Olefin Complexes of Low-Valent Rhenium

Aldjia Choualeb,^[a] Olivier Blacque,^[a] Helmut W. Schmalle,^[a] Thomas Fox,^[a] Thomas Hiltebrand,^[a] and Heinz Berke^{*[a]}

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Replacement of the MeCN group in the acetonitrile-cisdibromo(nitrosyl)-trans-bis(phosphane)rhenium compounds **1a**, **b** ($\mathbf{R} = i\mathbf{Pr} \mathbf{a}$, $\mathbf{R} = \mathbf{Cy} \mathbf{b}$) with ethylene afforded the olefin derivatives $[\operatorname{Re}(\eta^2 - H_2C = CH_2)(\operatorname{NO})(\operatorname{PR}_3)_2\operatorname{Br}_2]$ (2a,b) (R = *i*Pr a, R = Cy b). Compound **1a** could be converted into the dimethyl species [Re(MeCN)(NO)(PiPr₃)₂Me₂] (3a) applying MeLi in toluene; the related methylation of 1b, however, failed. Abstraction of a Br⁻ ion from 1a,b with [Na][BAr'₄] in acetontrile yields the air-stable salts [Re(MeCN)₂(NO)(PR₃)₂-Br]⁺[BAr'₄]⁻ (**4a**,**b**) (R = *i*Pr **a**, R = Cy **b**) and under 1 bar of H₂ complexes 1a,b were converted into the known dihydrogen species $[\text{Re}(\eta^2 - H_2)(\text{NO})(\text{PR}_3)_2(\text{Br})_2]$ (**5a**,**b**) (R = *i*Pr **a**, R = Cy **b**). Reduction of [Re(MeCN)(NO)(PR₃)₂Br₂] (**1a**,**b**) with Na/ Hg under 1 bar of C_2H_4 afforded the butadiene complex $[\text{Re}(\eta^4-\text{C}_4\text{H}_6)(\eta^2-\text{H}_2\text{C}=\text{CH}_2)(\text{NO})(\text{PR}_3)_2]$ (6a,b) (R = *i*Pr a, R = Cy b) via oxidative coupling of two coordinated ethylene

Introduction

Over a large range of oxidation states rhenium shows generally high bond strengths to carbon donors. However, its affinity to π acceptor ligands can vary with the oxidation state of the metal center, since π back-bonding is expected to depend on the metal-d-electron count. Complexes with rhenium in high oxidation states thus show less propensity for olefin binding, a circumstance, which allows reversible olefin binding in catalytic intermediates, such as those in epoxidations,^[1a] olefin metathesis reactions^[1b] and in processes, which crucially involve C-H activations.^[2] Compounds with rhenium in lower oxidation states are expected to more strongly bind olefins, but such rhenium centers often do not perform well in catalysis, since they frequently show reluctance to form coordinatively unsaturated species. Special ancillary ligand sets may, however, assist dissociations of other ligands. Thus, π acceptors can labilize other π acceptors sharing the metal π electron density and furthermore π donor ligands may exert a kinetic *cis* labilizing effect on cis ligands.^[3] In this study we therefore wanted to evaluate ethylene binding to rhenium in lower oxidation states^[4a] and in various ligand environments. Earlier several

 [a] Anorganisch-chemisches Institut Universität Zürich, Winterthurerstrasse 190, 8057 Zürich, Switzerland Fax: +41-44-6356802 E-mail: hberke@aci.uzh.ch groups followed by double β -H shift and subsequent reductive H_2 elimination from the formed dihydride complex. Reduction of the complexes [Re(CO)(NO)(PR_3)_2Cl_2] (**7a**,**b**) (R = *i*Pr **a**, R = Cy **b**) with Na/Hg yields the pentacordinate species [Re(CO)(NO)(PR_3)_2(\eta^2-H_2C=CH_2)] (**8a**,**b**) (R = *i*Pr **a**, R = Cy **b**) under the same conditions as for **6a**,**b**. Reaction of **8a** with 1 equiv. of B(C₆F₅)_3 leads to the [Re(CO)_2[NOB(C₆F₅)_3]-(P*i*Pr_3)_2] compound (**9a**) and to the carbonyl nitrosyl complexes [Re(CO)_2(NO)(P*i*Pr_3)_2] (**10a**) with evolution of ethylene. The same reaction of **8a** and **8b**, but applying 1 bar of CO, leads to exclusive formation of **9a**,**b**. Complexes **4a**, **4b**, **6b**, **8a**, **9a**, and **9b** were characterized by X-ray diffraction studies.

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pseudo-octahedral or pentacoordinate olefin complexes with rhenium in low oxidation states and a partial π acceptor coordination sphere were studied for their conformational preferences in olefin rotation,^[4b] photochemical isomerization processes,^[4c] and in stoichiometric C-H activations,^[4d] which demonstrated in various ways the basic capability of such rhenium centers to strongly interact with olefins. Our group has recently focused on the development of rhenium bisphosphane nitrosyl systems containing $[\text{Re}(\text{NO})(\text{PR}_3)_2 X_2]^{[5]}$ (X = halogene) and $[\text{Re}(\text{NO})_2$ - $(PR_3)_2$ ^[6] fragments. The latter fragments were seen to react with olefins in metathesis catalyses^[6] and thus demonstrated affinity to olefins. For the earlier types of fragments a high propensity for olefin uptake was extrapolated based on their capability to bind $H_2^{[5]}$ and the close relationship in binding properties of both ligands.^[7] Our explorations on ethylene binding were therefore started using [Re(NO)- $(PR_3)_2X_2$] fragments possessing a "mixed type" ligand sphere of σ and π donors and π acceptors.

Results and Discussion

I. Reactions of [Re(CH₃CN)(NO)(PR₃)₂Br₂]

The reactions of the recently reported [Re(MeCN)-(NO)(PR₃)₂Br₂] complexes (R = *i*Pr **1a**, R = Cy **1b**)^[5] with ethylene produced indeed the ethylene complexes [Re(η^2 -



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Scheme 1.

 $H_2C=CH_2)(NO)(PR_3)_2Br_2]$ (R = *i*Pr **2a**, R = Cy **2b**) in good yields (Scheme 1). When ethylene was bubbled through the solutions of **1a**,**b** at 1 bar the color changed from light yellow to purple after 1 h for **2a** and 1.5 h for **2b**, but comparison of the ³¹P NMR spectra indicated only slight changes.^[5]

Complexes 2a,b were characterized further by spectroscopic means (IR, ¹H, and ¹³C NMR) and the pure products showed correct elemental analyses. Studies in solution were some times more difficult for 2b, since it exhibits low solubilities in many organic solvents. Besides a strong v(NO) band, the solid state IR spectra of 2a,b displayed v(CH) bands in the region of 2800 to 3000 cm⁻¹ indicating the presence of the Re-coordinated ethylene. v(C=C) absorptions could not be detected. The ¹H NMR spectrum of **2a** revealed two broad resonances at $\delta = 2.51$ and 2.47 ppm for two chemically different types of protons of the C₂H₄ ligand. Apparently there is hindered rotation around the rhenium-ethylene bond with a preferred orientation of the C=C bond parallel to the P-Re-P axis, which leads to distinction of pairs of Z-protons. Even at temperatures as high as 80 °C these signals did not coalesce. In the case of complex 2b the ¹H NMR signals of the olefin overlapped with those of the PCy₃ groups so that the hindered rotation of the olefin ligand could not be traced by ¹H NMR spectroscopy. However, DFT calculations (vide infra) suggest a substantial barrier of rotation for such types of bis(phosphane) complexes in general. In the ¹³C NMR spectra the two carbon atoms of the C₂H₄ moieties are chemically equivalent and appear for **2a** and **2b** as broad triplets at δ = 39.5 ppm confirming the preferred orientation of the olefin in the P-Re-P axis. In the ³¹P NMR spectra both phosphorus atoms are chemically equivalent and exhibit a singlet at $\delta = -13.3$ ppm for **2a** and -20.3 ppm for **2b** (40 °C).

Complex **1a** reacts with 2 equiv. of MeLi in toluene to produce the corresponding dimethyl derivative [Re(NO)-(MeCN)(P*i*Pr₃)₂Me₂] (**3a**) related to the [Re(NO)(CO)-(PR₃)₂Me₂] complexes (R = OMe, iOPr, Me, Et) reported earlier.^[8] Reaction of **2a** with only 1 equiv. of MeLi does not afford the monomethyl complex $[Re(NO)(MeCN)-(PiPr_3)_2MeBr]$, rather only half an equivalent of **3a**. This could be interpreted in terms of a faster second methylation, faster than the first one. Surprisingly, all attempts to access the dimethyl rhenium species **2b** did not meet with success. A variety of inseparable products were observed indicating a complicated course of the reaction with formation of radicals.

Complex **3a** was characterized by IR, ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR spectroscopy. Because of the liquid nature of the compound, satisfactory elemental analysis could not be obtained. The IR spectrum recorded in CH₂Cl₂ revealed a very strong band at 1588 cm⁻¹ for the NO group, as well as a weak band at 2360 cm⁻¹ for the coordinated MeCN ligand. Compared to **2a** the v(NO) absorption of **3a** is shifted to lower wavenumbers by about 100 cm⁻¹ indicating a relatively strong π -back-bonding.^[9] The ¹H NMR spectrum in C₆D₆ showed besides the signals of the *i*Pr and MeCN groups, two triplets at $\delta = 2.36$ ppm (*J*(PH) = 2.2 Hz) and 2.29 ppm (*J*(PH) = 2.0 Hz) for the chemically inequivalent methyl groups. In the ¹³C{¹H} NMR spectrum they give rise to broad signals at $\delta = 24.6$ and 20.6 ppm. Complex **3a** turned out to be very air-sensitive in solution.

Abstraction of a bromide atom from 1a,b using 1 equiv. of [Na][BAr'₄] (Ar' = m-(CF₃)₂C₆H₃) in acetonitrile occurred within 14 h and proceeded with regiospecific replacement of the bromide cis to the NO group affording the [Re(MeCN)₂(NO)(PR₃)₂Br][BAr'₄] salts 4a,b. The *trans*-to-NO bromide is apparently bound more strongly experiencing a push-pull stabilization of the π donor with the *trans* π acceptor. Complexes **4a**,**b** were isolated as pure vellow solids and are quite air-stable. The use of an excess of [Na]-[BAr'₄] did not lead to abstraction of the second bromide ion. Because of the cationic nature of the complexes, the solid-state IR spectra of 4a,b showed v(NO) bands shifted to higher wavenumbers in comparison with the starting materials. Bands for the two coordinated acetonitriles, which should appear in the range of 2350 to 2200 cm⁻¹, could not be detected. The NMR spectroscopic data of 4a,b con-

firmed the presence of {Re(MeCN)₂(NO)(PR₃)₂} fragments with two nitrile ligands. The ¹H NMR spectra displayed singlets at room temperature at $\delta = 2.89$ ppm for **4a** and at $\delta = 2.93$ ppm for **4b** attributed to the two chemically equivalent *trans* acetonitrile ligands. Singlets also appeared in the ³¹P{¹H} NMR spectra at $\delta = 0.4$ for **4a** and -10.2 ppm for **4b**.

The molecular structures of 4a,b were also determined by X-ray diffraction studies and the cations are shown in Figure 1. Complex 4b crystallized as a CH₂Cl₂ solvate. The rhenium coordination was found to be pseudo octahedral with the nitrosyl ligand located *trans* to the Br atom, while the two MeCN and the phosphane groups are disposed *trans*. Selected bond lengths and angles of **4a**,**b** are summarized in Table 1. The nitrosyl groups of both compounds were found disordered with the Br ligands.

As depicted in Scheme 1, H₂ rapidly displaces the coordinated MeCN group in **1a**,**b** producing the corresponding dihydrogen derivatives [Re(η^2 -H₂)(NO)(PR₃)₂Br₂] (**5a**,**b**) in quantitative spectroscopic yields. Complexes **5a**,**b** were identified by ¹H NMR spectroscopy based on the data of their earlier preparations from the reaction of [NEt₄]-[Re(NO)Br₅] with the corresponding phosphanes in ethanol.^[5]



Figure 1. ORTEP drawings of the molecular structures of the cations of 4a (left) and 4b (right) (thermal ellipsoids are drawn at the 20 and 30% probability levels, respectively). The rhenium atom of 4a lies on a center of inversion, only half of the molecule has been refined and the equivalent atoms (*) have been generated by the symmetry transformation 1/2 - x, 1/2 - y, 1/2 - z). The resulting disorder between the NO and Br ligands, the counterions [BAr'₄]⁻, the CH₂Cl₂ solvate molecule of 4b, as well as all hydrogen atoms have been omitted for clarity.

Table 1. Selected bond lengths [Å] and angles [°] for 4a and 4b.

4 a		4b	
$\overline{\text{Re}(1)-P(1)}$	2.5077(12)	Re(1)–P(1)	2.5319(19)
$Re(1) - P(1a)^{[a]}$	2.5077(12)	Re(1)-P(2)	2.5288(19)
Re(1) - N(1)	1.830(10)	$Re(1) - N(1)^{[b]}$	1.716(7)/1.662(17)
Re(1)-N(2)	2.056(3)	Re(1)-N(2)	2.071(7)
Re(1)-N(2a)	2.056(3)	Re(1)-N(3)	2.052(6)
$\operatorname{Re}(1)$ - $\operatorname{Br}(1)$	2.4733(16)	$Re(1) - Br(1)^{[b]}$	2.5582(11)/2.486(7)
N(1)–O(1)	1.208(10)	$N(1) - O(1)^{[b]}$	1.222(9)/1.178(15)
N(2)-C(22)	1.129(5)	N(2)-C(1)	1.133(10)
N(2a) - C(22a)	1.129(5)	N(3)-C(3)	1.148(10)
P(1) - Re(1) - P(1a)	180	P(1) - Re(1) - P(2)	177.25(6)
N(1)-Re(1)-Br(1)	173.7(3)	N(1)-Re(1)-Br(1)	176.7(2)
N(2)-Re(1)-N(2a)	180	N(2)-Re(1)-N(3)	173.5(3)
Re(1)-N(1)-O(1)	173.2(12)	Re(1)-N(1)-O(1)	173.2(6)/164(4)
Re(1)-N(2)-C(22)	178.1(4)	Re(1)-N(2)-C(1)	173.1(6)
Re(1) - N(2a) - C(22a)	178.1(4)	Re(1) - N(3) - C(3)	177.7(7)

[a] Symmetry operation: a = 1/2 - x, 1/2 - y, 1/2 - z. [b] Split atoms due to disorder are labeled N(11), N(12), O(11), O(12), Br(1), Br(2) in the cif file.



6a,b

Scheme 2.

We then attempted access to olefin complexes with the rhenium center in a still lower oxidation state than +I. Reduction of **1a,b** with sodium amalgam in THF leads at room temperature under 1 bar of ethylene to the butadiene ethylene species [Re(η^4 -C₄H₆)(η^2 -H₂C=CH₂)(NO)(PR₃)₂] (**6a,b**) (Scheme 2). These Re⁻¹ complexes were isolated as pale yellow powders in yields of 31% for **6a** and of 63% for **6b**.

In Scheme 2 a mechanism for the formation of **6a,b** is proposed. First generation of **2a,b** and then reduction to a transient Re(ethylene)₂ complex is suggested, which eventually converts into a metallacyclopentane structure with oxidative coupling of the two ethylene ligands.^[10–12] Double β -hydride elimination and H₂ reductive elimination^[2,13] is followed by the ethylene replacement of one phosphane ligand.

Single crystals of 6b were obtained from a mixture of pentane/dichloromethane, 10:1 (Figure 2, Table 2). The Xray diffraction study established the structure of 6b in detail. The coordination sphere of 6b can be viewed as a pseudo tetrahedron counting the butadiene as one ligand or as a pseudo square pyramid with the butadiene moiety occupying two coordination sites. According to the latter view the essentially planar η^4 -butadiene, η^2 -ethylene, and the NO ligand would form the base and the phosphane the apical position of the pyramid. Conformationally, the ethylene group is in parallel orientation with respect to the Re-P axis and the *cis*-butadiene ligand points with its open side toward the PCy₃ ligand. The ethylene and the butadiene group are disordered. The disorder could properly be resolved revealing reasonable bonding parameters. The average distance between the internal butadiene carbon atoms of 1.34(2) Å is significantly shorter by 0.09 Å than the average distances of the terminal carbon atoms of 1.43(2) Å speaking for a strong Re-butadiene back bonding with superimposition of the π_3 orbital of the butadiene moiety. For comparison, the free cis-butadiene bond possesses an internal C-C distance of 1.463(3) and terminal olefinic distances of 1.342(2) Å.^[14,15] The Re-C_{int} and Re-C_{term} distances are similar and fall into the range of 2.16(3) to 2.27(2) Å emphasizing a genuine η^4 coordination mode. The Re-Cterm bond length approximately trans to the ethylene group is shorter by 0.09(2) Å than the Re–C_{term} distance trans to the NO group. This can be explained via sizeable differences in the *trans* influences of ethylene and the NO group with the NO ligand having the stronger effect. The hydrogen atoms of the coordinated olefins could not be located in the Fourier difference maps and they have been calculated after each refinement cycle (riding model).



Figure 2. ORTEP drawing of the molecular structure of **6b** (thermal ellipsoids are drawn at the 30% probability level). The disorder observed between the ethylene and butadiene ligands as well as all hydrogen atoms have been omitted for clarity.

Table 2.	Selected	bond	lengths	[Å]	and	bond	angles	[°]	for (6b.
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Re(1) - N(1)	1.770(3)	N(1)–O(1)	1.197(4)
Re(1)-C(1A)	2.285(15)	C(1A)-C(2A)	1.434(17)
Re(1)-C(2A)	2.25(2)	C(3A)-C(4A)	1.417(17)
Re(1)-C(3A)	2.235(13)	C(4A)-C(5A)	1.344(14)
Re(1)-C(4A)	2.258(9)	C(5A)-C(6A)	1.42(2)
Re(1)-C(5A)	2.18(2)	C(1B)-C(2B)	1.43(3)
$\operatorname{Re}(1)$ – $\operatorname{C}(6A)$	2.170(18)	C(3B)-C(4B)	1.47(2)
$\operatorname{Re}(1) - \operatorname{C}(1B)$	2.30(3)	C(4B) - C(5B)	1.34(2)
$\operatorname{Re}(1)$ – $\operatorname{C}(2B)$	2.28(3)	C(5B)-C(6B)	1.42(2)
$\operatorname{Re}(1)$ – $\operatorname{C}(3B)$	2.272(18)	Re(1)-N(1)-O(1)	175.8(3)
Re(1)-C(4B)	2.224(11)	C(3A)-C(4A)-C(5A)	118.2(11)
$\operatorname{Re}(1)$ – $\operatorname{C}(5B)$	2.21(3)	C(4A)-C(5A)-C(6A)	115.4(14)
$\operatorname{Re}(1)$ – $\operatorname{C}(6B)$	2.16(3)	C(3B)-C(4B)-C(5B)	123.4(14)
Re(1) - P(1)	2.4585(10)	C(4B)-C(5B)-C(6B)	111.3(17)

Principally, butadiene can coordinate to a metal as a *cis*or *trans*-butadiene. The *trans*- η^4 -diene complexes are normally thermodynamically less stable and they may convert to the corresponding *cis*- η^4 -diene complexes.^[16,17] The *cis*- η^4 -diene complexes are known mainly with early transition metal centers, such as in Cp₂M(diene) (M = Ti, Zr, Hf),^[16] as well as with Ta.^[18]

Two extreme forms of butadiene *cis* coordination were found: the *cis*- η^4 -1,3-diene structure and the metallacyclopent-3-ene structure. NMR spectroscopy is able to distinguish the various coordination modes of the diene ligand on the basis of their coupling constants. In the *cis* coordination the majority of diene complexes reported so far exhibit the η^4 -1,3 diene structure possessing bond lengths of C_{int}-C_{int} \geq C_{term}-C_{term} and M-C_{term} \geq M-C_{term}, the dihedral angles between the planes defined by C_{term}, M, C_{term} and C_{term}, C_{int}, C_{int}, C_{term} atoms are generally <90°. When the dihedral angle is greater than 90° and the C_{int}-C_{int} bond is significantly shorter than C_{term}-C_{int}, the bent metallacyclopent-3-ene structure is adopted.^[12]

The ¹H NMR and the ¹³C NMR spectroscopic data of **6a,b** indeed confirmed their *cis* butadiene structure. Also on the basis of the ³¹P NMR spectra, **6a**, however, exists in solution as a mixture of two stereoisomers appearing in a 3:1 ratio. Suggested by the DFT calculations modeled with a PMe₃ ligand (vide infra) the isomerism is anticipated to be caused by butadiene rotation. Principally the three rotamers **A**, **B**, and **C** are conceivable (Figure 3). For electronic reasons any of these rotamers are expected to have one leg of the three-legged pianostool in the diene cleft.^[19] According to the calculations on a PMe₃ model isomer **A** is of

lowest energy. **B** and **C** of this derivative lie +3.9 and +8.6 kcal/mol higher in energy. In analogy **6a** is assumed to exist in the equilibrium conformations **A** and **B**. Another point of discussion concerns the kinetics. The barrier for the interconversion of rotamer **A** and **B** apparently is low enough that room temperature thermal energy (<15 kcal/mol) can equilibrate the two isomers of **6a**, however, at a rate which is slow on the NMR time scale. By the same token the energy difference of isomers **A** and **B** of **6b** and their barrier of rotation are expected to be substantially higher than those of **6a**, since the PCy₃ ligand possesses a still larger cone angle than $PiPr_3$. For the latter complex the butadiene rotation is therefore considered to be "frozen out" in the energetically preferred rotamer **A**.



Figure 3. Projections of the rotational isomers of **6a**,**b** and **6-Me** and proton assignment for the butadiene ligand.



Figure 4. TOCSY for the butadiene ligand of 6b recorded in C_6D_6 (r.t.) with irradiation of one *internal* CH group.

The ¹H NMR spectrum of **6b** indeed points to a solution structure according to rotamer A, which indeed is the structure in the solid state (Figure 2). Beside the signals of the PCy₃ ligand, overlapping with those of the C_2H_4 group, the resonances of the butadiene group are attributed to two anti, two syn, and two internal protons. Any of the isomeric structures A, B, and C of 6a,b possesses C_1 symmetry and "left/right" asymmetry of the butadiene so that the various types of butadiene protons are doubled and each butadiene proton appears at a distinct chemical shift. For 6b this could nicely be demonstrated by a TOCSY experiment with irradiation of one *internal* CH group (Figure 4 and Table 3). For 6a, however, the chemical shift differences between the signals of the butadiene and the ethylene groups of the rotamers A and B are very small and lead to overlap. The differences in chemical shifts between the syn and the anti protons of 6a,b were found to be in the range of 0.25–1.42 ppm comparable with the $\Delta\delta$ values of Fe(CO)₃(η^4 -C₄H₆)^[20] and of RhCp(η^4 -C₄H₆) (1.3–2.3 ppm) (Table 3). A coupling between the syn protons and the phosphorus nuclei was not observed for both complexes.

Table 3. ¹H NMR chemical shift [ppm] for the butadiene ligand of the rotamers A and B of **6a** and A of **6b**.

	H_{syn1}	Hanti1	H _{int1}	H _{int2}	H _{anti2}	H _{syn2}
6a(A)	-0.21	-0.52	5.72	5.25	0.56	1.98
6a(B)	-0.21	-0.72	5.72	5.25	0.43	2.06
6b(A)	-0.17	-0.42	5.76	5.29	0.70	2.01

The coupling constants $J(H_{syn1}H_{anti1})$, $J(H_{syn1}H_{int1})$, $J(H_{anti1}H_{int1})$, $J(H_{int1}H_{int2})$, $J(H_{anti2}H_{int2})$, $J(H_{syn2}H_{int2})$ of isomer **A** of **6a,b** and isomer **B** of **6a** are 7 and 6 Hz and $J(H_{anti2}H_{syn2})$ 4 and 3 Hz, respectively. On the basis of the couplings of the *anti* protons with the phosphorus nuclei (ca. 7 Hz) it was concluded that the butadiene units in **6a,b** have structures close to a *cis*- η^2 -1,3-diene ligand with a minor admixture of a metallacyclo-3-pentene structure. The coordination of the ethylene group in **6a,b** was confirmed by ¹³C NMR and by NOE measurements. All ethylene protons of **6a** appear in the ¹H NMR spectrum as chemically distinguished signals indicating hindered rotation.

II. Reactions of [Re(NO)(CO)(PR₃)₂Cl₂]

In order to probe the accessibility of other Re^{-I}–olefin complexes, we attempted the reduction of the complexes [Re(NO)(CO)(PR₃)₂Cl₂] (7**a**,**b**) (R = *i*Pr **a**, Cy **b**), related to **1a**,**b** by replacement of the olefin ligand with CO. In the presence of 1.4 bar of ethylene and otherwise under the same conditions as for the reductions of **1a**,**b**, the ethylene derivatives [Re(NO)(CO)(η^2 -H₂C=CH₂)(PR₃)₂] (**8a**,**b**) were obtained in good yields (Scheme 3) after reaction times of 5 d.



Scheme 3.

The change from yellow to orange became visible after filtration from the amalgam. The formation of **8a,b** was accompanied by the formation of a very small amount (about 1%) of the known dihydride complex [Re(NO)(CO)(H₂)-(PR₃)₂],^[5] which was removed by washing of the solids with pentane. The dihydride complexes were formed in larger amounts (about 34%) when the reaction was carried out under a pressure of 10 bar of ethylene. It was concluded that the formation of the dihydride complex results from the presence of a H₂ impurity in the ethylene gas.

The IR spectra of **8a,b** reveal v(CO) and v(NO) absorptions, which are shifted both by more than 100 cm⁻¹ to lower wavenumbers compared to **7a,b**^[8] indicating increased π -back bonding. v(C=C) bonds are not observed, but the coordination of the ethylene group is indicated by the presence of characteristic v(C–H) vibrations. The ¹H NMR spectrum of **8b** is less informative with respect to a structural assignment, since the PCy₃ resonances cover other signals over a large area of chemical shifts. The ¹H NMR resonances of the ethylene group of **8a** could not be detected in the room temperature spectrum, but were observed at 100 °C as a broad triplet at $\delta = 1.86$ ppm for all chemically and magnetically inequivalent C₂H₄ protons.

The structures of **8a,b** were derived from their analytical and spectroscopic data and for **8a** it was confirmed by an exemplary X-ray diffraction study. The structure of **8a** is shown in Figure 5 and selected bond lengths and angles are given in Table 4.

The coordination geometry around the rhenium center corresponds to a distorted trigonal bipyramid with the CO and NO groups and both carbon atoms of the ethylene group located in the trigonal plane of the molecule. The two phosphane ligands occupy apical positions with a P(1)-Re(1)-P(2) angle of 178.16(3)° (Table 4). Contrary to complexes 2a,b the orientation of the C=C bond is perpendicular to the P-Re-P vector, which is indicated by the dihedral $90.37(10)^{\circ}$, P(1)-Re(1)-C(3) angles P(1)-Re(1)-C(2)90.73(9)°, P(2)–Re(1)–C(2) 90.75(10)°, and P(2)–Re(1)–C(3) 91.04(9)°. It is the electronically preferred orientation in d^8 trigonal bipyramidal structures. The C=C bond length of 1.420(8) Å is comparable to those found in other ethylene rhenium complexes.^[21] The Re-N bond length of 1.799(3) Å is in accord with the values found in the literature.^[22] The N1–O2 bond separation of 1.208(4) Å is in the range of 1.10 to 1.38 Å expected for a linear NO⁺ type coordination^[21–23] [Re–N–O angle of 172.7(3)°]. The positions of the hydrogen atoms of the ethylene ligand were located in a difference electron-density map and their coordinates were fixed, but their isotropic displacement parameters were freely refined.



Figure 5. ORTEP drawing of the molecular structure of 8a (thermal ellipsoids are drawn at the 50% probability level). All hydrogen atoms have been omitted for clarity.

Table 4. Selected bond lengths [Å] and bond angles [°] for 8a.

Re(1)–P(1)	2.4758(9)	C(2)-Re(1)-P(1)	90.37(10)
Re(1) - P(2)	2.4744(9)	C(2)-Re(1)-P(2)	90.75(10)
Re(1) - N(1)	1.799(3)	C(3)-Re(1)-P(1)	90.73(9)
Re(1)-C(1)	1.922(4)	C(3)-Re(1)-P(2)	91.04(9)
Re(1)-C(2)	2.239(4)	N(1)-Re(1)-C(1)	111.11(15)
Re(1)-C(3)	2.282(3)	N(1)-Re(1)-C(2)	128.67(15)
C(2)-C(3)	1.420(6)	N(1)-Re(1)-C(3)	165.26(14)
N(1)–O(2)	1.208(4)	N(1)-Re(1)-P(1)	89.32(9)
C(1)–O(1)	1.151(5)	N(1)-Re(1)-P(2)	88.84(9)
P(1)-Re(1)-P(2)	178.16(3)	Re(1)-C(1)-O(1)	176.4(3)
C(1)-Re(1)-C(2)	120.22(15)	Re(1)-N(1)-O(1)	172.7(3)
C(1)-Re(1)-P(1)	89.95(11)	C(2)-C(3)-Re(1)	70.1(2)
C(1)-Re(1)-P(2)	90.75(11)	C(3)-C(2)-Re(1)	73.3(2)
C(2)-Re(1)-C(3)	36.59(14)		

Olefin complexes can be activated by Lewis acids to become alkene polymerization catalysts.^[24–30] The olefin gets attacked by the Lewis acid forming a zwitterionic species. The metal cation and the Lewis acid attacked anionic group are covalently linked in some fashion. They have been found to represent a way to modulate ion pairing in these catalysts, thus increasing activity. One important class of these zwitterionic complexes is obtained when the counteranion is located on the alkyl group occupying the reactive wedge of the complex. These types of complexes are called Girdle-type zwitterionic compounds and have been accessed mainly through electrophilic attack of $B(C_6F_5)_3$ on suitable hydrocarbon ligands of neutral group 4 bent metallocenes.^[31,32]

With the objective to generate active rhenium-based catalysts, we exemplarily attempted activation of complex **8a** with a Lewis acid. Treatment of **8a** with one equivalent of $B(C_6F_5)_3$ in toluene or benzene at room temperature did, however, not lead to the mentioned zwitterionic species $[Re^+(NO)(CO)(PR_3)_2CH_2CH_2B^-(C_6F_5)_3]$. The structures of the product showed that the $B(C_6F_5)_3$ electrophile had attacked the more Lewis basic NO site to give eventually the nitrosyl/Lewis acid adduct $\{Re(CO)_2[NOB(C_6F_5)_3](PR_3)_2\}$ (**9a**) and in addition the known complex $[Re(CO)_2(NO)-(PR_3)_2]$ (**10a**) with loss of the ethylene ligand in both complexes as depicted in Scheme 4. Complex **10a** was identified



Scheme 4.



by its ³¹P NMR spectrum ($\delta = 81.6$ ppm) and its IR spectrum reported earlier.^[8] ¹H and ³¹P{¹H} NMR pursuit of the reaction confirmed generation of free ethylene and formation of **9a** and **10a** in a 1:1 ratio. Formation of the phosphane adduct *i*Pr₃PB(C₆F₅)₃ was not observed.^[33] Complex **9a** could be separated from **10a** in 38% yield.

Formation of **9a** with replacement of the ethylene group in **8a** by CO requires explanation of how free CO could have formed. It apparently originates from the partial decomposition of the $B(C_6F_5)_3$ adduct of **8a** to yield ethylene and CO. The presence of only low amounts of CO accounts for the low yield of **9a**.

With the objective to access **9a,b** in a better yield, we first prepared complex **10a,b** by the reaction of **8a,b** with CO. The reaction was very sluggish and took more than 5 d. But much to our surprise, no stable adduct formation



Figure 6. ORTEP drawings of the molecular structures of 9a and 9b (thermal ellipsoids are drawn at the 30% probability level). All hydrogen atoms have been omitted for clarity.

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could be observed between **10a**,**b** and $B(C_6F_5)_3$. We have to assume that the additions of $B(C_6F_5)_3$ to **10a**,**b** are kinetically hindered.

When, however, **8a**,**b**, $B(C_6F_5)_3$, and CO were mixed together **9a**,**b** was produced in high yield. This observation stresses the necessity for the involvement of initial $B(C_6F_5)_3$ adducts of **8a**,**b** promoting formation of **9a**,**b** by subsequent ethylene substitution with CO (Scheme 4).

The adducts apparently release ethylene much faster than **8a**,**b** in the presence of CO to trap the unsaturated intermediates. Single crystals of **9a**,**b** were obtained from $CH_2Cl_2/$ pentane solutions at -30 °C.

The molecular structures of 9a,b were determined and are shown in Figure 6. The coordination geometries are distorted trigonal bipyramids. The two CO groups and the $NOB(C_6F_5)_3$ fragment are located in the trigonal plane of the molecules and the two phosphanes occupy apical positions. The phosphane ligands are bent towards the two CO groups [(P(1)-Re-P(2) 161.20(5) and 161.92(6)° for 9a and 9b, respectively] (Table 5). Such substantial bending of the phosphane molecules may be caused by steric "bumping" of the phosphanes and the NOB(C_6F_5)₃ fragment. Significant bending of the phosphanes was also observed in the hydride Lewis acid adducts [Re(H)(NO)(NOBC₆F₅)₃- $(PiPr_3)_2$ ^[33] and [Re(H)(NO)(NOBF_3)(PiPr_3)_2^[5] with P(1)-Re(1)-P(2) 134.77(3) and 146.60(6)°, respectively. The electronic and steric factors favor the bending of the axial ligands towards the purely σ -donating hydride ligand and away from the nitrosyl group.^[34,35] Similar to the complexes {Re(H)(NO)[NOB(C_6F_5)₃](P*i*Pr₃)₂} and [Re(H)(NO)] $(NOBF_3)(PiPr_3)_2$] the Re–N distances of 1.790(4) and 1.785(6) Å are only slightly affected by the coordination of $B(C_6F_5)_3$, but compared to other η^1 rhenium nitrosyl complexes the N-OBX₃ bond is elongated. The nitrosyl ligands are slightly bent upon $B(C_6F_5)_3$ attachment (Re(1)-N(1)-O(3) 166.2(4) and 158.6(6)°); however, it was approximately linear in the cases of $\{\text{Re}(H)(\text{NO})[\text{NOB}(C_6F_5)_3](\text{P}i\text{Pr}_3)_2\}$ $[Re-N-O 175.0(3)^{\circ}]$ and $[Re(H)(NO)(NOBF_3)(PiPr_3)_2]$ $[Re-N-O 175.0(3)^{\circ}]$ N-O 170.0(4)°]. A significant structural effect was recognized upon coordination of BCl₃ to a NO group in the com-

Table 5. Selected bond lengths [Å] and angles [°] for 9a and 9b.

	9a	9b
Re(1)–P(1)	2.4639(17)	2.4840(19)
Re(1) - P(2)	2.4535(17)	2.480(2)
Re(1) - N(1)	1.790(4)	1.785(6)
$\operatorname{Re}(1) - \operatorname{C}(a)^{[a]}$	1.961(6)	1.988(9)
$Re(1)-C(b)^{[a]}$	1.912(6)	1.916(8)
C(a) - O(1)	1.146(8)	1.150(10)
C(b)-O(2)	1.166(8)	1.151(9)
N(1)–O(3)	1.276(6)	1.296(8)
P(1)-Re(1)-P(2)	161.20(5)	161.92(6)
C(a)-Re(1)-C(b)	101.2(3)	104.5(3)
N(1)-Re(1)-P(1)	101.06(16)	99.5(2)
N(1)-Re(1)-P(2)	97.00(16)	98.5(2)
Re(1)-N(1)-O(3)	166.2(4)	158.6(6)
N(1)–O(3)–B	124.1(4)	125.3(6)

[a] C(a) and C(b) are C(39) and C(40) for **9a**, and C(1) and C(2) for **9b**.

pound [Re(Cp)(SiMe₂Cl)(NOBCl₃)(PPh₃)].^[36] This compound reveals a marked N–O elongation [1.47(1) Å] accompanied by a shortening of the Re–N bond [1.568(9) Å]. In **9a,b** the N–O bond lengths are 1.276(6) and 1.296(8) Å. Nitrosyl/Lewis acid interactions were shown to play a key role in the catalytic oxidation of alcohols,^[37] as well as in catalytic hydrogenation and hydrosilylation of olefins and ketones.^[33]

III. Theoretical Studies on Ethylene Complexes

As a single-faced π acceptor an olefinic ligand quite often shows barriers to free rotation around the metal-olefin bond. Generally, the C=C bond is preferentially oriented in the trigonal plane of three-coordinate complexes, is perpendicular to the plane in four-coordinate square-planar complexes, and is in plane with the trigonal plane of fivecoordinate trigonal-bipyramidal complexes (Scheme 5).^[38] These prevailing orientations are thought to result mostly from electronic rather than from steric effects. In d⁶ octahedral complexes olefins do only rarely show rotational barriers, if the cis ligands are all the same. Barriers might appear only for cases where the π donor planes at the metal centers are electronically strongly distinguished (R₃P-M-PR₃ plane electronically more donating than the L_1-M-L_3 plane of Scheme 5). In d⁸ trigonal bipyramidal complexes the olefin is preferentially oriented in the trigonal plane regardless of the presence of an axial R₃P-M-PR₃ arrangement. For instance in the structure of 8a the olefin orientation is in accord with this general rule.



Scheme 5.

Five-coordinated d⁶ complexes, as for instance (μ^2 -Cl- $[(A1Me_2)_2C \equiv)]W(CH_3)(PMe_3)_2(C_2H_4),^{[39]}$ (bis-mesitylimido)W(PMe₃)₂(C₂H₄),^[40] and bis(2,6-diisopropylphenylimido)Mo(PMe₃)₂($C_{2}H_{4}$) show reorientation of the olefinic group.^[41] In pseudo-octahedral complexes with trans phosphane ligands cis to the olefin, structures are prevailing with a parallel orientation of the olefin with respect to the P-M-P axis.^[42-49] Nevertheless, some examples show the olefin lying perpendicular to the P-M-P axis.^[50-53] Several of these latter examples might be governed by special effects, since they mostly possess two ethylene ligands in trans^[50,51] or in cis position^[52] to each other with one C=C bond parallel to the P-M-P vector and the second one perpendicular to it. To the best of our knowledge, only in the ortho-metallated ruthenium complex RuH(C₂H₄)(2-phenylpyridine)($PiPr_3$)₂ has the coordinated ethylene not aligned with the P-Ru-P axis.^[53]

The most widely accepted model for the bonding of an olefin to transition metals is that proposed by Dewar^[54] and by Chatt and Duncanson.^[55] This model involves formation of a σ -bond by donation of π -electrons to the metal and formation of a π -bond by back donation from the d orbitals of the metal to the olefin π^* -orbital. The precise nature of this bond has been the subject of many theoretical and experimental studies.^[56] In order to study the structures of **2a**, **2b**, and **8a** more thoroughly with the olefinic C=C bond lying parallel to the P–Re–P axis in the six-coordinate octahedral complexes **2a** and **2b** and in the trigonal plane of **8a** DFT calculations^[57] were carried out on the model complexes Re(PMe₃)₂X₂(NO)(C₂H₄) (X = Br, **2-Me**) and Re(PMe₃)₂(CO)(NO)(C₂H₄) (**8-Me**).

We made use of a well-established bond partitioning scheme,^[58] which divides the overall bond energy BE into various contributions from different interactions [Equation (1)], to look at the bond-forming reaction between the metal fragment and ethylene.

$$\Delta E_{\rm int} = -[\Delta E_{\rm elstat} + \Delta E_{\rm Pauli} + \Delta E_{\rm oi}] = -[\Delta E^0 + \Delta E_{\rm oi}] \tag{1}$$

The interaction energy between both fragments ΔE_{int} is partitioned into three physically meaningful terms, namely the electrostatic interaction ΔE_{elstat} , the Pauli repulsion ΔE_{Pauli} , and the orbital interaction term, ΔE_{oi} . When two suitable, bond-forming fragments are brought together to adapt the geometry of the final molecule, the term ΔE_{elstat} describes the classical Coulomb interaction between the unmodified and interpenetrating charge distributions of the two fragments. We further have to consider the Pauli repulsion ΔE_{Pauli} , which takes into account destabilizing two-orbital four-electron interactions between occupied orbitals on both fragments. The sum of Pauli repulsion and electrostatic interaction is called the *steric interaction* ΔE^0 . The last term in Equation (1), ΔE_{oi} introduces the attractive orbital interaction between occupied and virtual orbitals on the two fragments, and includes polarization and charge-transfer contributions. Although ΔE_{int} values are not defined in the same way as bond dissociation enthalpies ΔH , they are reasonable approximations of bond enthalpy terms, which in turn provide a good description for the bond strength.^[59] The bonding analysis for 2-Me and 8-Me is presented in Table 6.

Table 6. Bond analysis of the $[Re]\!\!-\!\!(\eta^2\!\!-\!\!C_2H_4)$ bond for $2\!\!-\!\!Me$ and $8\!\!-\!\!Me$

System	ΔE	$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{\rm elstat}$	ΔE^0	$\Delta E_{\rm oi}$	$\Delta E_{\rm int}$
2-Me ″	0.0	+225.23	-163.13	+62.10	-120.86	-58.76
2-Me ⊥	+23.1	+127.25	-90.57	+36.68	-59.23	-22.55
8-Me ″	+10.2	+217.96	-159.16	+58.79	-111.64	-52.84
8-Me ⊥	0.0	+194.45	-143.07	+51.38	-113.15	-61.77

For the three studied model complexes, both conformations with the C=C bond of ethylene parallel (") or perpendicular (\perp) to the P–M–P axis have been optimized without any constraints. The relative total energies confirm the structural observations since the parallel orientation is favored for 2-Me by 23.1 kcal/mol with respect to the corresponding perpendicular conformation and the perpendicular orientation is favored for 8-Me (by 10.2 kcal/mol with respect to the corresponding parallel conformation). The results from the bond analysis of **2-Me** show that ΔE_{oi} is the main factor determining the strength of the Re- $(\eta^2$ - C_2H_4) bond. The steric interaction term ΔE^0 is dominated by the Pauli repulsion ΔE_{Pauli} , and thus represents a nonbonding contribution. Despite the fact that the perpendicular orientation of ethylene reduces the steric repulsion between fragments from +62 to +37 kcal/mol (2-Me) the attractive orbital interaction ΔE_{oi} greatly stabilizes the parallel molecular arrangement from about 120 kcal/mol to only 59 kcal/mol for 2-Me \perp , respectively. In the case of the trigonal-bipyramidal complex 8-Me, the three main contributions of 9-Me" are very similar to those for 2-Me" (differences are less than 8 kcal/mol). The major change which leads to a favored perpendicular arrangement for 8-Me comes from the electronic contribution ΔE_{oi} . Calculated ΔE_{oi} increases from 56 kcal/mol to 113 kcal/mol on going from $2-Me \perp$ to $8-Me \perp$, even larger than the value for 8-Me" (112 kcal/mol). For 8-Me, both steric (+51 vs. +59 kcal/mol) and electronic terms (-113 vs. -112 kcal/mol) contribute to a better stabilization of the perpendicular arrangement.

According to the Dewar–Chatt–Duncanson model, two molecular orbitals from the metallic fragments $\text{Re}(\text{PMe}_3)_2$ -(NO)(CO) or $\text{Re}(\text{PMe}_3)_2(\text{NO})\text{Br}_2$ can compete for the formation of the π -bond by back donation to ethylene. The metal contribution to these two highest occupied molecular orbitals is mainly d_{xz} and d_{yz} (Scheme 6).



Scheme 6.

Both orbitals can interact with the olefin π^* -orbital in a bonding fashion depending on the orientation of ethylene. The LUMO is mainly Re-d_{z²} and is responsible for the σ bond by interaction with the filled π_{C2H4} orbital. The energy levels of these crucial orbitals of the metal fragments of **2-Me** and **8-Me** in their structures of the optimized molecules are presented in Figure 7 and Table 7. In the pseudo

System	Br–Re–Br	Br-Re-N _{NO}	P-Re-Br	P-Re-P	N _{NO} -Re-C _{CO}	LUMO	НОМО	HOMO – 1
2-Me″ 2-Me⊥	91.8 88.9	91.4 89.3	81.1 85.9	143.1 168.1		$\begin{array}{c} -4.677 \ ({\rm d}_{z^2}) \\ -4.679 \ ({\rm d}_{z^2}) \end{array}$	$-5.685 (d_{xz})$ $-5.805 (d_{xz})$	$-6.648 (d_{yz})$ $-6.590 (d_{yz})$
8-Me″ 8-Me⊥				159.1 175.0	136.8 112	$\begin{array}{c} -3.462 \ (d_{z^2}) \\ -3.566 \ (d_{z^2}) \end{array}$	$\begin{array}{c} -5.084 \ (\mathrm{d}_{xz}) \\ -4.488 \ (\mathrm{d}_{yz}) \end{array}$	$-5.147 (d_{yz})$ -5.820 (d _{xz})

Table 7. Optimized bond angles [°] and energy levels [eV] of the metallic fragments $Re(PMe_3)_2(NO)Br_2$ of **2-Me** and $Re(PMe_3)_2(NO)(CO)$ of **8-Me**.

octahedral complex **2-Me** the three ligands of the equatorial plane, two halides and one nitrosyl keep more or less their positions during ethylene rotation. The Br–Re–Br and Br–Re–N_{NO} bond angles remain in the range 88.9–91.8° and P–Re–Br increases by only 5° when the ethylene lies in the ReBr₂(NO) plane (Table 7). The orbitals are well separated by about 1 eV and the HOMO is mainly built from Re-d_{xz} which favors the parallel orientation of ethylene with respect to the P–Re–P axis. The second occupied π -type orbital is low in energy through the bonding interaction with the nitrosyl ligand not allowing for efficient further backbonding with the ethylene.



Figure 7. Energy diagram for the d_{xz} , d_{yz} , d_{z^2} orbitals of the fragments Re(PMe₃)₂(NO)(CO) of **2-Me** and Re(PMe₃)₂(NO)Br₂ of **8-Me** in their structures of the optimized molecules.

In the case of the trigonal-bipyramidal complex 8-Me, the bending distortion of the ligands in both planes and in the opposite direction of the ethylene is easier than for 2-Me and polarizes the d_{xz} or d_{yz} orbital of the metal for increased back-donation to the ethylene. Nevertheless, the degree of bending of the PMe₃ is limited by steric repulsions between PMe₃ and CO and NO and between the phosphorus ligands themselves whereas the bending of the carbonyl and nitrosyl group is only limited by electronic and steric interactions between themselves in the equatorial plane. While the P–Re–P angle decreases by 16° from 175.0 (8-Me \perp) to 159.1° (8-Me^{*II*}) the N_{NO}–Re–C_{CO} bond angle can become narrower by 25° from the parallel to the perpendicular orientation of ethylene (from 136.8 to 112°). The result is a greater destabilization of the occupied orbital built with Re-d_{yz}, since the overlap between Re-d_{yz} and p_y/p_z of the carbonyl and nitrosyl groups is reduced which becomes the HOMO of the metallic fragment. Back bonding to ethylene becomes stronger in the equatorial plane and favors the perpendicular orientation of ethylene with respect to the P– Re–P axis.

It was also challenging to provide understanding for the solution structures of the polyolefin complexes $Re(C_2H_4)(C_4H_6)(PR_3)(NO)$ 6a and 6b. In particular the Xray structure of **6b** provides a good idea about the ground states of 6a and 6b which is pseudo tetrahedral with one ethylene group coordinated to the rhenium center in parallel orientation with respect to the Re-P axis, one cis-butadiene ligand bound in an η^4 -coordination mode with an essentially planar carbon skeleton, one phosphane and one nitrosyl group. Complex 6a exists in solution as a mixture of two stereoisomers A and B with either the phosphane or the olefin in the cleft of the butadiene appearing in a 3:1 ratio on the basis of the ³¹P NMR spectra. Complex 6b is expected to exclusively exist in the butadiene rotameric form A with the phosphane ligand oriented in the cleft of the diolefin. The potential energy surface of the model complex $\text{Re}(C_2H_4)(C_4H_6)(\text{PMe}_3)(\text{NO})$ 6-Me could not be fully explored, but the geometries of the global or local minima corresponding to the three possible rotational isomers A, B, and **C** were fully optimized with the help of the density functional theory (Figure 8).^[60] The computed bonding energies of 6-Me give isomer A as the most stable calculated structure, while B and C lie +3.9 and +8.6 kcal/mol higher in energy and thus confirm the given structural assignments for rotational isomers of 6a and 6b. Ethylene rotation was also checked in rotamer A of 6-Me, but no other energetic minimum than the orientation parallel to the Re-P axis was found. The observed isomerism of 6a could thus not be explained on the basis of ethylene rotational isomerism. The energy differences between structures A and B or C is expected to have a significant steric component and to depend on the size of the phosphane. The larger the phosphane the stronger the preference for structure A, since the cleft of the butadiene ligand is the only place in the molecule that provides abundant space. That would explain why 6b with the bulky PCy₃ shows only isomer A and 6a with the smaller PiPr3 leads to rational isomerism.





Figure 8. Optimized isomeric structures of the model complex $Re(C_2H_4)(C_4H_6)(PMe_3)(NO)$ 6-Me.

Conclusions

This work focused on the chemistry of new olefin rhenium complexes. The ethylene complexes 2a,b were isolated in good yields by replacement of a MeCN group from 1a,b. The ethylene ligand showed an unexpectedly high preference for the orientation parallel to the P-Re-P axis. Reduction of **1a**,**b** with sodium amalgam under 1 bar of ethylene affords the butadiene complexes 6a.b. The salient features in bonding and the coordination geometry of 6a,b have been clarified on the basis of NMR and X-ray analysis coupled with a theoretical treatment. The pentacoordinate d⁸-olefin complexes demonstrated the olefin to be oriented in the trigonal plane of a trigonal bipyramid. This type of complex revealed a primary attack of the Lewis acid $B(C_6F_5)_3$ at the nitrosyl group rather than on the olefin, which eventually furnished $Re(CO)_2[NOB(C_6F_5)_3](PR_3)_2$ complexes with ethylene replacement in the presence of CO.

Experimental Section

All operations were carried out under a nitrogen atmosphere using a M. Braun 150 G-B glove box. The solvents were dried with sodium/benzophenone (THF, Et₂O, hydrocarbons) or P_2O_5 (CH₂Cl₂, CH₃CN) and distilled under N₂ prior to use. The deuterated solvents used in the NMR experiments were dried with sodium/benzophenone (C₆D₆, [D₈]toluene, [D₈]THF) or P_2O_5 (CD₂Cl₂, CD₃CN) and vacuum transferred for storage in Schlenk flasks fitted with Teflon valves. NMR experiments were carried out with Varian Gemini 300, Varian Mercury 200, or Bruker DRX 500 spectrometers using 5-mm diameter NMR tubes equipped with Teflon valves, which allow degassing and further introduction of gases into the probe. Chemical shifts are given in ppm. ¹H and ¹³C{¹H} NMR spectra were referenced to the residual proton or ¹³C resonances of the deuterated solvent. ³¹P chemical shifts are relative to 85% H₃PO₄. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zürich. IR spectra were recorded with a Bio-Rad FTS-45 spectrometer. The following reagents were purchased from commercial suppliers and used without further purification: MeLi (Fluka), P*i*Pr₃ (STREM), ethylene (99.9999% purity, MESSER or 99.9995% purity, PanGas), and H₂ (99.99995% purity, PanGas). Complexes **1a,b** were obtained according to literature procedures.^[5]

Synthesis of [Re(NO)(PiPr₃)₂(η²-C₂H₄)Br₂] (2a): Ethylene was bubbled through a solution of **1a** (0.100 g, 0.135 mmol) in toluene (20 mL) at room temperature for 1 h. After removal of the volatiles under vacuum, the residue was chromatographed on a SiO₂ column with toluene as a eluent yielding after drying in vacuo **2a** as a pale yellow powder (0.072 g, 0.1 mmol, 74%). IR (KBr): $\tilde{v} = 2963, 2920$ and 2879 (s, vC–H), 1693 (vs, vNO) cm⁻¹. ¹H NMR (300.1 MHz, C₆D₆): $\delta = 3.12-2.95$ (m, 6 H, (CH₃)₂CHP), 2.51 and 2.47 (2 br. signals, 4 H, H₂C=CH₂), 1.45–1.32 and 1.35–1.19 (2 m, 36 H, (CH₃)₂CHP) ppm. ³¹P{¹H} NMR (80.9 MHz, C₆D₆): $\delta = -13.3$ (s) ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆): $\delta = 39.5$ (br., H₂C=CH₂), 26.2 (t, *J*(PC) = 11 Hz, (CH₃)₂CHP), 19.9 and 19.6 (2 s, (CH₃)₂CHP) ppm. C₂₀H₄₆Br₂NOP₂Re (724.55): calcd. C 33.19, H 6.41, N 1.94; found C 33.39, H 6.52, N 1.93.

Synthesis of [Re(NO)(PCy₃)₂(η²-C₂H₄)Br₂] (2b): Complex **1b** (0.086 g, 0.088 mmol) in 100 mL of toluene was heated at 60 °C for one night. After cooling to room temperature, ethylene was bubbled through the solution for 1.5 h. The precipitate was collected and washed with cold THF (3×5 mL) and MeCN (3×5 mL) to afford **2b** as a pure pale yellow solid (0.066 g, 0.068 mmol, 78%). IR (KBr): $\tilde{v} = 2926$ and 2879 (s, vC–H), 1696 (vs, vNO) cm⁻¹. ¹H NMR (300.1 MHz, CD₂Cl₂, 40 °C): $\delta = 3.00-1.32$ (H₂C=CH₂ and P(C₆H₁₁)₃) ppm. ³¹P{¹H} MMR (80.9 MHz, CD₂Cl₂, 40 °C): $\delta = -20.3$ (br. s) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂, 40 °C): $\delta = 39.5$ (br., H₂C=CH₂), 36.5 (t, *J*(PC) = 9 Hz, P(C₆H₁₁)₃), 29.4, 28.6 and 27.1 (3 s, P(C₆H₁₁)₃) ppm. C₃₈H₇₀Br₂NOP₂Re (964.93): calcd. C 47.30, H 7.31, N 1.45; found C 47.21, H 7.55, N 1.63.

Synthesis of [Re(NO)(PiPr₃)₂(MeCN)Me₂] (3a): To a solution of 1a (0.081 g, 0.105 mmol) in 10 mL of toluene, cooled to -30 °C was added rapidly MeLi 1.6 M in Et₂O (132 µL, 0.210 mmol). The color changed immediately from light orange to red. The mixture was stirred at -30 °C for 30 min then allowed to come to room temperature and stirred for additional 30 min. The solution was filtered through celite and the solvent was evaporated under vacuum. The extraction with pentane affords the red beet viscous complex 3a (0.078 g, 0.128 mmol, 82%). IR (CH_2Cl_2) : $\tilde{v} = 2360 \text{ (w, vMe}C \equiv N)$, 1588 (vs, vNO) cm⁻¹. ¹H NMR (300.1 MHz, C₆D₆): δ = 2.61–2.43 (m, 6 H, (CH₃)₂CHP), 2.36 (t, J(PH) = 2.20 Hz, 3 H, ReMe), 2.29 (t, J(PH) = 2.03 Hz, 3 H, ReMe), 1.97 (s, 3 H, MeCNRe), 1.32–1.22 (m, 36 H, (CH₃)₂CHP) ppm. ³¹P{¹H} NMR (80.9 MHz, C₆D₆): δ = -15.9 (s) ppm. ¹³C{¹H} NMR (125.8 MHz, C₆D₆): δ = 24.6 (t, $J(PC) = 11 \text{ Hz}, (CH_3)_2 CHP), 20.6 (br. s, ReMe), 20.5 (br. s, ReMe),$ 20.2 and 20.1 (2s,(CH₃)₂CHP) ppm.

Synthesis of $[Re(NO)(PiPr_3)_2(MeCN)_2Br][BAr^F_4]$ (4a): A solid Na-BAr^F₄ (0.131 g, 0.148 mmol) was added to a solution of 1a (0.114 g, 0.148 mmol) dissolved in 10 mL of MeCN. The mixture was stirred for 14 h at room temperature. The yellow solution was

filtered and the solvent was removed under vacuum. Extraction by CH₂Cl₂ and recrystallization from CH₂Cl₂/pentane at room temperature affords, after one day, yellow crystals of 4a (0.188 g, 0.120 mmol, 81%). IR (KBr): $\tilde{v} = 1712$ (vs, vNO) cm⁻¹. ¹H NMR (300.1 MHz, CD₂Cl₂): δ = 7.73 (m, 8 H, BAr^F₄), 7.56 (m, 4 H, BAr^F₄), 2.89 (s, 6 H, MeCNRe), 2.83–2.71 (m, 6 H, (CH₃)₂CHP), 1.42–1.33 (m, 36 H, (CH₃)₂CHP) ppm. ${}^{31}P{}^{1}H$ NMR (121.47 MHz, CD₂Cl₂): $\delta = 0.4$ (s) ppm. ¹³C{¹H} NMR (125.8 MHz, CD₂Cl₂): δ = 162.0 (q, ¹*J*(BC) = 50 Hz, *ipso*-BAr^F), 137.7 (s, H₃CCNRe), 135.1 (s, o-BAr^F), 129.1 (br., m-BAr^F), 126.0 $(q, {}^{1}J(CF) = 50 \text{ Hz}, CF_{3}), 117.8 \text{ (br., } p\text{-BAr}^{F_{4}}), 24.8 \text{ (t, } J(PC) =$ 11 Hz, (CH₃)₂CHP), 19.1 (s, (CH₃)₂CHP), 5.2 (s, H₃CCNRe) ppm. ¹⁹F NMR (125.8 MHz, CD_2Cl_2 : $\delta =$ -64.4 ppm. C₅₄H₆₀BBrF₂₄N₃OP₂Re (1561.91): calcd. C 41.95, H 3.91, N 2.72; found C 42.03, H 4.01, N 2.67.

Synthesis of [Re(NO)(PCy₃)₂(MeCN)₂Br][BAr^F₄] (4b): 4b (0.078 g, 0.042 mmol, 84%) was obtained by the same procedure described for **4a** by reaction of **1b** (0.050 g, 0.051 mmol) and NaBAr^F₄ (0.045 g, 0.051 mmol) in a mixture of THF/MeCN (15:1 mL) at room temperature after 30 h. IR (ATR): $\tilde{v} = 1703$ (vs, vNO) cm⁻¹. ¹H NMR (300.1 MHz, CD₂Cl₂): $\delta = 2.94$ (s, 6 H, CH₃CN-Re), 2.57–1.28 (m, 66 H, P(C₆H₁₁)₃) ppm. ³¹P{¹H} NMR (121.47 MHz, CD₂Cl₂): = -10.2 (s) ppm. ¹³C{¹H} NMR (75.5 MHz, CD₂Cl₂): $\delta = 164.0$ (m, *ipso*-BAr^F), 137.7 (s, H₃CCNRe), 135.2 (s, *o*-BAr^F), 129.4 (br., *m*-BAr^F), 129.0 (m, CF₃), 118.0 (br., *p*-BAr^F₄), 35.2 (t, *J*(PC) = 10 Hz, P(C₆H₁₁)₃), 29.6, 28.9 and 26.8 (3 s, P(C₆H₁₁)₃), 5.7 (s, CH₃CN-Re) ppm. ¹⁹F NMR (125.8 MHz, CD₂Cl₂): $\delta = -63.9$ ppm. C₇₂H₈₄BBrF₂₄N₃O₂P₂Re (1818.28): calcd. C 47.56, H 4.65, N 2.31; found C 47.71, H 4.67, N 2.20.

Synthesis of $[\text{Re}(\eta^4-C_4H_6)(\eta^2-H_2C=CH_2)(\text{NO})(PiPr_3)_2]$ (6a): In a 50 mL Young tap Schlenk tube the complex [Re(NO)(MeCN)-(PiPr₃)₂Br₂] (1a) (0.100 g, 0.135 mmol) was dissolved in 20 mL of THF and 10 g of 0.7% sodium amalgam was added. Without stirring, the solution was frozen and kept under pressure of 1.4 bar of C_2H_4 for 5 min. The mixture was warmed to room temperature, and stirred for 3 d. Filtration over celite and removal of the solvent left a yellow residue, which was extracted with toluene and then dried. Final extraction with pentane affords a pure pale yellow powder of **6a** (0.020 g, 0.042 mmol, 31%). IR (ATR): $\tilde{v} = 2964$, 2930 and 2872 (s, vC-H), 1646 (vs, vNO) cm⁻¹. ¹H NMR $(500.25 \text{ MHz}, C_6 D_6)$: $\delta = 5.72 \text{ (q, } J(\text{HH}) = 6.7 \text{ Hz}, 1 \text{ H},$ $H_{int}C=CH_{int}$), 5.25 (q, J(HH) = 6.7 Hz, 1 H, $H_{int}C=CH_{int}$), 2.20 (m, 1 H, (HHC=CHH)Re), 2.06 (m, 0.34 H, H_{svn2}H_{anti2}CRe, isomer **B**), 1.98 (dd, ${}^{3}J(HH) = 6.7$, ${}^{2}J(HH) = 3.5$ Hz, 0.66 H, $H_{syn2}H_{anti2}CRe$, isomer A), 1.82 (m, 5 H, (CH₃)₂CHP and (HHC=CHH)Re), 1.48 (m, 1 H, (HHC=CHH)Re), 1.18-0.98 and 0.95–0.87 (2 m, 18 H, (CH₃)₂CHP), 0.56 (td, ${}^{3}J(HH) = {}^{3}J(PH) =$ 6.7 Hz, ${}^{2}J(\text{HH}) = 3.5$ Hz, 0.66 H, $H_{syn2}H_{anti2}$ CRe, isomer A), 0.43 $(td, {}^{3}J(HH) = {}^{3}J(PH) = 6.7 Hz, {}^{2}J(HH) = 3.5 Hz, 0.34 H,$ H_{syn2}H_{anti2}CRe, isomer B), -0.21 (m, 1 H, H_{syn1}H_{anti1}CRe), -0.52 $(q, J(HH) = J(PH) = 6.7 \text{ Hz}, 0.66 \text{ H}, H_{syn1}H_{anti1}CRe, \text{ isomer A}),$ -0.72 (q, J(HH) = J(PH) = 6.7 Hz, 0.34 H, H_{syn1}H_{antil}CRe, isomer **B**) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 21.3 (br. s, isomer A), 12.9 (br. s, isomer B) ppm. ${}^{13}C{}^{1}H$ NMR (125.8 MHz, C₆D₆): δ = 97.5 (d, J(CP) = 2 Hz, H_{int}C=CH_{int}, isomer **B**), 96.14 (d, J(CP) = 2 Hz, $H_{int}C=CH_{int}$, isomer A), 83.0 (br. s, $H_{int}C=CH_{int}$, isomer A), 81.97 (br. s, $H_{int}C=CH_{int}$, isomer B), 34.0 (d, J(CP) = 5 Hz, $H_{svn1}H_{anti1}CRe$, isomer **B**), 32.8 (d, J(CP) = 5 Hz, $H_{svn1}H_{anti1}CRe$, isomer A), 30.5 (d, J(CP) = 6 Hz, $H_{anti2}H_{syn2}CRe$, isomer A), 29.7 (d, J(CP) = 6 Hz, $H_{anti2}H_{syn2}CRe$, isomer **B**), 29.2 (br. s, $(CH_3)_2$ -CHP, isomer A), 29.0 (br. s, (CH₃)₂CHP, isomer B), 25.5 (d, J(CP) = 8 Hz, (HHC=CHH)Re, isomer A), 24.9 (d, J(CP) = 8 Hz, (HHC=CHH)Re, isomer **B**), 24.7 (d, J(CP) = 3 Hz, (HHC=CHH)-

Re, isomer A), 23.7 (d, J(CP) = 3 Hz, (HHC=CHH)Re, isomer B), 19.4 (s, (CH₃)₂CHP isomer A), 19.0 (s, (CH₃)₂CHP, isomer B) ppm. C₁₅H₃₁NOPRe (458.59): calcd. C 39.28, H 6.81, N 3.05; found C 39.46, H 6.93, N 3.18.

Synthesis of $[\text{Re}(\eta^4-C_4H_6)(\eta^2-H_2C=CH_2)(\text{NO})(\text{PCy}_3)_2]$ (6b): Complex 6b (0.026 g, 0.045 mmol, 63%) was obtained by the same procedure described for 6a by reduction of 1b (0.070 g, 0.071 mmol) under a pressure of 1.4 bar of ethylene. IR (ATR): $\tilde{v} = 2924$ and 2846 (vs, vC-H), 1643 (vs, vNO) cm⁻¹. ¹H NMR (500.25 MHz, C_6D_6): $\delta = 5.76$ (q, J(HH) = 6.4 Hz, 1 H, $H_{int}C=CH_{int}$), 5.29 (q, ${}^{3}J(\text{HH}) = 6.4 \text{ Hz}, 1 \text{ H}, \text{ H}_{\text{int}}\text{C}=\text{C}H_{\text{int}}, 2.40-1.05 \text{ (m, } 37 \text{ H},$ $(H_2C=CH_2)Re \text{ and } P(C_6H_{11})_3), 2.01 \text{ (dd, } {}^2J(H_{syn2}H_{anti2}) = 3.3,$ $J(\text{HH}) = 6.4 \text{ Hz}, 1 \text{ H}, H_{syn2}\text{H}_{anti2}\text{CRe}), 0.70 \text{ (td, } J(\text{HH}) = 3.3,$ $J(HH) = J(PH) = 6.4 \text{ Hz}, 1 \text{ H}, H_{syn2}H_{anti2}CRe), -0.17 \text{ (m, 1 H,}$ $H_{syn1}H_{antil}CRe$, -0.42 (q, J(HH) = J(PH) = 6.1 Hz, 1 H, $H_{syn1}H_{anti1}CRe$) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆): δ = 10.0 (s) ppm. ¹³C{¹H} NMR (125.8 MHz, C₆D₆): $\delta = 95.7$ (s, $H_{int}C=CH_{int}$), 83.6 (s, $H_{int}C=CH_{int}$), 33.6 (d, J(CP) = 5 Hz, $H_{syn1}H_{anti1}CRe$, 32.2 (d, J(CP) = 19 Hz, $P(C_6H_{11})_3$), 31.7 (d, J(CP)= 13, $P(C_6H_{11})_3$, 30.5 (d, J(CP) = 5, $H_{anti2}H_{syn2}CRe$), 29.8 (br. s, $P(C_6H_{11})_3$, 27.9 (br. s, $P(C_6H_{11})_3$, 28.0 (d, J(CP) = 9 Hz, $P(C_6H_{11})_3)$, 26.9 (br. s, $P(C_6H_{11})_3)$, 25.3 (d, J(CP) = 8 Hz, (HHC=CHH)Re), 25.1 (d, J(CP) = 3 Hz, (HHC=CHH)Re) ppm. C₂₄H₄₃NOPRe (578.78): calcd. C 49.80, H 7.48, N 2.42; found C 50.02, H 7.61, N 2.26.

 $[Re(NO)(CO)(PiPr_3)_2(\eta^2-C_2H_4)]$ (8a): In a 60 mL Young tap Schlenk tube 7b (0.100 g, 0.157 mmol) was dissolved in 30 mL of THF and 10 g of 0.7% sodium amalgam was added. Without stirring, the solution was frozen and kept under pressure of 1.4 bar of C₂H₄ for 5 min. The mixture was warmed to room temperature, and stirred for 5 d. The mixture was filtered through celite and the solvent was removed under vacuum. The orange residue was extracted with toluene and washed with cold pentane to afford pure 8a (0.081 g, 0.136 mmol, 87%). Suitable X-ray crystals were obtained from a solution of 8a in 3 mL of pentane at -30 °C. IR (ATR): $\tilde{v} = 2963$, 2927 and 2872 (s, vC–H), 1879 (s, vCO), 1576 (s, vNO) cm⁻¹. ¹H NMR (300.1 MHz, C₆D₆, room temp.): $\delta = 2.16$ -1.84 (m, 6 H, (CH₃)₂CHP), 1.38–1.19 (m, 36 H, (CH₃)₂CHP) ppm. $\rm C_2H_4$ not observed. $^1\rm H$ NMR (300.1 MHz, [D_8]toluene, 100 °C): δ = 2.42–1.31 (m, $(CH_3)_2CHP$ partly overlap with signal of toluene CH₃), 1.86 (br. t, 4 H, H₂C=CH₂), 1.25-1.09 (m, 36 H, (CH₃)₂-CHP) ppm. ³¹P{¹H} NMR (121.5 MHz, C₆D₆, room temp.): δ = 13.4 (s) ppm. ¹³C{¹H} NMR (75.5 MHz, [D₈]toluene, 90 °C): δ = 218.4 (t, J(PC) = 12 Hz, C=O), 25.1 (t, J(PC) = 23 Hz, $(CH_3)_2$ -CHP), 23.0 (br. s, H₂C=CH₂), 20.6 and 19.3 (2 s, (CH₃)₂-CHP) ppm. C₂₁H₄₆NO₂P₂Re (592.75): calcd. C 42.55, H 7.82, N 2.36; found C 42.69, H 8.12, N 2.35.

[Re(NO)(CO)(PCy₃)₂(\eta^2-C₂H₄)] (8b): Complex **8b** (0.086 g, 0.103 mmol, 90%) was obtained by the same procedure as described for **8a** via reduction of [Re(NO)(CO)(PCy₃)₂Cl₂] (0.100 g, 0. 114 mmol) using 10 g of 0.7% sodium amalgam and 1.4 bar C₂H₄. IR (ATR): $\tilde{v} = 2925$ and 2848 (s, vCO), 1883 (s, vCO), 1585 (vs, vNO) cm⁻¹. ¹H NMR (300.1 MHz, C₆D₆, room temp.): $\delta = 2.17-1.17$ (H₂C=CH₂ and P(C₆H₁₁)₃) ppm. ³¹P{¹H} NMR (80.9 MHz, C₆D₆): $\delta = 5.7$ (s) ppm. ¹³C{¹H} NMR (75.5 MHz, [D₈]toluene, -20 °C): $\delta = 218.5$ (t, *J*(PC) = 12 Hz, C=O), 34.4 (br., P(C₆H₁₁)₃), 30.7, 30.3, 27.3 (3 s, P(C₆H₁₁)₃), 23.0 (br. s, H₂C=CH₂) ppm. C₃₉H₇₀NO₂P₂Re (833.13): calcd. C 56.22, H 8.47, N 1.68; found C 56.67, H 8.59, N 1.61.

NMR Tube Reactions. Synthesis of $[\text{Re}(\eta^2-\text{H}_2)(\text{NO})(\text{PR}_3)_2\text{Br}_2]$ (R = *i*Pr 5a, R = Cy 5b): A solution of 1a (0.010 g, 0.013 mmol) in 0.5 mL C₆D₆ or 1b (0.012 g, 0.012 mmol) in 0.5 mL of CD₂Cl₂ was



sealed under 1 bar of H₂. Formation of **5a,b** takes place immediately upon shaking of the tubes. All NMR spectroscopic data are in agreement with those previously reported.^[5]

1 mL of toluene was added dropwise with stirring to a solution of **8a** (0.056 g, 0.094 mmol) in the same solvent. The mixture was stirred further at room temperature for 22 h. The solvent was then removed in vacuo and the residue extracted with pentane and recrystallized from the same solvent at -30 °C to afford orange crystals of **9a**; yield 0.039 g, 0.036 mmol, 38%. **9a** and **10a** were identified by their IR spectra: **9a** IR (ATR): $\tilde{v} = 1968$ (s, vCO),

Table 8. Summary of crystallographic data for complexes 4a, 4b, 6b, 8a, 9a, and 9b.

	4a	4b	6b
Empirical formula	C54H60BBrF24N2OP2Re	C72He4BBrF24N2OP2Re•CH2Cl2	C24H42NOPRe
Molecular weight	1561 91	1887 21	578 76
Color	vellow	vellow	pale vellow
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	C^{2}/c	Pna?,	$P_{2,lc}$
a [Å]	20.330(2)	33849(2)	14 1035(9)
$h \begin{bmatrix} A \end{bmatrix}$	15.0650(11)	123816(11)	11 3650(6)
c [Å]	21 790(2)	19.0254(18)	17 4160(12)
	90	90	90
<i>R</i> [9]	109 124(11)	90	121 264(7)
<i>P</i> []	90	90	90
/ L] V [Å ³]	6305 4(10)	7073 7(12)	2386 2(3)
7	4	Δ	4
$a \to [g \text{ cm}^{-3}]$	1 645	1 572	1 611
$\mu \text{ [mm^{-1}]}$	2 722	2 232	5 174
Transmission range	0.7098_0.5185	0 7135-0 4660	0 5464_0 3401
Crystal size [mm]	$0.15 \times 0.21 \times 0.27$	$0.18 \times 0.34 \times 0.43$	$0.22 \times 0.21 \times 0.13$
hkl limiting indices	-26/25 + 19 + 28	-38/40 + 15 + 23	-20/17 + 16 + 24
F(000)	3006	3702	-20/17, = 10, = 24
θ limits [°]	2 15-28 05	1 75_25 92	2 96_30 43
Number of meased reflections	26224	53030	51454
Number of unique reflections	7504	15066	7130
Number of parameters	A15	960	272
$R^{[a]}[I > 2\sigma(D)]$ all data	0.0356 0.0721	0.0467 0.0565	0.0264 0.0374
$R_1^{[b]}[I > \sigma(I)]$, an data	0.0829 0.0883	0.1182 0.1237	0.0744 0.0752
WR_2^{r-1} [$I > 0(I)$], all data GOE (for F^2)	0.831	0.027	0.071
	1 001 1 576	1 130 1 686	0.670 2.011
$\Delta p_{\text{max/min}}$	-1.071, 1.370	-1.150, 1.000	-0.070, 2.011
	0 -	0-	
	88	9a	96
Empirical formula	$C_{21}H_{46}NO_2P_2Re$	$\frac{9a}{C_{43}H_{54}BF_{15}NO_{3}P_{2}Re}$	9b C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re
Empirical formula Molecular weight	8a C ₂₁ H ₄₆ NO ₂ P ₂ Re 592.74	9a C ₄₃ H ₅₄ BF ₁₅ NO ₃ P ₂ Re 1176.83	96 C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06
Empirical formula Molecular weight Color	8a C ₂₁ H ₄₆ NO ₂ P ₂ Re 592.74 orange	9a C ₄₃ H ₅₄ BF ₁₅ NO ₃ P ₂ Re 1176.83 orange	96 C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06 orange
Empirical formula Molecular weight Color Crystal system	C ₂₁ H ₄₆ NO ₂ P ₂ Re 592.74 orange monoclinic	Grand Straight Straig	C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06 orange triclinic
Empirical formula Molecular weight Color Crystal system Space group	$C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$	$C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\bar{1}$	C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06 orange triclinic <i>P</i> 1
Empirical formula Molecular weight Color Crystal system Space group <i>a</i> [Å]	ba $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13)	$C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic <i>P</i> I 11.2503(17)	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic <i>P</i> I 12.5747(8)
Empirical formula Molecular weight Color Crystal system Space group <i>a</i> [Å] <i>b</i> [Å]	$\begin{array}{c} \mathbf{5a} \\ C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ \text{orange} \\ \text{monoclinic} \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \end{array}$	$\begin{array}{c} \textbf{9a} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ orange \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \end{array}$	$\begin{array}{c} \mathbf{y_{0}} \\ \mathbf{C}_{56}\mathbf{H}_{66}\mathbf{BF}_{15}\mathbf{NO_{3}P_{2}Re} \\ 1345.06 \\ \text{orange} \\ \text{triclinic} \\ P\bar{1} \\ 12.5747(8) \\ 14.6063(10) \end{array}$
Empirical formula Molecular weight Color Crystal system Space group <i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å]	$\begin{array}{c} \mathbf{5a} \\ C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ \text{orange} \\ \text{monoclinic} \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \end{array}$	$\begin{array}{c} \textbf{9a} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ orange \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \end{array}$	$\begin{array}{c} \textbf{96} \\ \textbf{C}_{56}\textbf{H}_{66}\textbf{B}\textbf{F}_{15}\textbf{N}\textbf{O}_{3}\textbf{P}_{2}\textbf{R}e \\ \textbf{1345.06} \\ \textbf{orange} \\ \textbf{triclinic} \\ P\bar{\textbf{1}} \\ \textbf{12.5747(8)} \\ \textbf{14.6063(10)} \\ \textbf{16.5491(10)} \end{array}$
Empirical formula Molecular weight Color Crystal system Space group <i>a</i> [Å] <i>b</i> [Å] <i>c</i> [Å] <i>a</i> [°]	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ orange \\ monoclinic \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \end{array}$	$9a$ $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\bar{1}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19)	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8)
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ orange \\ monoclinic \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \end{array}$	$\begin{array}{c} \textbf{9a} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ orange \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \end{array}$	96 C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06 orange triclinic P1 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8)
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ orange \\ monoclinic \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \\ 90.00 \end{array}$	$\begin{array}{c} \textbf{9a} \\ \hline C_{43}H_{54}BF_{15}NO_3P_2Re \\ 1176.83 \\ \text{orange} \\ \text{triclinic} \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \end{array}$	$\begin{array}{c} \textbf{96} \\ \hline C_{56}H_{66}BF_{15}NO_{3}P_{2}Re \\ 1345.06 \\ orange \\ triclinic \\ P\bar{1} \\ 12.5747(8) \\ 14.6063(10) \\ 16.5491(10) \\ 86.834(8) \\ 88.538(8) \\ 67.138(7) \end{array}$
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] γ [°] γ [Å]	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ orange \\ monoclinic \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \\ 90.00 \\ 2551.1(4) \end{array}$	$\begin{array}{c} \textbf{9a} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ \text{orange} \\ \text{triclinic} \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \end{array}$	$\begin{array}{c} \textbf{9b} \\ \hline \\ C_{56}H_{66}BF_{15}NO_3P_2Re \\ 1345.06 \\ orange \\ triclinic \\ P\bar{1} \\ 12.5747(8) \\ 14.6063(10) \\ 16.5491(10) \\ 86.834(8) \\ 88.538(8) \\ 67.138(7) \\ 2796.5(3) \end{array}$
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] γ [°] Z	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ orange \\ monoclinic \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \\ 90.00 \\ 2551.1(4) \\ 4 \end{array}$	$\begin{array}{c} \textbf{y_a} \\ \hline C_{43}H_{54}BF_{15}NO_3P_2Re \\ 1176.83 \\ orange \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \end{array}$	$\begin{array}{c} \textbf{9b} \\ \hline \\ C_{56}H_{66}BF_{15}NO_3P_2Re \\ 1345.06 \\ orange \\ triclinic \\ P\bar{1} \\ 12.5747(8) \\ 14.6063(10) \\ 16.5491(10) \\ 86.834(8) \\ 88.538(8) \\ 67.138(7) \\ 2796.5(3) \\ 2 \end{array}$
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] γ [°] V [Å3] Z ρ_{calcd} [g cm ⁻³]	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ orange \\ monoclinic \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \\ 90.00 \\ 2551.1(4) \\ 4 \\ 1.543 \end{array}$	$\begin{array}{c} \textbf{y_a} \\ \hline C_{43}H_{54}BF_{15}NO_3P_2Re \\ 1176.83 \\ orange \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \end{array}$	96 C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06 orange triclinic P1 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å3] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹]	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ \text{orange} \\ \text{monoclinic} \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \\ 90.00 \\ 2551.1(4) \\ 4 \\ 1.543 \\ 4.904 \end{array}$	$\begin{array}{c} \textbf{y_a} \\ \hline C_{43}H_{54}BF_{15}NO_3P_2Re \\ 1176.83 \\ orange \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \end{array}$	96 C ₅₆ H ₆₆ BF ₁₅ NO ₃ P ₂ Re 1345.06 orange triclinic P1 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å3] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range	$8a$ $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13) 14.0278(10) 15.4531(16) 90.00 100.370(13) 90.00 2551.1(4) 4 1.543 4.904 0.1262–0.5018	y_a $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\bar{1}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19) 85.913(19) 75.505(18) 2385.6(7) 2 1.638 2.712 0.652–0.407	$\begin{array}{c} \textbf{9b} \\ \hline \\ C_{56}H_{66}BF_{15}NO_3P_2Re \\ 1345.06 \\ orange \\ triclinic \\ P\bar{1} \\ 12.5747(8) \\ 14.6063(10) \\ 16.5491(10) \\ 86.834(8) \\ 88.538(8) \\ 67.138(7) \\ 2796.5(3) \\ 2 \\ 1.597 \\ 2.324 \\ 0.666-0.845 \end{array}$
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å3] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm]	$8a$ $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13) 14.0278(10) 15.4531(16) 90.00 100.370(13) 90.00 2551.1(4) 4 1.543 4.904 0.1262–0.5018 0.14 × 0.48 × 0.57	$9a$ $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\overline{1}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19) 85.913(19) 75.505(18) 2385.6(7) 2 1.638 2.712 0.652-0.407 0.27 × 0.28 × 0.44	$9b$ $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å3] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices	8a $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13) 14.0278(10) 15.4531(16) 90.00 100.370(13) 90.00 2551.1(4) 4 1.543 4.904 0.1262–0.5018 0.14 × 0.48 × 0.57 ±16, ±19, ±21	$9a$ $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\overline{1}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19) 85.913(19) 75.505(18) 2385.6(7) 2 1.638 2.712 0.652-0.407 0.27 × 0.28 × 0.44 -15/16, -17/18, ±24	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å ³] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000)	$8a$ $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ $11.9641(13)$ $14.0278(10)$ $15.4531(16)$ 90.00 $100.370(13)$ 90.00 $2551.1(4)$ 4 1.543 4.904 $0.1262-0.5018$ $0.14 \times 0.48 \times 0.57$ $\pm 16, \pm 19, \pm 21$ 1200	$\begin{array}{c} \mathbf{y_{a}} \\ \hline \mathbf{C}_{43}\mathbf{H}_{54}\mathbf{BF}_{15}\mathbf{NO}_{3}\mathbf{P}_{2}\mathbf{Re} \\ 1176.83 \\ \text{orange} \\ \text{triclinic} \\ P\bar{\mathbf{I}} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \\ 0.652-0.407 \\ 0.27 \times 0.28 \times 0.44 \\ -15/16, -17/18, \pm 24 \\ 1176 \end{array}$	95 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°]	8a $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13) 14.0278(10) 15.4531(16) 90.00 100.370(13) 90.00 2551.1(4) 4 1.543 4.904 0.1262–0.5018 0.14 × 0.48 × 0.57 $\pm 16, \pm 19, \pm 21$ 1200 3.20–30.39	$9a$ $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\bar{I}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19) 85.913(19) 75.505(18) 2385.6(7) 2 1.638 2.712 0.652-0.407 0.27 × 0.28 × 0.44 -15/16, -17/18, ±24 1176 2.79-30.39	95 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83–30.39
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections	8a $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13) 14.0278(10) 15.4531(16) 90.00 100.370(13) 90.00 2551.1(4) 4 1.543 4.904 0.1262–0.5018 0.14 × 0.48 × 0.57 $\pm 16, \pm 19, \pm 21$ 1200 3.20–30.39 29650	$9a$ $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\bar{I}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19) 85.913(19) 75.505(18) 2385.6(7) 2 1.638 2.712 0.652–0.407 0.27 × 0.28 × 0.44 -15/16, -17/18, ±24 1176 2.79–30.39 51447	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] $\beta [°]$ $\gamma [°]$ $V [Å^3]$ Z $\rho_{calcd.} [g cm^{-3}]$ $\mu [mm^{-1}]$ Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections	8a $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ 11.9641(13) 14.0278(10) 15.4531(16) 90.00 100.370(13) 90.00 2551.1(4) 4 1.543 4.904 0.1262–0.5018 0.14 × 0.48 × 0.57 $\pm 16, \pm 19, \pm 21$ 1200 3.20–30.39 29650 7583	$9a$ $C_{43}H_{54}BF_{15}NO_3P_2Re$ 1176.83 orange triclinic $P\bar{1}$ 11.2503(17) 12.818(2) 17.353(3) 80.100(19) 85.913(19) 75.505(18) 2385.6(7) 2 1.638 2.712 0.652-0.407 0.27 × 0.28 × 0.44 -15/16, -17/18, ±24 1176 2.79-30.39 51447 13094	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505 15287
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å ³] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections Number of unique reflections	$\begin{array}{c} \mathbf{8a} \\ \hline C_{21}H_{46}NO_2P_2Re \\ 592.74 \\ \text{orange} \\ \text{monoclinic} \\ P2_1/n \\ 11.9641(13) \\ 14.0278(10) \\ 15.4531(16) \\ 90.00 \\ 100.370(13) \\ 90.00 \\ 2551.1(4) \\ 4 \\ 1.543 \\ 4.904 \\ 0.1262-0.5018 \\ 0.14 \times 0.48 \times 0.57 \\ \pm 16, \pm 19, \pm 21 \\ 1200 \\ 3.20-30.39 \\ 29650 \\ 7583 \\ 260 \end{array}$	$\begin{array}{c} \textbf{y_{a}} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ \text{orange} \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \\ 0.652-0.407 \\ 0.27 \times 0.28 \times 0.44 \\ -15/16, -17/18, \pm 24 \\ 1176 \\ 2.79-30.39 \\ 51447 \\ 13094 \\ 575 \end{array}$	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505 15287 712
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [Å] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections Number of unique reflections Number of parameters $R_1^{[a]}$ [$I > 2\sigma(I)$], all data	δa $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ $11.9641(13)$ $14.0278(10)$ $15.4531(16)$ 90.00 $2551.1(4)$ 4 1.543 4.904 $0.1262-0.5018$ $0.14 \times 0.48 \times 0.57$ $\pm 16, \pm 19, \pm 21$ 1200 $3.20-30.39$ 29650 7583 260 $0.0267, 0.0380$	$\begin{array}{c} \textbf{y_{a}} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ \text{orange} \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \\ 0.652-0.407 \\ 0.27 \times 0.28 \times 0.44 \\ -15/16, -17/18, \pm 24 \\ 1176 \\ 2.79-30.39 \\ 51447 \\ 13094 \\ 575 \\ 0.0522, 0.0635 \end{array}$	$9b$ $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505 15287 712 0.0362, 0.0487
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [ų] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections Number of maneters Number of parameters $R_1^{[a]}$ [$I > 2\sigma(I)$], all data $wR_3^{[b]}$ [$I > \sigma(I)$], all data	$8a$ $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ $11.9641(13)$ $14.0278(10)$ $15.4531(16)$ 90.00 $100.370(13)$ 90.00 $2551.1(4)$ 4 1.543 4.904 0.1262 - 0.5018 $0.14 \times 0.48 \times 0.57$ $\pm 16, \pm 19, \pm 21$ 1200 3.20 - 30.39 29650 7583 260 $0.0267, 0.0380$ $0.0685, 0.0706$	$\begin{array}{c} \textbf{y_{a}} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ \text{orange} \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \\ 0.652-0.407 \\ 0.27 \times 0.28 \times 0.44 \\ -15/16, -17/18, \pm 24 \\ 1176 \\ 2.79-30.39 \\ 51447 \\ 13094 \\ 575 \\ 0.0522, 0.0635 \\ 0.1412, 0.1478 \end{array}$	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505 15287 712 0.0362, 0.0487 0.1262, 0.1277
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [ų] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections Number of unique reflections Number of parameters $R_1^{[a]}$ [$I > \sigma(I)$], all data $WR_2^{[b]}$ [$I > \sigma(I)$], all data	$8a$ $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ $11.9641(13)$ $14.0278(10)$ $15.4531(16)$ 90.00 $100.370(13)$ 90.00 $2551.1(4)$ 4 1.543 4.904 $0.1262-0.5018$ $0.14 \times 0.48 \times 0.57$ $\pm 16, \pm 19, \pm 21$ 1200 $3.20-30.39$ 29650 7583 260 $0.0267, 0.0380$ $0.0685, 0.0706$ 1.061	$\begin{array}{c} \textbf{y_{a}} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ \text{orange} \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \\ 0.652-0.407 \\ 0.27 \times 0.28 \times 0.44 \\ -15/16, -17/18, \pm 24 \\ 1176 \\ 2.79-30.39 \\ 51447 \\ 13094 \\ 575 \\ 0.0522, 0.0635 \\ 0.1412, 0.1478 \\ 1.081 \\ \end{array}$	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505 15287 712 0.0362, 0.0487 0.1262, 0.1277 1.067
Empirical formula Molecular weight Color Crystal system Space group a [Å] b [Å] c [Å] a [°] β [°] γ [°] V [ų] Z $\rho_{calcd.}$ [g cm ⁻³] μ [mm ⁻¹] Transmission range Crystal size [mm] hkl limiting indices F(000) θ limits [°] Number of measd. reflections Number of unique reflections Number of unique reflections Number of parameters $R_1^{[a]}$ [$I > \sigma(I)$], all data $WR_2^{[b]}$ [$I > \sigma(I)$], all data GOF (for F^2) $\Delta \rho_{max/min}$	$8a$ $C_{21}H_{46}NO_2P_2Re$ 592.74 orange monoclinic $P2_1/n$ $11.9641(13)$ $14.0278(10)$ $15.4531(16)$ 90.00 $100.370(13)$ 90.00 $2551.1(4)$ 4 1.543 4.904 $0.1262-0.5018$ $0.14 \times 0.48 \times 0.57$ $\pm 16, \pm 19, \pm 21$ 1200 $3.20-30.39$ 29650 7583 260 $0.0267, 0.0380$ $0.0685, 0.0706$ 1.061 $-2.543, 1.111$	$\begin{array}{c} \textbf{y_{a}} \\ \hline C_{43}H_{54}BF_{15}NO_{3}P_{2}Re \\ 1176.83 \\ \text{orange} \\ triclinic \\ P\bar{1} \\ 11.2503(17) \\ 12.818(2) \\ 17.353(3) \\ 80.100(19) \\ 85.913(19) \\ 75.505(18) \\ 2385.6(7) \\ 2 \\ 1.638 \\ 2.712 \\ 0.652-0.407 \\ 0.27 \times 0.28 \times 0.44 \\ -15/16, -17/18, \pm 24 \\ 1176 \\ 2.79-30.39 \\ 51447 \\ 13094 \\ 575 \\ 0.0522, 0.0635 \\ 0.1412, 0.1478 \\ 1.081 \\ -7.462, 4.098 \end{array}$	96 $C_{56}H_{66}BF_{15}NO_3P_2Re$ 1345.06 orange triclinic $P\overline{1}$ 12.5747(8) 14.6063(10) 16.5491(10) 86.834(8) 88.538(8) 67.138(7) 2796.5(3) 2 1.597 2.324 0.666-0.845 0.17 × 0.13 × 0.08 -14/14, -17/17, ±19 1356 2.83-30.39 43505 15287 712 0.0362, 0.0487 0.1262, 0.1277 1.067 1.788, -0.579

[a] $R_1 = \sum (F_o - F_c) / \sum F_o$; $I > 2 \sigma(I)$. [b] $wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2 \}^{1/2}$.

1883 (s, vCO), 1458 (s, vNO) cm⁻¹. **10a** IR (hexane): $\tilde{v} = 1940$ (s, vCO), 1852 (s, vCO), 1605 (s, vNO) cm⁻¹.

Synthesis of [Re(CO)₂{NOB(C₆F₅)₃}(PiPr₃)₂] (9a): A solution of $B(C_6F_5)_3$ (0.064 g, 0.124 mmol) in 2 mL of toluene was added to a solution of 8a (0.074 g, 0.124 mmol) in 15 mL of the same solvent in a Young tap Schlenk tube. Without stirring the mixture was frozen and kept under pressure of 1 bar of CO for 3 min. The mixture was warmed to room temperature and stirred for 15 min. The gas and the solvent were removed in vacuo and the orange residue was extracted with CH₂Cl₂ and washed several times using cold pentane to afford pure 9a (0.126 g, 0.114 mmol, 92%). IR (ATR): $\tilde{v} = 1968$ (s, vCO), 1883 (s, vCO), 1458 (s, vNO) cm⁻¹. ¹H NMR $(300.1 \text{ MHz}, [D_8] \text{toluene}): \delta = 0.92-0.80 \text{ (m, 6 H, (CH_3)_2CHP)},$ 1.82–1.71 (m, 36 H, $(CH_3)_2$ CHP) ppm. ³¹P{¹H} NMR (121.5 MHz, [D₈]toluene): δ = 32.3 (s) ppm. ¹³C{¹H} NMR (125.8 MHz, [D₈]toluene): δ = 215.9 (br., C=O), 24.0 (t, J(PC) = 11 Hz, (CH₃)₂CHP), 18.6 and 18.4 (2 s, (CH₃)₂CHP) ppm. C₃₈H₄₂BF₁₅NO₃P₂Re (1104.68): calcd. C 41.31, H 3.83, N 1.27; found C 41.75, H 3.78, N 1.30.

Synthesis of [Re(CO)₂{NOB(C₆F₅)₃}(PCy₃)₂] (9b): Complex 9b (0.088 g, 0.066 mmol, 90%) was obtained using the same procedure as described for 9a (method B) via the reaction of 8b (0.062 g, 0.074 mmol), B(C₆F₅) (0.038 g, 0.074 mmol) under 1 bar of CO. IR (ATR): $\tilde{v} = 1974$ (s, vCO), 1875 (s, vCO), 1457 (s, vN–OB) cm⁻¹. ¹H NMR (200.0 MHz, C₆D₆, room temp.): $\delta = 2.20$ –0.81 (m, P(C₆H₁₁)₃) ppm. ³¹P{¹H} NMR (80.9 MHz, C₆D₆): $\delta = 24.6$ (s) ppm. ¹³C{¹H} NMR (75.5 MHz, C₆D₆): $\delta = 211.5$ (br., C=O), 37.7 (t, *J*(PC) = 13 Hz, P(C₆H₁₁)₃, 30.5, 27.4 and 26.0 (3s, P(C₆H₁₁)₃) ppm. C₅₆H₆₆BF₁₅NO₃P₂Re (1345.07): calcd. C 50.00, H 4.94, N 1.04; found C 50.09, H 5.03, N 1.00.

X-ray Structure Analyses of Compounds 4a, 4b, 6b, 8a, 9a, and 9b: All six crystals were protected in hydrocarbon oil and prepared for the X-ray experiment by using a polarizing microscope. Selected crystals of 4a, 4b, 6b, 8a, 9a, and 9b (Table 8) were mounted on the tip of a glass fiber and immediately transferred to the goniometer of an imaging plate detector system (Stoe IPDS diffractometer). The crystals were cooled to 183(2) K and 193(2) K (8a) in an Oxford Cryogenic System. The crystal-to-image distances were set to 60, 70, 50, 50, 50, and 50 mm resulting in θ_{max} values of 28.05, 25.92, 30.43, 30.39, 30.39, and 30.39°. For compounds 8a, 9a, and 9b rotation, and for 4a, 4b, and 6b oscillation scan modes were applied. 8000 (5000 for 9a) reflections with $I > 6\sigma(I)$ were selected for the cell parameter refinements. A total of 26224 (4a), 53039 (4b), 51454 (6b), 29650 (8a), 51447 (9a), and 43505 (9b) diffraction intensities were collected of which 7594, 15066, 7139, 7583, 13094, and 15287 were unique (R_{int} = 6.52, 8.59, 6.13, 5.01, 14.04, and 8.64%) after data reduction. Numerical absorption corrections based on 12, 17, 8, 10, 15, and 7 crystal faces were applied with FACEitVIDEO and XRED.^[60] The structures were solved by the Patterson (for 4a, 6b, 8a, 9a, 9b) and by direct methods (for 4b) using the SHELXS-97 program.^[61] Interpretation of the difference electron density maps, preliminary plot generation, and checking for higher symmetry were done with PLATON^[62] (1990, 1991-2005) and with the LEPAGE program.^[63] All structures were refined with the program SHELXL-97^[61] using anisotropic displacement parameters for heavy atoms, some exceptions in disordered structures 4a and 4b are given in the CIF files (see CCDC deposition numbers, see below). Positions of H-atoms were calculated after each refinement cycle (riding model). Structural plots were generated using ORTEP III.^[64] For the achiral non-centrosymmetric structure of 4b the correct space group choice (Pna21, no. 33) was confirmed by Flack's parameter $x^{[65]}$ and PLATON.^[62] Refinement details are given in the "_exptl_special_details" in the respective cif files.

Computational Details: DFT calculations were carried out using the Amsterdam Density Functional program package ADF, release 2004.01.[57] We used the Vosko-Wilk-Nusair[66] local density approximation (LDA) and the generalized gradient approximation (GGA) with corrections for exchange and correlation according to Becke^[67] and Lee-Yang-Parr,^[68] respectively (BLYP). The ADF approach to DFT-GGA calculations is based on the use of Slatertype orbitals (STO) as basis functions. The valence shells of all atoms were described by double- ξ basis sets augmented by one polarization function (ADF database DZP), except for rhenium for which a triple- ξ basis set was applied (ADF database TZP). The frozen-core approximation was applied for the 1s electrons of carbon, oxygen, and nitrogen, for the 1s-2p electrons of phosphorus and chlorine, for the 1s-3d electrons of bromine and for the 1s-4f electrons of rhenium. Relativistic effects were taken into account in all calculations using the zero order regular approximation (ZORA).^[69] The relativistic atomic potentials necessary for the relativistic calculations for each atom were calculated using the auxiliary program DIRAC, which is supplied with the ADF program package. The geometry optimizations were considered converged when the change in the maximum gradient element was smaller than 5.0×10^{-4} Hartrees Å⁻¹. The other convergence criteria referring to changes in total energy, Cartesian or internal coordinates had to converge to the default values proposed by the program.

CCDC-297768 to -297771 (for **4a**, **4b**, **8a**, **9a**) and -609682 to -609683 (for **6b** and **9b**) 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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