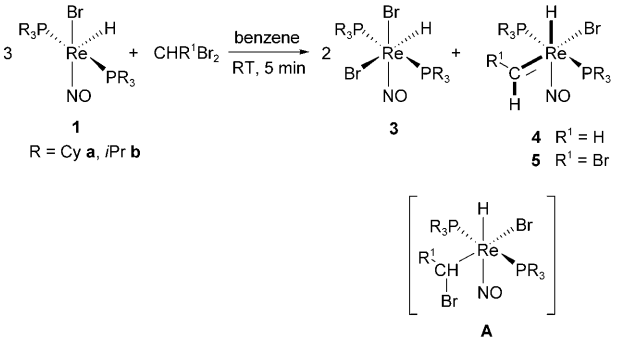


Figure 3. Temperature-dependent magnetic susceptibility data of **3a** recorded in the range of 5–300 K.

THF, most probably due to further reactions of the hydride ligand in the cation proton loss[18] or of irreversible Br^- ligand loss from the anion.

The reactivity of other alkyl halides towards **1a** or **1b** was also examined. Bromoethane and *tert*-butylbromide proved to be inert toward **1a** or **1b** even at higher temperatures (80 °C). The reaction with allylbromide was found to be complicated and could not be unraveled, since the allyl group might also coordinate to the rhenium vacant site, thereby leading to a 18-electron Re^{I} complex. Interestingly, dibromomethane does react with **1a** or **1b**, but in a different manner than benzylbromide did. Treatment of a violet solution of **1a**,**b** in benzene with CH_2Br_2 (0.5 equiv) immediately afforded a deep brown solution, from which a mixture containing the Re^{II} hydride **3a**,**b** and a Re^{I} carbene hydride complex $[Re(=CH_2)(Br)(H)(NO)(PCy_3)_2]$ (R = Cy **4a**, *i*Pr **4b**) was obtained (Scheme 2). In the ^{1}H NMR spectra, a doublet at $\delta=14.79$ (**4a**, J(H,H) = 4 Hz) or 14.92 ppm (**4b**,



Scheme 2.

J(H,H) = 4 Hz) was assigned to one of the carbene protons. The resonance of the other proton of the carbene ligand appeared as a doublet of doublets at $\delta=14.59$ (**4a**, J(H,H) = 4 Hz, J(=CH,ReH) = 10 Hz) or 14.76 ppm (**4b**, J(H,H) = 4 Hz, J(=CH,ReH) = 10 Hz). This is interpreted in terms of a *transoid* ^{3}J coupling with the rhenium hydride (see Scheme 2), which was observed as a triplet of doublets at $\delta=2.42$ (**4a**, ^{2}J(H,P) = 34 Hz, ^{3}J(=CH,ReH) = 10 Hz) or 2.40 ppm (**4b**, ^{2}J(H,P) = 34 Hz, ^{3}J(=CH,ReH) = 10 Hz). This indicates that the carbene shows hindered rotation around the Re=CH_2 bond and the two $C_{carbene}$–H bonds are in a same plane with the H-Re-NO plane so as to maximize the π back-donation from rhenium to the empty p orbital of the carbene carbon atom. This hypothesis was further substantiated by a ^{1}H TOCSY experiment for **4a**, in which the dipolar H···H coupling (NOE) detectable through irradiation of the carbene proton signal at $\delta=14.59$ ppm indicates their spatial proximity. This demands the *cis* position of the hydride and the carbene ligand. The preference for this geometry requires rearrangement of the initial coordination sphere, which stresses the need for geometrical flexibility of such rhenium nitrosyl systems. One main driving force for

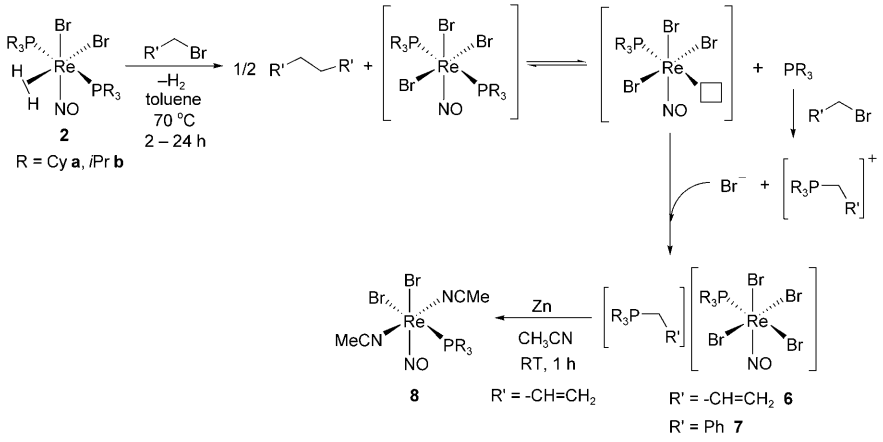
such a geometrical change could be the "push–pull" type *trans* arrangement of the π-donor bromide and the π-acceptor carbene ligand (=CH_2). In the $^{13}C\{^1H\}$ NMR spectra, the multiplet resonance at $\delta = 278.1$ (**4a**) or 279.0 ppm (**4b**) was assigned to the $C_{carbene}$ atom, which was further supported by $^{13}C,^1H$ correlation spectra that demonstrated a correlation between this signal and the proton signal of the rhenium hydride. In the $^{31}P\{^1H\}$ NMR spectra, a singlet at $\delta = 46.0$ (**4a**) or 52.6 ppm (**4b**) was observed in accord with the *trans* disposition of the phosphine ligands. In the IR spectra, besides the ν(NO) absorption for **3a,b**, a strong stretching vibration of the NO group at 1670 (**4a**) or 1661 cm^{-1} (**4b**) was observed. It should be noted that products based on the appearance of a free bromomethylene radical (•CH_2Br), like, for instance, its recombination product dibromoethane, were not observed by in situ NMR spectroscopy and GC–MS. No obvious formation of other organic products was observed. We therefore assume primary intermediacy of the bromoalkyl Re^{II} species (**A**) shown in Scheme 2, which is thought to be subjected to another bromide abstraction by **1** so that an overall stoichiometry of 2:1 arises between the products **3** and **4**. Although **3a** and **3b** could be isolated from the mixture in 27 and 34% yield, respectively, attempts to separate **4a** and **4b** failed.

Similarly, the reaction of **1a**,**b** with bromoform (0.5 equiv) afforded within 5 min a mixture that contained **3a**,**b** and a Re^I carbene hydride complex [Re(=CHBr)(Br)(H)(NO)-$(PCy_3)_2$] (R = Cy **5a**, *i*Pr **5b**; Scheme 2). In the ^1H NMR spectra, a doublet at $\delta = 14.20$ (**5a**) or 14.30 ppm (**5b**) was assigned to the carbene proton. The magnitude of the coupling constant (11 Hz) indicated, like in complexes **4**, a *transoid* alignment of the carbene C–H and the Re–H ligand. The resonance for the hydride was observed as a triplet of doublets at $\delta = 2.20$ (**5a**, $^2J(H,P) = 35$ Hz, $^3J(=CH,ReH) = 11$ Hz) or 2.04 ppm (**5b**, $^2J(H,P) = 35$ Hz, $^3J(=CH,ReH) = 11$ Hz). In the $^{13}C\{^1H\}$ NMR spectra, a singlet at $\delta = 250.8$ (**5a**) or 252.3 ppm (**5b**) was assigned to the $C_{carbene}$ atom. The $^{31}P\{^1H\}$ NMR spectra showed a singlet at $\delta =$ 38.8 ppm for **5a** and at 46.9 ppm for **5b**.

In the presence of radical scavengers such as tetramethylpiperidine oxide (TEMPO), the reaction of **1a** with $PhCH_2Br$ afforded **3a** and the primary radical trapped product TEMPO–CH_2Ph, as proven by ^1H NMR spectroscopy ($\delta =$ 4.89 ppm, s; CH_2). Formation of 1,2-diphenylethane was not observed. In the reaction of **1a** with CH_2Br_2, the presence of TEMPO in benzene blocked the formation of the carbene compound **4a** completely. The •CH_2Br radical was trapped by TEMPO to give the adduct TEMPO–CH_2Br, which was detected by ^1H NMR spectroscopy ($\delta = 5.58$ ppm, s; CH_2). Similarly, formation of **4a** was not observed, even when other single-electron transfer (SET) scavengers such as *p*-dinitrobenzene were used.[19] These results indicate that **4a** is derived from the bromomethylene radical •CH_2Br through the bromomethyl rhenium(II) intermediate.

A plausible pathway for the reaction of **1** with $PhCH_2Br$ and CH_2Br_2 was thus proposed. Single-electron transfer (SET) from **1** to the C–Br bond of benzylbromide occurs to afford **3** along with the formation of the benzyl radical ($PhCH_2$•), which undergoes dimerization to afford 1,2-diphenylethane. In the case of CH_2Br_2, the reaction takes place probably through the coordination of the C–Br bond to the vacant site of **1**. The formed intermediate reacts with another equivalent of **1**, thus yielding **3** and the bromomethylene radical (•CH_2Br) coordinated species. As one C–Br bond is still present, it further accepts one electron from **1**, thereby resulting in the formation of the carbene hydride **4** and another equivalent of **3**. The geometry change might also occur in this process. It should also be pointed out that activation of *gem*-dihalide by late-transition-metal compounds such as those with rhodium centers have been widely explored.[20] However, they all take place by means of oxidative addition of carbon halogen bonds to metals, thus resulting in oxidation states increased by two. Furthermore, one-pot syntheses of carbene compounds from the reactions of ruthenium complexes with *gem*-dihalide have also been reported through oxidative addition followed by an α-halide elimination process.[21] In comparison, CH_2Br_2 or $CHBr_3$ act in the reaction with **1a**,**b** as a double single-electron acceptor.

Reactions of $[Re(Br)_2(NO)(PR_3)_2(\eta^2\text{-}H_2)]$ (2) with allyl- and benzylbromide: Treatment of a solution of **2a** in toluene with an excess amount of allylbromide (10 equiv) afforded at 70 °C within 24 h the monophosphine-coordinated Re^{II} complex salt $[Cy_3PCH_2CH{=}CH_2][Re(Br)_4(NO)(PCy_3)]$ (**6a**), which was isolated as a red solid in 53% yield (Scheme 3). By comparison, the reaction of **2b** bearing $PiPr_3$ ligands was



Scheme 3.

much faster, and a reaction time of 2 h was enough to achieve $[i\mathrm{Pr_3PCH_2CH{=}CH_2}][\mathrm{Re(Br)_4(NO)(P}i\mathrm{Pr_3)}]$ (**6b**) in 90% isolated yield. In both cases, one phosphine ligand dissociated from the rhenium center and was found bonded to the cationic allyl group. The allyl-dimerization product hexa-1,5-diene was detected by GC–MS in both reaction mixtures. Compounds **6a** and **6b** were characterized by various spectroscopic methods, gave correct elemental analyses, and were studied by single-crystal X-ray diffraction. IR spectroscopy confirmed the presence of one nitrosyl ligand that displayed strong ν(NO) absorptions at 1728 for **6a** and at 1731 cm^{-1} for **6b**. The X-ray diffraction study of **6a** (Figure 4) revealed a pseudo-octahedral rhenium center.[22] The ON-Re-Br angles of 169.8(3) and 170.8(3)° were found to deviate somewhat from the ideal 180°. The nitrosyl ligands were only slightly bent with O-N-Re angles of 173.6(11) and 171.6(11)° with relatively short N–O distances, which spoke to linear nitrosyl ligands.[23]

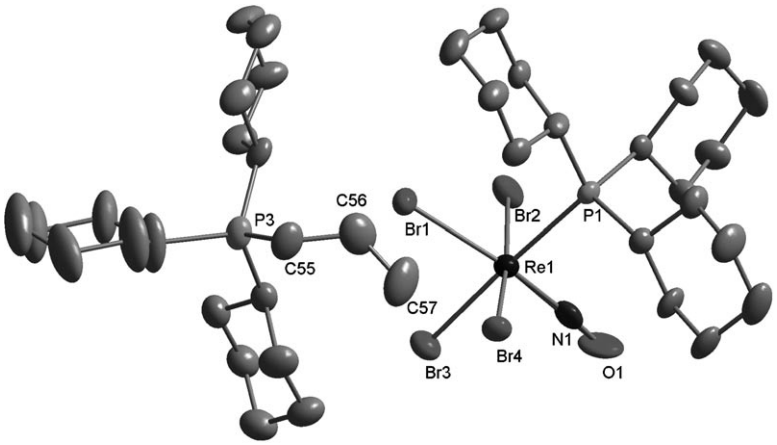
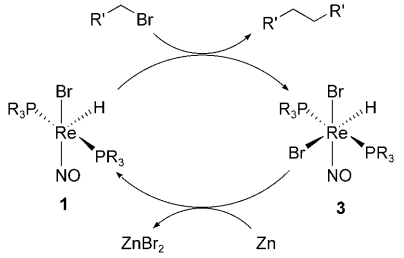


Figure 4. Molecular structure of $[\mathrm{Cy_3PCH_2CH{=}CH_2}][\mathrm{Re(Br)_4(NO)(PCy_3)}]$ (**6a**) with 20% probability displacement ellipsoids. Two of the four independent molecules are shown. All hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: Re1–N1 1.793(11), Re1–Br2 2.5147(11), Re1–Br4 2.5215(11), Re1–P1 2.546(3), Re1–Br3 2.5618(11), Re1–Br1 2.5718(11), N1–O1 1.046(12). Selected bond angles [°]: N1-Re1-Br1 169.8(3), P1-Re1-Br3 176.32(6), N1-Re1-Br2 89.3(3), N1-Re1-Br4 97.8(3), O1-N1-Re1 173.6(11).

In the same manner as allylbromide, **2a** and **2b** reacted with benzylbromide to give the monophosphine Re^{II} salts $[\mathrm{R_3PCH_2Ph}][\mathrm{Re(Br)_4(NO)(PR_3)}]$ (R = Cy **7a**, *i*Pr **7b**) in good yields. 1,2-Diphenylethane was detected by GC–MS in the reaction mixtures. Satisfactory elemental analyses were obtained for both compounds. The molecular structures of **7a** and **7b** were also established by X-ray diffraction studies given in the Supporting Information.

It should be noted at this point that other alkyl bromides such as bromoethane, *tert*-butylbromide, and dibromomethane were also tested in their reactions with **2a** and **2b**, but were found inert under various more forceful conditions, presumably due to stronger C–Br bonds in these cases and the accompanying higher barriers to homolysis or heterolysis relative to those of allyl- and benzylbromide. ^{1}H NMR spectroscopy analyses carried out on samples in the presence of TEMPO shows that the reaction of **2a** with allylbromide proceeded through the intermediacy of the allyl radical, thereby affording in benzene at 70°C the radical trapping product TEMPO–$CH_2CH{=}CH_2$. No evidence for allyl dimerization was given. Thus, a SET pathway is proposed in which the allyl- or benzylbromide acts not only as a single-electron acceptor but also as a phosphine trap. Therefore, for proper reactivity, 2 equiv of these reagents are needed. The reaction presumably proceeds through the initial loss of the labile H_2 ligand to afford five-coordinated, 16-electron intermediates, which further interact with the alkyl bromides by SET from rhenium to the C–Br bond, thereby leading in a redox process to the formation of the neutral transient $[\mathrm{Re^{II}Br_3(NO)(PR_3)_2}]$ complexes and alkyl radicals ($^{sp^2}$C–CHR•), which undergo recombination (Scheme 3). Presumably due to the presence of three bromide ligands, which cumulatively exert a strong *cis*-labilization effect, one phosphine ligand dissociates from the rhenium center of $[\mathrm{ReBr_3(NO)(PR_3)_2}]$ and gets replaced by a bromide ion. The bromide originates from the allyl- or benzylbromides by phosphine substitution to generate the phosphonium cations, which together with the anionic $[\mathrm{Re^{II}Br_4(NO)(PR_3)}]^-$ component form salts that precipitate from the toluene solution.

Reduction of Re^{II} complexes and their applications in catalyses: For the reduction of the Re^{II} complex, the brown solution of **3a** or **3b** was treated in THF with an excess of zinc at room temperature. A purple solution was formed within 30 min with the recovery of Re^{I} hydride in 82 (**1a**) or 78% (**1b**) yield obtained in situ by means of NMR spectroscopy. This result enables the development of rhenium-catalyzed homocoupling reactions of benzylbromide. As sketched in Scheme 4, the reaction of benzylbromide with zinc (0.5 equiv) in the presence of 1% of **3a** or **3b** as a catalyst in THF afforded 1,2-diphenylethane in a turnover frequency



TOF (h^{-1})	Ph	$CH{=}CH_2$
3a	150	575
3b	134	562

Scheme 4.

(TOF) value of 150 (**3a**) or 134 h^{-1} (**3b**). Interestingly, despite the complexity of their stoichiometric reactions with allylbromide, **3a** and **3b** proved to be highly active catalysts for the homocoupling of allylbromide. One percent of **3a** or **3b** with 0.25 equiv of zinc are enough to afford hexa-1,5-diene in THF at room temperature with good TOF values of 575 (**3a**) and 562 h^{-1} (**3b**), respectively. The catalytic reaction was found to be solvent dependent. No conversion was achieved when the reaction was carried out in nonpolar solvents such as benzene or toluene. This might be due to passivation of zinc caused by the formed zinc bromide that is insoluble in nonpolar solvents.

For comparison, the reduction of the orange-red solution of **6a** or **6b** with an excess of Zn powder (10 equiv) in acetonitrile took 1 h at room temperature to produce yellow mixtures, from which the monophosphine Re^{I} complexes $[Re(Br)_2(NO)(MeCN)_2(PR_3)]$ (R = Cy **8a**, *i*Pr **8b**) were isolated in 61 (**8a**) and 79% (**8b**) yield, respectively. Both compounds were fully characterized by elemental analyses and various spectroscopic methods. In the IR spectra, strong ν(NO) absorptions appeared at 1682 for **8a** and at 1685 cm^{-1} for **8b**. In the ^1H NMR spectra, singlets were detected at $\delta = 1.26$ for **8a** and at 1.25 ppm for **8b**, which were assigned to the protons of two identical acetonitrile ligands. This implies that the two acetonitrile ligands are arranged in a *trans* orientation. Integrations of the ^1H NMR spectroscopic signals of **8b** indicated a 2:1 ratio of the acetonitrile to phosphine ligands. In the ^{31}P NMR spectra, the resonances of the phosphorus ligands are shifted in comparison with the related bisphosphine monoacetonitrile Re^{I} complexes to lower field to $\delta = 3.2$ ppm for **8a** and 13.9 ppm for **8b**.[9f] The molecular structure of **8a** was also established by an X-ray diffraction study presented in Figure 5.[24] The molecule

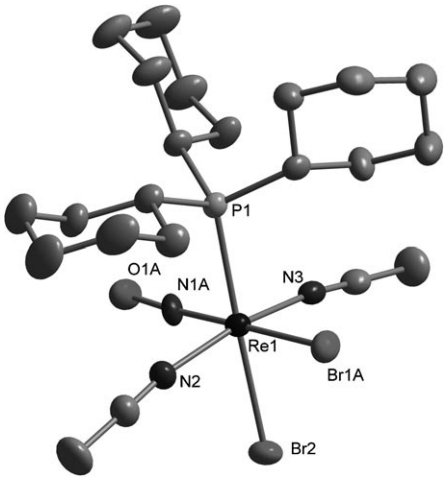
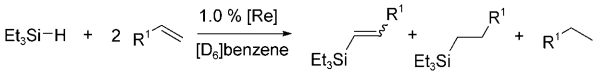


Figure 5. Molecular structure of $[Re(Br)_2(NO)(MeCN)_2(PCy_3)]$ (**8a**) with 30% probability displacement ellipsoids. The *trans*-NO/Br disorder and all hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: P1–Re1 2.4311(7), N1A–Re1 1.831(7), N2–Re1 2.060(2), N3–Re1 2.054(2), N1A–O1A 1.226(8). Selected bond angles [°]: P1-Re1-Br2 178.461(18), N1A-Re1-Br1A 178.7(3), N3-Re1-N2 168.66(9), O1A-N1A-Re1 173.5(10), Br1A-Re1-P1 92.28(5).

adopts a pseudo-octahedral geometry around the rhenium center with the phosphine in *trans* position to one of the bromides (P1-Re1-Br2 with an angle of 178.461(18)°). The *trans*-acetonitrile ligands are slightly bent with a N3-Re1-N2 angle of 168.66(9)°. The NO group is practically linearly aligned with the *trans* bromide with an average N-Re-Br angle of 177.5°.

Recently we reported that the bisphosphine compounds **2a** and **2b** are efficient catalysts for highly selective dehydrogenative silylation of alkenes.[10] However, the reaction can only be conducted at temperatures over 100 °C, which presumably was connected to the quite high energy barrier for the required dissociation of one phosphine ligand from the precatalyst to initiate the catalytic cycle. The application of the monophosphine compounds **8a** and **8b** as catalyst precursors would allow one to circumvent this difficulty in, for instance, dehydrogenative silylations of styrenes with Et_3SiH. Indeed, using **8a**, we found that the reaction temperature for this type of catalysis could be lowered

Table 1. Dehydrogenative silylation of styrenes catalyzed by Re^{I} complexes.[a]



Entry	R^1	[Re]	T [°C]	t [h]	Yield [%][b]	dehydro(*E*/*Z*)/hydro[c]
1	*p*-$CH_3C_6H_4$	**2a**	70	24	30	–
2	*p*-$CH_3C_6H_4$	**2b**	70	24	25	–
3	*p*-$CH_3C_6H_4$	**8a**	70	1.0	61	99(96:4):1
4	*p*-$CH_3C_6H_4$	**8b**	70	6.0	81	98(96:4):2
5	*p*-$CH_3C_6H_4$	**8a**	70	5.0	91	99(96:4):1
6	*p*-$CH_3C_6H_4$	**8a**	70	19	>99	99(96:4):1
7[d]	*p*-$CH_3C_6H_4$	**8a**	100	0.5	77	99(96:4):1
8[d]	*p*-$CH_3C_6H_4$	**8a**	100	2.0	>99	99(96:4):1
9	*p*-$CH_3OC_6H_4$	**8a**	70	20	92	99(>99:1):1
10	*p*-$CH_3OC_6H_4$	**8b**	70	20	90	99(>99:1):1
11	*p*-FC_6H_4	**8a**	70	5.0	92	99(>99:1):1
12	*p*-FC_6H_4	**8b**	70	4.0	89	99(>99:1):1
13[d]	$(EtO)_3Si$	**8a**	100	18	64	79(>99:1):21
14[d]	$(EtO)_3Si$	**8b**	700	20	51	75(>99:1):25
15	H	**8a**	70	4.0	>99	68:32
16	H	**8b**	70	7.0	>99	79:21

[a] 0.25 mmol of silane and 0.50 mmol of olefin. [b] From ^1H NMR spectroscopic integration. Hydrosilylation byproducts add up to 100%. [c] Determined by GC–MS. [d] In $[D_8]$toluene.

(Table 1). An exemplary experiment with **8a** (1.6 mg, 1.0%) dissolved in $[D_6]$benzene (0.5 mL) containing Et_3SiH (0.25 mmol) and *p*-methylstyrene (0.50 mmol) was carried out at 70 °C. It reached a TOF value of 61 h^{-1} after 1 h and 91% conversion within 6 h. This amounts to a reaction rate over 12 times faster than that catalyzed by **2a** under otherwise similar conditions. ^1H NMR spectroscopy and GC–MS indicated a selectivity of 99% for dehydrogenative silylation with the product 1-(*p*-methylstyryl)-2-(triethylsilyl)ethylene, for which *E* and *Z* isomers were determined in a 96:4 ratio. The formation of branched dehydrogenative silylation products was not detected. The high selectivity remained even

when the reaction was conducted at 100 °C, and conversion over 99 % was then achieved within 2 h (Table 1, entries 7, 8). Thus we can conclude that addition of 2 equiv of olefin is enough to achieve high selectivity. Similarly, rate enhancement was observed for the dehydrogenative silylation of *p*-methylstyrene at 70 °C by using **8b** as a catalyst (entry 4). In general, **8b** was found to be less active than **8a**. Other substituted styrenes, such as *p*-methoxy- and *p*-fluorostyrene, have also been tested as substrates, which not only gave high yields, but also higher selectivities (over 99.6 %) for *trans*-dehydrogenative silylation products (entries 9–12). With aliphatic alkenes such as triethoxylvinylsilane, both the conversion rate and the selectivity for dehydrogenative silylation became poor (entries 13, 14). In the case of ethylene gas, a high yield but low dehydrogenative silylation/hydrosilylation selectivity (less than 4:1) was observed (entries 15, 16). Based on all these results, it is evident that monophosphine Re^{I} complexes exhibit higher activity than bisphosphine ones. The rate enhancement is anticipated to originate from the more facile dissociation of an acetonitrile ligand in comparison with a phosphine ligand, which facilitates the initial coordination of alkenes and the oxidative addition of the Si–H bond to the rhenium center.

Conclusion

A facile synthetic route to mononuclear Re^{II} hydride complexes $[Re(H)(Br)_2(NO)(PR_3)_2]$ (**3**) was developed by exploiting the propensity of Re^{I} complexes of type **1** for SET pathways with benzyl bromide. In comparison, dibromomethane or bromoform act as a double SET acceptor toward **1** to lead to the formation of Re^{I} carbene hydrides compounds **4** or **5** along with **3**. In contrast, the SET reaction mode **2** of allyl- or benzylbromide with the $[Re^{I}Br(H_2)(NO)(PR_3)_2]$ dihydrogen complex led to the paramagnetic monophosphine salts **6** and **7** bearing the $[Re^{II}Br_4(NO)(PR_3)]^-$ anions. Compound **6** was found to be an appropriate precursor to prepare the monophosphine $[Re^{I}Br_2(NO)(MeCN)_2(PR_3)]$ (**8**), which exhibit improved catalytic activity in highly selective dehydrogenative silylations of styrenes. In combination with zinc, complexes **3** were also applied as highly active catalysts for homocoupling of allyl- and benzylbromide. This work therefore not only presents the first example of Re^{II} hydride complexes in the realm of Re^{II} chemistry, but also offers a practical synthetic route to monophosphine Re^{I} compounds.

Finally, evidence was provided that Re^{II} hydrides of type **3** may be converted to σ-type radicals with small activation barriers. Therefore their applications in new radical-driven catalyses are now under investigation in our group.

Experimental Section

General: All manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glove box (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze–thaw cycles prior to use. The deuterated solvents were dried with sodium/benzophenone ([D_8]THF, [D_8]toluene, [D_6]benzene) and vacuum-transferred for storage in Schlenk flasks fitted with Teflon valves. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopic data were recorded using a Varian Gemini-300, Varian Mercury 200, or Bruker DRX 500 spectrometers by using 5 mm diameter NMR spectroscopy tubes equipped with Teflon valves, which allow degassing and further introduction of gases into the probe. Chemical shifts are expressed in parts per million (ppm). ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton or ^{13}C resonances of the deuterated solvent. All chemical shifts for the $^{31}P\{^1H\}$ NMR spectroscopic data are reported downfield in ppm relative to external 85 % H_3PO_4 at $\delta = 0.0$ ppm. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were obtained by ATR methods using a Bio-Rad FTS-45 FTIR spectrometer. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich. Benzylbromide, allylbromide, TEMPO, and *p*-dinitrobenzene were purchased from Aldrich and used without further purification. Dibromomethane and bromoform were used after distillation.

$[Re(Br)_2(H)(NO)(PCy_3)_2]$ (3a): In a 20 mL vial in a glove box, $[Re(Br)(H)(NO)(PCy_3)_2]$ (86 mg, 0.10 mmol) was dissolved in benzene (2 mL). Then benzylbromide (13 μL, 0.11 mmol) was added and the violet solution immediately turned dark brown. After 5 min, the solution was evaporated in vacuo. The residue was washed with pentane (2 × 2 mL) and dried in vacuo to give a brown solid. Yield: 83 mg, 89 %. The formation of 1,2-diphenylethane was proven by ^1H NMR spectroscopy, with characteristic resonances at $\delta = 6.97$ (m; Ph), 2.73 ppm (s; PhCH_2-), and by GC–MS measurements: m/z: 182.2 [M^+]. IR (ATR): $\tilde{\nu} = 2924$ (ν-(C-H)), 2848 (ν(C-H)), 2013 (ν(Re-H)), 1703 cm^{-1} (ν(NO)); EPR (toluene, 298 K): $a_i = 24.5$–31.5 mT (sextet), central field: 3480 G, $g = 2.0018$; elemental analysis calcd (%) for $C_{36}H_{67}Br_2NOP_2Re$ (936.26): C 46.10, H 7.20, N 1.49; found: C 46.26, H 7.12, N 1.47.

$[Re(Br)_2(H)(NO)(PiPr_3)_2]$ (3b): In a 20 mL vial in a glove box, $[Re(Br)(H)(NO)(PiPr_3)_2]$ (31 mg, 0.05 mmol) was dissolved in benzene (1 mL). Then benzylbromide (7 μL, 0.06 mmol) was added and the violet solution immediately turned dark brown. After 5 min, the solution was evaporated in vacuo. The residue was washed with pentane (1 × 2 mL) and dried in vacuo to give a dark-brown solid. Yield: 28 mg, 80 %. IR (ATR): $\tilde{\nu} = 2963$ (ν(C-H)), 2927 (ν(C-H)), 2872 (ν(C-H)), 2032 (ν(Re-H)), 1694 cm^{-1} (ν(NO)); elemental analysis calcd (%) for $C_{18}H_{43}Br_2NOP_2Re$ (696.07): C 31.00, H 6.21, N 2.01; found: C 31.12, H 6.29, N 2.00; EPR (toluene, 298 K): $a_i = 22.0$–29.1 mT (sextet), central field = 3480 G, $g = 2.0018$.

Reaction of 1a with CH_2Br_2: In a 20 mL vial in a glove box, $[Re(Br)(H)(NO)(PCy_3)_2]$ (35 mg, 0.04 mmol) was dissolved in benzene (1 mL). Then CH_2Br_2 (2 μL) was added and the violet solution immediately turned dark brown. After 5 min, the solution was evaporated in vacuo. The residue was washed with pentane (2 × 2 mL) and dried in vacuo to give a green-brown solid that contained a mixture of $[Re(=CH_2)(Br)(H)(NO)(PCy_3)_2]$ (**4a**) and Re^{II} hydride **3a**. By washing with a benzene/pentane mixing solution (1:20, 2 × 2 mL), pure **3a** could be obtained as a brown solid in 27 % yield (10 mg). However, attempt to isolate pure **4a** failed. In situ spectroscopic data for **4a**: ^1H NMR (500.25 MHz, [D_8]toluene): $\delta = 14.79$ (d, J(H,H) = 4 Hz, 1H; Re=CH_2), 14.59 (dd, J(H,H) = 4 Hz, J(=CH,ReH) = 10 Hz, 1H; Re=CH_2), 2.42 (dt, J(=CH,ReH) = 10 Hz, J(H,P) = 34 Hz, 1H; Re-H), 1.13–2.78 ppm (m, 66H; P(C_6H_{11})$_3$); $^{13}C\{^1H\}$ NMR (125.8 MHz, [D_8]toluene): $\delta = 278.1$ (brs; Re=CH_2), 33.7 (t, $J = 12$ Hz; P-*C*H), 30.2, 29.7, 29.5, 27.9 (t, $J = 5$ Hz), 27.2, 26.8, 19.0 ppm; $^{31}P\{^1H\}$ NMR (202.5 MHz, [D_8]toluene): $\delta =$ 46.0 ppm (s; 2P); IR (ATR): $\tilde{\nu} = 2924$ (ν(C-H)), 2850 (ν(C-H)), 1670 cm^{-1} (ν(NO)).

Reaction of 1b with CH_2Br_2: In a 20 mL vial in a glove box, $[Re(Br)(H)(NO)(PiPr_3)_2]$ (31 mg, 0.05 mmol) was dissolved in benzene (1 mL). Then CH_2Br_2 (2 μL) was added and the violet solution immediately turned dark brown. After 5 min, the solution was evaporated in vacuo. The residue was washed with pentane (2 × 2 mL) and dried in vacuo to give a green-brown solid that contained a mixture of [Re(=

CH_2)(Br)(H)(NO)(P*i*Pr$_3$)$_2$] (**4b**) and the Re^{II} hydride **3b**. By washing with pentane (5×2 mL), pure **3b** could be obtained as a brown solid in 34% yield (12 mg). However, pure **4b** could not be obtained. In situ spectroscopic data for **4b**: ^{1}H NMR (500.25 MHz, [D$_8$]toluene): δ=14.92 (d, J(H,H)=4 Hz, 1H; Re=C*H*$_2$), 14.76 (dd, J(H,H)=4 Hz, J(=CH,ReH)=10 Hz, 1H; Re=C*H*$_2$), 2.47 (m, 6H; P-C*H*(CH$_3$)$_2$), 2.40 (dt, J(=CH,ReH)=10 Hz, J(H,P)=34 Hz, 1H; Re-H), 1.25 ppm (m, 36H; P-CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_8$]toluene): δ=279.0 (brs; Re=CH$_2$), 24.0 (t, J(P,C)=11 Hz; P-*C*H(CH$_3$)$_2$), 19.1 (s), 18.7 ppm (s); ^{31}P{^{1}H} NMR (202.5 MHz, [D$_8$]toluene): δ=52.65 ppm (s, 2P); IR (ATR): $\tilde{\nu}$= 2961 (ν(C-H)), 2927 (ν(C-H)), 2030 (ν(Re-H)), 1661 cm^{-1} (ν(NO)).

Reaction of 1a with CHBr$_3$: In a 20 mL vial in a glove box, [Re(Br)(H)(NO)(PCy$_3$)$_2$] (35 mg, 0.04 mmol) was dissolved in benzene (1 mL). Then CHBr$_3$ (1.5 μL) was added, and the violet solution immediately turned dark brown. After 5 min, the solution was evaporated in vacuo. The residue was washed with pentane (2×2 mL) and dried in vacuo to give a green-brown solid that contained a mixture of Re^{II} hydride **3a** and [Re(=CHBr)(Br)(H)(NO)(PCy$_3$)$_2$] (**5a**). In situ characteristic data for **5a**: ^{1}H NMR (500.25 MHz, [D$_6$]benzene): δ=14.20 (d, J(=CH,ReH)=11 Hz, 1H; Re=CHBr), 2.20 (dt, J(=CH,ReH)=11 Hz, J-(H,P)=35 Hz, 1H; Re-H), 1.14–2.86 ppm (m, 66H; P(C$_6$H$_{11}$)$_3$); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_6$]benzene): δ=250.8 (brs; Re=CHBr), 34.7 (t, J= 12 Hz; P-*C*H), 30.1, 29.5, 29.4, 27.8 (t, J=5 Hz), 27.5, 26.8, 21.4 ppm; ^{31}P{^{1}H} NMR (202.5 MHz, [D$_6$]benzene): δ=38.8 ppm (s; 2P); IR (ATR, cm^{-1}): $\tilde{\nu}$=1728 cm^{-1} (ν(NO)).

Reaction of 1b with CHBr$_3$: In a 20 mL vial in a glove box, [Re(Br)(H)(NO)(P*i*Pr$_3$)$_2$] (25 mg, 0.04 mmol) was dissolved in benzene (1 mL). Then CHBr$_3$ (1.5 μL) was added and the violet solution immediately turned dark brown. After 5 min, the solution was evaporated in vacuo. The residue was washed with pentane (2×2 mL) and dried in vacuo to give a green-brown solid that contained a mixture of Re^{II} hydride **3b** and [Re(=CHBr)(Br)(H)(NO)(P*i*Pr$_3$)$_2$] (**5b**). In situ characteristic data for **5b**: ^{1}H NMR (500.25 MHz, [D$_6$]benzene): δ=14.30 (d, J(=CH,ReH)=11 Hz, 1H; Re=CHBr), 2.50 (m, 6H; P-C*H*(CH$_3$)$_2$), 2.04 (dt, J(=CH,ReH)=11 Hz, J(H,P)=35 Hz, 1H; Re-H), 1.23 (m, 18H; P-CH-(C*H*$_3$)$_2$), 1.09 ppm (m, 18H; P-CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (125.8 MHz, [D$_6$]benzene): δ=252.3 (brs; Re=CHBr), 25.4 (t, J(P,C)=12 Hz; P-*C*H-(CH$_3$)$_2$), 19.0 (s), 18.9 ppm (s); ^{31}P{^{1}H} NMR (202.5 MHz, [D$_6$]benzene): δ=47.9 ppm (s; 2P); IR (ATR): $\tilde{\nu}$=1734 cm^{-1} (ν(NO)).

[Cy$_3$PCH$_2$CH=CH$_2$][Re(Br)$_4$(NO)(PCy$_3$)] (6a): In a 50 mL Schlenk tube equipped with a Young tap, [Re(Br)$_2$(NO)(PCy$_3$)$_2$(η^2-H$_2$)] (160 mg, 0.16 mmol) and allylbromide (16 μL, 1.60 mmol) were mixed in toluene (5 mL). The mixture was stirred at 70°C for 24 h. During the reaction, a blood-red leaflike precipitate was formed gradually. The precipitate was separated and washed with toluene (2×5 mL) and dried in vacuo to give a blood-red solid. Yield: 93 mg, 53%. IR (ATR): $\tilde{\nu}$=2924 (ν(C-H)), 2846 (ν(C-H)), 1728 cm^{-1} (ν(NO)); elemental analysis calcd (%) for C$_{39}$H$_{71}$Br$_4$NOP$_2$Re (1137.76): C 41.17, H 6.29, N 1.23; found: C 41.30, H 6.23, N 1.26.

[*i*Pr$_3$PCH$_2$CH=CH$_2$][Re(Br)$_4$(NO)(P*i*Pr$_3$)] (6b): In a 50 mL Schlenk tube equipped with a Young tap, [Re(Br)$_2$(NO)(P*i*Pr$_3$)$_2$(η^2-H$_2$)] (65 mg, 0.10 mmol) and allylbromide (70 μL, 0.7 mmol) were mixed in toluene (5 mL). The mixture was stirred at 70°C. After 30 min, the color of the solution changed from light yellow to blood-red. After another 1.5 h, a blood-red leaflike precipitate was formed, which was separated and washed with toluene (2×5 mL) and dried in vacuo to give a blood-red solid. Yield: 75 mg, 90%. IR (ATR): $\tilde{\nu}$=2970 (ν(C-H)), 2886 (ν(C-H)), 1731 cm^{-1} (ν(NO)); elemental analysis calcd (%) for C$_{21}$H$_{47}$Br$_4$NOP$_2$Re (897.38): C 28.11, H 5.28, N 1.56; found: C 28.39, H 5.44, N 1.62.

[Cy$_3$PCH$_2$Ph][Re(Br)$_4$(NO)(PCy$_3$)] (7a): In a 50 mL Schlenk tube equipped with a Young tap, [Re(Br)$_2$(NO)(PCy$_3$)$_2$(η^2-H$_2$)] (100 mg, 0.10 mmol) and benzylbromide (50 μL, 0.40 mmol) were mixed in toluene (5 mL). The mixture was stirred at 70°C for 15 h. After cooling to room temperature, a blood-red precipitate was formed. The precipitate was separated and washed with toluene (2×2 mL) and pentane (5×2 mL) and dried in vacuo to give an orange-red solid. Yield: 60 mg, 51%. IR (ATR): $\tilde{\nu}$=2930 (ν(C-H)), 2849 (ν(C-H)), 1730 cm^{-1} (ν(NO)); elemental analysis calcd (%) for C$_{43}$H$_{73}$Br$_4$NOP$_2$Re (1184.15): C 43.48, H 6.19, N 1.18; found: C 43.62, H 6.34, N 1.21.

[*i*Pr$_3$PCH$_2$Ph][Re(Br)$_4$(NO)(P*i*Pr$_3$)] (7b): In a 50 mL Schlenk tube equipped with a Young tap, [Re(Br)$_2$(NO)(P*i*Pr$_3$)$_2$(η^2-H$_2$)] (20 mg, 0.03 mmol) and benzylbromide (24 μL, 0.20 mmol) were mixed in toluene (5 mL). The mixture was stirred at 70°C for 24 h. After cooling, a blood-red precipitate was formed. The precipitate was separated and washed with toluene (1×2 mL) and pentane (5×2 mL) and dried in vacuo to give an orange-red solid. Yield: 15 mg, 53%. IR (ATR): $\tilde{\nu}$=1728 cm^{-1} (ν(NO)); elemental analysis calcd (%) for C$_{25}$H$_{49}$Br$_4$NOP$_2$Re (947.40): C 31.69, H 5.21, N 1.48; found: C 31.79, H 5.31, N 1.50.

[Re(Br)$_2$(NO)(MeCN)$_2$(PCy$_3$)] (8a): In a 30 mL Schlenk tube equipped with a Young tap, **6a** (50 mg, 0.05 mmol) and Zn powder (26 mg, 0.4 mmol) were mixed in acetonitrile (5 mL). The mixture was stirred at room temperature for 1 h to afford a yellow mixture. The excess of Zn was removed by filtration through Celite. The yellow filtrate was dried in vacuo and was further extracted with benzene (3×1 mL). The benzene solution was dried in vacuo again and further washed with cold benzene (1×0.5 mL). The residue was dried in vacuo to afford an orange solid. Yield: 23 mg, 61%. ^{1}H NMR (200.0 MHz, [D$_6$]benzene): δ=1.07–2.73 (m, 33H; P(C$_6$H$_{11}$)$_2$), 1.26 ppm (s, 6H; CH$_3$CN); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene): δ=134.6 (s; CH$_3$*C*N), 36.4 (s), 36.0 (s), 28.9 (s), 27.7 (s), 26.8 (s), 26.7 (s), 2.1 ppm (br; *C*H$_3$CN); ^{31}P{^{1}H} NMR (80.9 MHz, [D$_6$]benzene): δ=3.2 ppm (s); IR (ATR): $\tilde{\nu}$=2928 (ν(C-H)), 2913 (ν(C-H)), 2849 (ν(C-H)), 2274 (ν(CN)), 1682 cm^{-1} (ν(NO)); elemental analysis calcd (%) for C$_{22}$H$_{39}$Br$_2$N$_3$OPRe (738.55): C 35.78, H 5.32, N 5.69; found: C 36.21, H 4.99, N 5.28.

[Re(Br)$_2$(NO)(MeCN)$_2$(P*i*Pr$_3$)] (8b): In a 50 mL Schlenk tube equipped with a Young tap, **6b** (96 mg, 0.11 mmol) and Zn powder (65 mg, 1.0 mmol) were mixed in acetonitrile (5 mL). The mixture was stirred at room temperature for 1 h to afford a yellow mixture. The excess of Zn was removed by filtration through Celite. The yellow filtrate was dried in vacuo and was further extracted with benzene (6×2 mL). The benzene solution was concentrated to 1 mL and pentane (6 mL) was added to afford orange precipitates, which were isolated and dried in vacuo to give an orange solid. Yield: 52 mg, 79%. ^{1}H NMR (200.0 MHz, [D$_6$]benzene): δ=2.78 (m, 3H; P-C*H*(CH$_3$)$_2$), 1.25 (s, 6H; CH$_3$CN), 1.17 ppm (m, 18H; P-CH(C*H*$_3$)$_2$); ^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]benzene): δ=134.5 (s; CH$_3$*C*N), 26. 6 (s), 26.3 (s), 18.8 (t, J(P,C)=5 Hz; P-*C*H(CH$_3$)$_2$), 2.6 ppm (br; *C*H$_3$CN); ^{31}P{^{1}H} NMR (80.9 MHz, [D$_6$]benzene): δ=13.9 ppm (s); IR (ATR): $\tilde{\nu}$=2961 (ν(C-H)), 2906 (ν(C-H)), 2874 (ν(C-H)), 2275 (ν(CN)), 1685 cm^{-1} (ν(NO)); elemental analysis calcd (%) for C$_{13}$H$_{27}$Br$_2$N$_3$OPRe (618.36): C 25.25, H 4.40, N 6.80; found: C 25.42, H 4.48, N 6.47.

Proof of SET mechanism for the formation of 6b: In a 3 mL NMR spectroscopic tube equipped with a Young tap, [Re(Br)$_2$(NO)(P*i*Pr$_3$)$_2$(η^2-H$_2$)] (7 mg, 0.01 mmol), TEMPO (3.1 mg, 0.02 mmol), and allylbromide (1 μL, 0.01 mmol) were mixed in [D$_6$]benzene (0.5 mL). The mixture was kept at 70°C for 5 h to give a deep purple solution. ^{1}H NMR spectroscopy indicated the formation of allyl-radical trapped product TEMPO–CH$_2$CH=CH$_2$ in 41% yield. ^{1}H NMR (200.0 MHz, [D$_6$]benzene): δ=5.85 (m, 1H; -C*H*=CH2), 5.28 (d, ^3J(H,H)=18H, 1H; -CH=CH*H*$_{(trans)}$), 5.04 (d, ^3J-(H,H)=10H, 1H; -CH=CH*H*$_{(cis)}$), 4.36 (d, ^3J(H,H)=4H, 2H; C*H*$_2$-CH=CH2), 0.93–1.48 (m, 6H; -CH$_2$-), 1.17 (s, 6H; CH$_3$), 1.22 ppm (s, 6H; CH$_3$).

Blank reaction of TEMPO and allylbromide: In a 3 mL NMR spectroscopic tube, TEMPO (4.5 mg, 0.03 mmol) and allylbromide (1 μL, 0.01 mmol) were mixed in [D$_6$]benzene (0.5 mL) and were kept at 70°C for 5 h. ^{1}H NMR spectroscopy indicated that no reaction occurred.

Homocoupling of benzyl- or allylbromide with Zn catalyzed by Re^{II} complexes: In a 20 mL vial in a glove box, benzyl- or allylbromide (0.5 mmol), zinc (13 mg, 0.25 mmol), and Re^{II} catalyst **3a** or **3b** (0.005 mmol) were mixed in [D$_8$]THF (0.5 mL). The mixture was violently stirred at room temperature for 10 min. The yield of the homocoupling product was determined by ^{1}H NMR spectroscopy and GC–MS. In the case of allylbromide, the color of the solution was observed to turn from brown to gray-yellow and the zinc was almost consumed within 10 min.

Dehydrogenative silylation of alkenes with Et_3SiH catalyzed by monophosphine Re^{I} complexes: In a Schlenk tube equipped with a Young tap, Et_3SiH (0.25 mmol), alkene (0.50 mmol), and an appropriate amount of rhenium catalyst (0.0025) were mixed in [D_6]benzene (0.5 mL). The mixture was kept stirring in the closed system at 70 or 100 °C. After an appropriate reaction time, the yield and product distribution were determined by ^{1}H NMR spectroscopy and GC–MS.

Crystal structure analyses of 3a, 6a, and 8a: Crystallographic data were collected at 183(2) K using an Oxford Xcalibur diffractometer (4-circle kappa platform, Ruby CCD detector and a single-wavelength Enhance X-ray source with $Mo_{K\alpha}$ radiation, $\lambda = 0.7107$ Å).[25] The selected suitable single crystals were mounted using polybutene oil on the top of a glass fiber fixed on a goniometer head and were immediately transferred to the diffractometer. Pre-experiment, data collection, face-indexing analytical absorption correction,[26] and data reduction were performed using the Oxford program suite CrysAlisPro.[27] The structures were initially solved from heavy-atom location by Patterson interpretation (SHELXS-97) and were refined by full-matrix least-squares methods on F^2 (SHELXL-97).[28] All programs used during the crystal-structure determination processes are included in the WINGX software.[29] The program PLATON[30] was used to check the result of the X-ray analyses. More detailed information about the structure refinements of **3a**, **6a**, and **8a** and the crystal structures of **6b**, **7a**, and **7b** are given in the Supporting Information. The X-ray crystal-structure data for **3a**, **6a**, and **8a** can be found in references [14, 22, 24], respectively. CCDC-748180 (**3a**), -748181 (**6a**), -748182 (**6b**), -748183 (**8a**), -748184 (**7a**), and -748185 (**7b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] C. P. Casey, *Science* **1993**, *259*, 1552.
[2] a) E. J. Schelter, F. Karadas, C. Avendano, A. V. Prosvirin, W. Wernsdorfer, K. R. Dunbar, *J. Am. Chem. Soc.* **2007**, *129*, 8139; b) E. J. Schelter, A. V. Prosvirin, K. R. Dunbar, *J. Am. Chem. Soc.* **2004**, *126*, 15004; c) E. J. Schelter, A. V. Prosvirin, W. M. Reiff, K. R. Dunbar, *Angew. Chem.* **2004**, *116*, 5020; *Angew. Chem. Int. Ed.* **2004**, *43*, 4912.
[3] a) J. D. Allison, P. E. Fanwick, R. A. Walton, *Organometallics* **1984**, *3*, 1515; b) C. A. Hertzer, R. E. Myers, P. Brant, R. A. Walton, *Inorg. Chem.* **1978**, *17*, 2383; c) T. Nimry, R. A. Walton, *Inorg. Chem.* **1977**, *16*, 2829; d) E. J. Schelter, J. K. Bera, J. Bacsa, J. R. Galan-Mascaros, K. R. Dunbar, *Inorg. Chem.* **2003**, *42*, 4256.
[4] a) M. Bakir, P. E. Fanwick, R. A. Walton, *Polyhedron* **1987**, *6*, 907; b) S. Das, I. Chakraborty, A. Chakravorty, *Inorg. Chem.* **2003**, *42*, 6545; c) D. Giusto, G. Cova, *Gazz. Chim. Ital.* **1972**, *102*, 265.
[5] a) M. Carvalho, M. T. Duarte, A. M. Galvao, A. J. L. Pombeiro, R. Henderson, H. Fuess, I. Svoboda, *J. Organomet. Chem.* **1999**, *583*, 56; b) M. Carvalho, A. M. Galvao, A. J. L. Pombeiro, *J. Chem. Soc. Dalton Trans.* **2000**, 3393.
[6] a) R. M. Chin, J. Barrera, R. H. Dubois, L. E. Helberg, M. Sabat, T. Y. Bartucz, A. J. Lough, R. H. Morris, W. D. Harman, *Inorg. Chem.* **1997**, *36*, 3553; b) L. E. Helberg, J. Barrera, M. Sabat, W. D. Harman, *Inorg. Chem.* **1995**, *34*, 2033.
[7] F. Zobi, B. Spingler, R. Alberto, *Dalton Trans.* **2008**, 5287.
[8] a) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721; b) S. Maria, F. Stoffelbach, J. Mata, J.-C. Daran, P. Richard, R. Poli, *J. Am. Chem. Soc.* **2005**, *127*, 5946; c) R. Poli, *Acc. Chem. Res.* **1997**, *30*, 494; d) E. Le Grognec, J. Claverie, R. Poli, *J. Am. Chem. Soc.* **2001**, *123*, 9513; e) C. Aguilar-Lugo, R. L. Lagadec, D. R. Alexander, G. C. Valverde, S. L. Morales, L. Alexandrova, *J. Polym. Sci. Part A* **2009**, *47*, 3814; f) Y. Kotani, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 2420; g) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921; h) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689; i) H. Takahashi, T. Ando, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 6461; j) I. del Rio, G. van Koten, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 361.
[9] a) A. Choualeb, O. Blacque, H. W. Schmalle, T. Fox, T. Hiltebrand, H. Berke, *Eur. J. Inorg. Chem.* **2007**, 5246; b) A. Llamazares, H. W. Schmalle, H. Berke, *Organometallics* **2001**, *20*, 5277; c) D. Gusev, A. Llamazares, G. Artus, H. Jacobsen, H. Berke, *Organometallics* **1999**, *18*, 75; d) H. Jacobsen, V. Jonas, D. Werner, A. Messmer, J. C. Panitz, H. Berke, W. Thiel, *Helv. Chim. Acta* **1999**, *82*, 297; e) H. Berke, P. Burger, *Comments Inorg. Chem.* **1994**, *16*, 279; f) A. Choualeb, E. Maccaroni, O. Blacque, H. W. Schmalle, H. Berke, *Organometallics* **2008**, *27*, 3474; g) Y. Jiang, H. Berke, *Chem. Commun.* **2007**, 3571.
[10] Y. F. Jiang, O. Blacque, T. Fox, C. M. Frech, H. Berke, *Chem. Eur. J.* **2009**, *15*, 2121.
[11] a) Y. F. Jiang, O. Blacque, T. Fox, C. M. Frech, H. Berke, *Organometallics* **2009**, 28, 5493; b) Y. F. Jiang, O. Blacque, T. Fox, C. M. Frech, H. Berke, *Organometallics* **2009**, *28*, 4670.
[12] A. Houmam, *Chem. Rev.* **2008**, *108*, 2180.
[13] J. M. Khurana, S. Chauhan, G. C. Maikap, *Org. Biomol. Chem.* **2003**, *1*, 1737.
[14] X-ray crystal-structure data for **3a**: brown crystals; $C_{36}H_{67}Br_2NOP_2Re$; $M_r = 937.86$; crystal size: $0.36 \times 0.15 \times 0.13$ mm^3; orthorhombic, space group $P2_12_12_1$; $a = 12.5510(1)$, $b = 17.0330(2)$, $c = 18.3518(2)$ Å; $V = 3923.27(7)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.588$ Mg m^{-3}; $F(000) = 1892$; $\mu = 5.243$ mm^{-1}; 58426 reflections ($2\theta_{max} = 61°$), 11968 unique; ($R_{int} = 0.0528$), 406 parameters; $R1$ ($I > 2\sigma(I)$) = 0.0252; $wR2$ (all data) = 0.0514; GOF = 0.989; largest difference peak and hole: 1.192 and −1.129 e Å^{-3}.
[15] D. G. Gusev, R. Kuhlman, J. R. Rambo, H. Berke, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1995**, *117*, 281.
[16] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Dover, Oxford, p. 163.
[17] a) S. Banerjee, B. K. Dirghangi, M. Menon, A. Pramanik, A. Chakravorty, *J. Chem. Soc. Dalton Trans.* **1997**, 2149; b) B. K. Dirghangi, M. Menon, S. Banerjee, A. Chakravorty, *Inorg. Chem.* **1997**, *36*, 3595; c) L. A. Delearie, R. C. Haltiwanger, C. G. Pierpont, *Inorg. Chem.* **1987**, *26*, 817.
[18] a) O. B. Ryan, M. Tilset, V. D. Parker, *J. Am. Chem. Soc.* **1990**, *112*, 2618; b) O. B. Ryan, M. Tilset, *J. Am. Chem. Soc.* **1991**, *113*, 9554; c) O. B. Ryan, M. Tilset, V. D. Parker, *Organometallics* **1991**, *10*, 298; d) M. Peruzzini, R. Poli in *Recent Advances in Hydride Chemistry*, Elsevier, Amsterdam, **2001**.
[19] Q. Y. Chen, Y. B. He, Z. Y. Yang, *J. Chem. Soc. Chem. Commun.* **1986**, 1452.
[20] a) E. G. Burns, S. S. C. Chu, P. Demeester, M. Lattman, *Organometallics* **1986**, *5*, 2383; b) H. Nishiyama, M. Horihata, T. Hirai, S. Wakamatsu, K. Itoh, *Organometallics* **1991**, *10*, 2706; c) B. Blank, G. Glatz, R. Kempe, *Chem. Asian J.* **2009**, *4*, 321; d) C. Tejel, M. A. Ciriano, L. A. Oro, A. Tiripicchio, F. Ugozzoli, *Organometallics* **2001**, *20*, 1676; e) Y. W. Ge, P. R. Sharp, *J. Am. Chem. Soc.* **1990**, *112*, 3667; f) B. C. de Pater, E. J. Zijp, H. W. Fruhauf, J. M. Ernsting, C. J. Elsevier, K. Vrieze, *Organometallics* **2004**, *23*, 269.
[21] a) M. Oliván, K. G. Caulton, *Inorg. Chem.* **1999**, *38*, 566; b) J. Wolf, W. Stuer, C. Grunwald, H. Werner, P. Schwab, M. Schulz, *Angew. Chem.* **1998**, *110*, 1165; *Angew. Chem. Int. Ed.* **1998**, *37*, 1124; c) D. J. Huang, J. C. Huffman, J. C. Bollinger, O. Eisenstein, K. G. Caulton, *J. Am. Chem. Soc.* **1997**, *119*, 7398; d) M. Oliván, K. G. Caulton, *Chem. Commun.* **1997**, 1733; e) T. E. Wilhelm, T. R. Belderrain, S. N. Brown, R. H. Grubbs, *Organometallics* **1997**, *16*, 3867; f) T. R. Belderrain, R. H. Grubbs, *Organometallics* **1997**, *16*, 4001.
[22] X-ray crystal-structure data for **6a**: red crystals; $C_{39}H_{71}Br_4NOP_2Re$; $M_r = 1139.73$; crystal size: $0.22 \times 0.12 \times 0.10$ mm^3; triclinic, space

group $P\bar{1}$; $a=10.94810(10)$; $b=14.1262(3)$, $c=28.4646(7)$ Å; $\alpha=93.6436(19)$, $\beta=91.4048(15)$, $\gamma=90.2123(14)°$; $V=4391.91(15)$ Å^3; $Z=4$; $\rho_{calcd}=1.721$ Mg m^{-3}; $F(000)=2260$; $\mu=6.509$ mm^{-1}; 51426 reflections ($2\theta_{max}=54°$); 18732 unique ($R_{int}=0.0386$); 865 parameters; $R1$ ($I>2\sigma(I)$)$=0.0652$; $wR2$ (all data)$=0.1754$; GOF$=1.109$; largest difference peak and hole: 3.061 and -1.889 e Å^{-3}.

[23] B. Machura, *Coord. Chem. Rev.* **2005**, *249*, 2277.

[24] X-ray crystal-structure data for **8a**: brown crystals, $C_{40}H_{57}Br_2N_3OPRe$; $M_r=972.98$; crystal size: $0.45\times0.19\times0.10$ mm^3; triclinic, space group $P\bar{1}$; $a=12.3974(2)$, $b=13.5874(2)$, $c=14.2977(3)$ Å; $\alpha=68.242(2)$, $\beta=71.012(2)$, $\gamma=83.211(1)°$; $V=2115.12(8)$ Å^3; $Z=2$; $\rho_{calcd}=1.528$ Mg m^{-3}; $F(000)=972$; $\mu=4.832$ mm^{-1}; 46946 reflections ($2\theta_{max}=61°$), 12924 unique ($R_{int}=0.0681$); 445 parameters; $R1$ ($I>2\sigma(I)$)$=0.0338$; $wR2$ (all data)$=0.0661$; GOF$=0.917$; largest difference peak and hole: 1.468 and -0.968 e Å^{-3}.

[25] Oxford Diffraction, Xcalibur CCD system, Oxford Diffraction Ltd, Abingdon, England, **2007**.

[26] R. C. Clark, J. S. Reid, *Acta Crystallogr. Sect. A* **1995**, *51*, 887–897.

[27] CrysAlisPro, Versions 1.171.32/34d, Oxford Diffraction Ltd, Abingdon, England.

[28] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122.

[29] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837.

[30] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

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