

58. Chemistry of (Carbonyl)(nitrosyl)[bis(phosphorus donor)]rhenium Complexes

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The chemistry of $[\text{Re}(\text{CO})(\text{NO})\text{L}_2]$ fragments (L = phosphorus donor) was explored. Starting from $[\text{Re}(\text{CO})_5\text{Cl}]$ the synthesis of $[\text{Re}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{CO})_4(\text{NO})_2]$ (1) was accomplished via the preparation of $[\text{Et}_4\text{N}]_2[\text{Re}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{CO})_6]$ and nitrosylation of this compound with $[\text{NO}][\text{BF}_4]$. Complex 1 was converted to $[\text{ReCl}_2(\text{CO})(\text{NO})\text{L}_2]$ complexes **2** (a L = $(\text{MeO})_3\text{P}$; b L = $(\text{EtO})_3\text{P}$; c L = $(i\text{-PrO})_3\text{P}$; d L = Me_3P ; e L = Et_3P ; f L = Cy_3P) by heating with L in MeCN. In the case of the reaction of L = $(\text{MeO})_3\text{P}$, a trisubstituted compound *mer*- $[\text{ReCl}_2(\text{NO})\text{P}(\text{OMe})_3]_3$ **3** was also obtained. Replacement of the Cl ligands in **2a–e** with Me groups was achieved by reacting them with MeLi in Et_2O yielding *cis,trans*- $[\text{Re}(\text{CO})(\text{NO})\text{Me}_2\text{L}_2]$ complexes **4a–e**. Reaction of **2a–e** with $\text{Li}[\text{BHEt}_3]$ led to substitution of one Cl by an H ligand with formation of $[\text{ReCl}(\text{CO})\text{H}(\text{NO})\text{L}_2]$ compounds **5a–e**, displaying *trans*-H,NO geometries. The hydride-transfer agent $\text{Na}[\text{AlH}_2(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2]$ transformed **2** into the *cis*-dihydride systems $[\text{Re}(\text{CO})\text{H}_2(\text{NO})\text{L}_2]$ **6a–f**. Reductive carbonylation of **2a–d** in the presence of Na/Hg and CO gave pentacoordinate $[\text{Re}(\text{CO})_2(\text{NO})\text{L}_2]$ complexes **7b–d**, and under comparable conditions the Cl substituents of **2b–f** were replaced by toluene using Mg or *t*-BuLi giving trigonal bipyramidal $[\text{Re}(\text{CO})(\text{NO})\text{L}_2(\text{PhC}\equiv\text{CPh})]$ compounds **8b–f**. Complexes **5c**, **6a**, and **8d** were characterized by X-ray crystal-structure analysis.

Introduction. – $d^8 \text{ML}_4$ fragments play an important role in organo-transition-metal chemistry. They act either as monovalent molecular units displaying a triplet or a singlet electronic state. This feature has a great impact on the chemistry of such species [1]. On the other hand, $d^8 \text{ML}_4$ moieties can provide bivalency under oxidative conditions which normally leads to d^6 octahedral systems. Thus, these fragments demonstrate chemical versatility, which is also reflected in their frequent occurrence in cycles of homogeneous catalysis that often require this property.

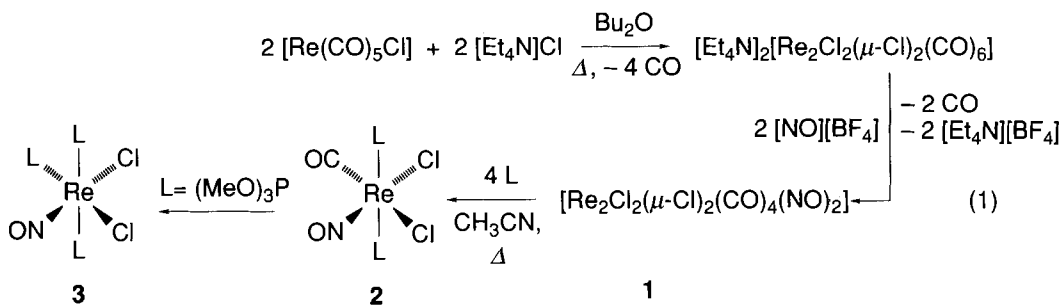
The actual reactive character of such unsaturated species is dependent on the nature of the ligands and the transition-metal center. Tuning of both of these factors would allow proper adjustment to bring about a desired type of chemistry. Following this idea, in earlier papers we have extensively investigated the chemistry of $[\text{Fe}(\text{CO})_2\text{L}_2]$ fragments [2]. In continuation of this work and to widen the scope of ligand and metal influence in L_4M species, we set out to examine the synthetic access to and the reactivity of isoelectronic complexes with $[\text{Re}(\text{CO})(\text{NO})\text{L}_2]$ moieties (L = phosphorus donor), which have, up to now, only scarcely been subjected to thorough studies [3].

Results and Discussions. – To establish a $[\text{Re}(\text{CO})(\text{NO})\text{L}_2]$ chemistry, it seemed best to aim at the utilization of $[\text{Re}(\text{CO})(\text{NO})\text{L}_2\text{Cl}_2]$ compounds **2** (L = phosphorous donor) as easily accessible synthetic precursors. Derivatives with L = Ph_3P , MePh_2P , $(\text{PhO})_3\text{P}$ were reported earlier [3d][4]. Their synthesis, however, could not be extended to the preparation of other types of phosphorus-donor complexes. It was, therefore, necessary to find a

more general synthetic route to this type of compounds. Our approach was based on the assembly of known reaction steps [4] [5], which, at some stages, needed modifications.

The compound $[\text{Et}_4\text{N}]_2[\text{Re}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{CO})_6]$ was synthesized in a first step by heating $[\text{Re}(\text{CO})_5\text{Cl}]$ with $[\text{Et}_4\text{N}]\text{Cl}$ in Bu_2O as a high-boiling solvent (Scheme 1). A subsequent nitrosylation of the Re center was accomplished by the reaction of $[\text{Et}_4\text{N}]_2[\text{Re}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{CO})_6]$ with 2 equiv. of $[\text{NO}][\text{BF}_4]$, which resulted in a much better overall yield compared with the direct transformation of $[\text{Re}(\text{CO})_5\text{Cl}]$ into **1** in the presence of NO [5b]. The substitution of **1** with 4 equiv. of a phosphorus ligand produced the desired complexes *cis,trans*- $[\text{ReCl}_2(\text{CO})(\text{NO})\text{L}_2]$, **2** (**a** L = $(\text{MeO})_3\text{P}$; **b** L = $(\text{EtO})_3\text{P}$; **c** L = $(i\text{-PrO})_3\text{P}$; **d** L = Me_3P ; **e** L = Et_3P ; **f** L = Cy_3P), again in high yield, when a coordinating solvent such as MeCN was used. It is proposed, that the primary and, therefore, key step in this substitutional process is the cleavage of the Cl bridges of **1** by solvent molecules indicated by a shift of the $\nu(\text{NO})$ band in the solution IR spectrum on going from CCl_4 to CH_3CN (14 cm^{-1}).

Scheme 1

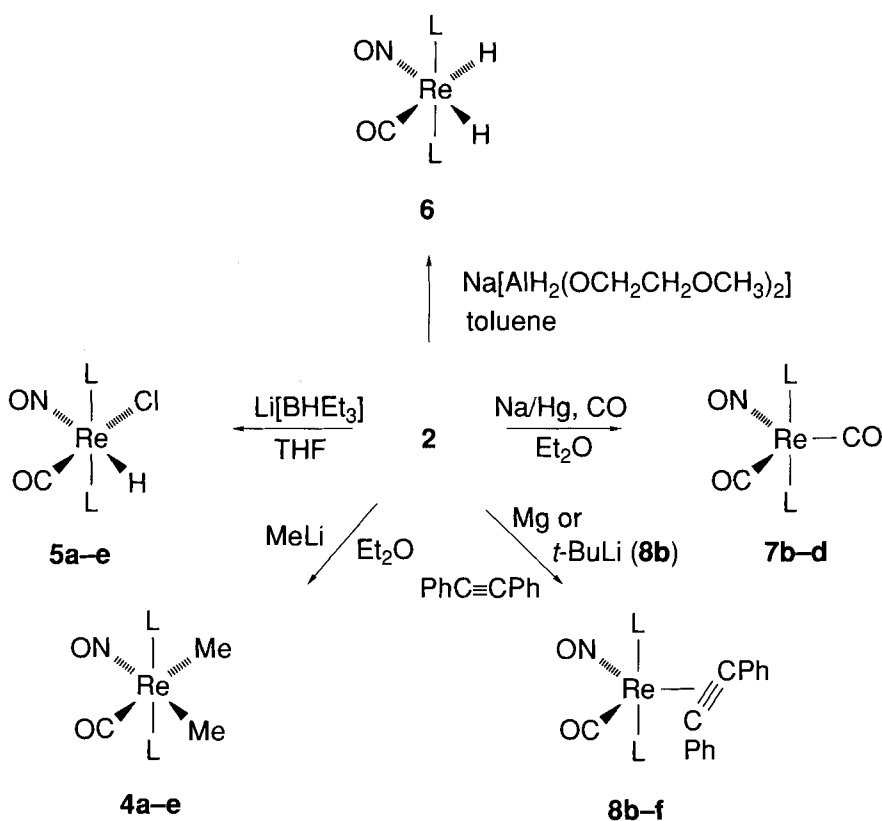


Mass-spectrometric data suggest that all yellow and air stable congeners **2** are mononuclear pseudo octahedral complexes. They display a *cis,trans*- $[\text{Re}(\text{CO})(\text{NO})\text{L}_2\text{Cl}_2]$ coordination geometry, which was supported by IR and ^1H - and ^{31}P -NMR spectroscopy. The synthesis of **2a** revealed a second product $\{\text{ReCl}_2(\text{NO})[\text{P}(\text{OMe})_3]_3\}$ (**3**), which became predominant when stoichiometric excess of $(\text{MeO})_3\text{P}$ was applied. **3** has been assigned a meridional $(\text{MeO})_3\text{P}$ *cis*- Cl_2 substitution pattern on the basis of IR and mainly ^1H - and ^{31}P -NMR spectroscopy.

Derivatives of **2** were transformed to either methyl or hydrido species by formal exchange of one or two Cl ligands. Applying MeLi in Et_2O the carbonyl-*cis*-dimethyl(nitrosyl)-*trans*-bis(phosphorus donor)rhenium compounds **4a–e** were obtained, however, in yields varying between 30 and 75%, depending on the nature of the phosphorus moiety. The reaction from **2** to **4** obviously proceeded without change of ligand positions in the $[\text{Re}(\text{CO})(\text{NO})\text{L}_2]$ fragment. Although **4a–e** are light yellow complexes, the reaction solutions from which they were isolated were red, indicating formation of (non-isolable) side-products, which are probably due one-electron reductive processes initiated by the organyl lithium component.

Reaction of **2** with $\text{Li}[\text{BHET}_3]$ in THF afforded (carbonyl)(chloro)(hydrido)nitrosyl-*trans*-bis(phosphorus donor)rhenium compounds **5a–e** (Scheme 2). They show great spectroscopic resemblance to the related compounds of the series **2** which suggests that

Scheme 2



a (MeO)₃P; **b** (i-PrO)₃P; **c** Me₃P; **d** Et₃P; **e** (i-Pr)₃P; **f** Cy₃P

the Re centers in both cases have similar coordinative environment. The ¹H-NMR resonances of the Re-bound H-atoms in all compounds **5** appear as a *triplet* with a *J*(P,H) indicative of a *cis*-phosphorus donor/hydride arrangement. It is difficult to assign the specific position of these H ligands, *i.e.*, whether they are located *trans* to the NO or CO group. The IR spectra of **5** reveal a significant shift of the $\nu(\text{NO})$ absorption to greater wave numbers in comparison with **2**, which is significantly larger than the observed shift of $\nu(\text{CO})$. This may be interpreted in terms of an electronic perturbation originating from the H/Cl ligand exchange in *trans*-position to the NO group. However, this is not sufficient evidence for a reliable assignment of structures of **5**, and, therefore, a single-crystal X-ray diffraction study was carried out on **5c** which clearly confirmed the *trans*-NO,H arrangement.

The $\nu(\text{ReH})$ absorptions of **5** shift to lower wavelengths with increasing electron-donating power of the phosphorus-donor substituent as expressed by their *Tolman's* electronic parameter. While the $\nu(\text{ReH})$ of **5d**, **5a**, and **5b** show a linear regression with the latter parameters, $\nu(\text{ReH})$ of **5e** is found to be off the line. The origin of this observation is yet unclear.

In contrast to our conclusions for the configuration of **5**, Grundy and coworkers [3d] reported a series of Re complexes of the type *trans*-[ReHX(NO)(CO)(PPh₃)₂] (X = F, MeO, Cl, Br, N₃, NCO, I, SCN) where the hydride ligand was described in *trans*-position to the CO ligand. Only for the derivative with X = F, a second isomer was detected with the hydride ligand *trans* to the NO group.

Treatment of the dichloro complexes **2** with Na[AlH₂(OCH₂CH₂OCH₃)₂] (Red Al) caused substitution of both Cl ligands in **2** with formation of the dihydride complexes *cis,trans*-[Re(CO)H₂(NO)L₂] (**6**). Best yields were obtained using a slight excess of Na[AlH₂(OCH₂CH₂OCH₃)₂] in toluene solution at ambient temperature. In analogy to [Re(CO)H₂(NO)(PPh₃)₂] [3b], the complexes **6** display a *trans*-phosphorus donor and *cis*-hydride configuration as confirmed by an X-ray diffraction study of **6a**.

The hydride ligands having H *trans* to NO show quite different ¹H-NMR chemical shifts than those *trans* to CO. One type of hydride signals of **6** falls into the region between -0.8 and -2.0 ppm (H *trans* to NO), whereas the other is found in the range of -4.2 to -5.4 ppm (H *trans* to CO). The differences of their chemical shifts amount, therefore, to 3.2–4.0 ppm. A similar situation was observed in isoelectronic cationic complexes [OsH₂(CO)(NO)(PR₃)₂]⁺ [6], in which, however, the H ligands are reported to undergo exchange processes at ambient temperature. Phosphite derivatives of **6** show this phenomenon at room temperature, while phosphane-substituted complexes **6c–f** exhibit fluctional behavior only when they are heated to 80°. These are now being studied in greater detail [7].

The reduction of **2b, c**, and **d** with Na sand or Na/Hg in Et₂O in the presence of 1 bar of CO yields (dicarbonyl)(nitrosyl)-*trans*-bis(phosphorus donor)rhenium compounds **7b–d** (L = (i-PrO)₃P, Me₃P, and Et₃P, respectively). Reductive ligand additions to transition-metal centers are a common synthetic tool especially for the case of replacement of two one-electron donors by CO. The trigonal bipyramidal structures of **7** are supported by their IR, and ¹H-, ¹³C-, and ³¹P-NMR spectroscopic properties. The observation of two ν(CO) IR bands for all compounds account for a *cis*-(CO)₂-arrangement, while the splitting pattern of the ¹³C-NMR resonances of these groups indicate that the two P nuclei are in chemically equivalent *cis*-positions to them. These two observations have led to the given structural assignment of **7**.

The formation of compounds **7** may actually proceed *via* a pseudo carbenoid [Re(CO)(NO)L₂] fragment. The question arises, whether it would be possible to trap these species with other π acceptor molecules such as acetylenes. The syntheses of [Re(CO)(NO)L₂(PhC≡CPh)] complexes **8b** (L = (i-PrO)₃P), **8c** (L = Me₃P), **8d** (L = Et₃P), **8e** (L = (i-Pr)₃P), and **8f** (L = Cy₃P) were accomplished *via* the reactions of **2b–f**, respectively, with Mg or t-BuLi and toluene using reductive condition similar to those which lead to the formation of **7**. Complex **8d** was characterized by an X-ray structure analysis, which confirmed the axial positions of the phosphorus donors and the theoretically expected equatorial arrangement of the π acceptor ligands. This configuration of **8** became also evident from their spectroscopic data. The IR spectra exhibit two strong bands in the region of 2200–1500 cm⁻¹ which were assigned to ν(CO) and ν(NO) vibrations. Both bands appear at relatively long wavelengths. This supports strong π donation from the Re centers, which is typical of interactions with ligands in the equatorial plane of d⁸ trigonal pyramids. Absorptions of ν(C≡C) vibrations which were expected to appear in the region of 1850 to 1700 cm⁻¹ were not observed.

It was not surprising that, in the ^{13}C -NMR spectra of **8**, different chemical shifts were found for the acetylenic C-atoms, but unexpectedly the $J(\text{P},\text{C})$ values were also differing significantly by *ca.* 2 Hz. This indicated that these nuclei are asymmetrically bound to the Re center which was assured by an X-ray structure determination of **8d**.

Crystal-Structure Determination of 5c, 6a, and 8d¹⁾. – Suitable crystals were grown from a saturated hexane (for **6a**) or hexane/ CH_2Cl_2 solution (for **5c** and **8d**) by cooling to -30° . For crystallographic and refinement data of **5c**, **6a**, and **8d**, see the *Table*.

Table. *Crystal, Structure-Solution, and Refinement Data of 5c, 6a, and 8d*

	5c	6a	8d
Empirical formula	$\text{C}_7\text{H}_{19}\text{NO}_2\text{P}_2\text{ClRe}$	$\text{C}_7\text{H}_{20}\text{NO}_8\text{P}_2\text{Re}$	$\text{C}_{27}\text{H}_{40}\text{NO}_2\text{P}_2\text{Re}$
Color; habit	yellow prism	yellow irregular	yellow cube
Crystal size (mm)	$0.3 \times 0.3 \times 0.2$	$0.25 \times 0.20 \times 0.15$	$0.5 \times 0.4 \times 0.1$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$C2/c$	$P\bar{1}$
a [Å]	13.349(4)	19.562(4)	8.670(2)
b [Å]	8.394(3)	6.6982(12)	10.520(3)
c [Å]	13.367(4)	13.568(2)	16.176(4)
α [°]			84.44(2)
β [°]	100.95(2)	113.675(13)	82.89(2)
γ [°]			76.57(2)
Volume [Å ³]	1470.6(8)	1628.2(5)	1420.4(6)
Z	4	4	2
Formula weight	432.8	494.4	658.7
Density (calc.)	1.955 Mg/m ³	2.017 Mg/m ³	1.540 Mg/m ³
Absorption coefficient	8.756 mm ⁻¹	7.785 mm ⁻¹	4.468 mm ⁻¹
$F(000)$	824	952	660
Solution	Patterson Method (<i>Siemens</i> SHELXTL PLUS [8]; <i>Micro VAX II</i>)		
Diffractometer used	<i>Siemens R3m/V</i>		
Radiation	MoK_α ($\lambda = 0.71073$ Å)		
Temperature [K]	235	215	209
Monochromator	Highly oriented graphite crystal		
2θ Range	6.0 to 58.0°	4.0 to 58.0°	3.0 to 48.0°
Scan type	<i>Wyckoff</i>	ω	<i>Wyckoff</i>
Scan speed	Variable;	Variable;	Variable;
	2.00 to 15.00°/min in ω	1.50 to 15.00°/min in ω	1.50 to 15.00°/min in ω
Scan range (ω)	1.60°	1.40°	1.20°
Independent reflections	3940 ($R_{\text{int}} = 3.72\%$)	2081 ($R_{\text{int}} = 4.79\%$)	4465 ($R_{\text{int}} = 0.00\%$)
Observed reflections	3459 ($F > 6.0\sigma(F)$)	2019 ($F > 6.0\sigma(F)$)	4450 ($F > 3.0\sigma(F)$)
Absorption correction	Semi-empirical		
Min./Max transmission	0.0115/0.0367	0.0432/0.0831	0.1043/0.3868
R_F	4.72	1.89	3.05
R_{F2}	3.99	2.14	3.59
Goodness of fit	3.33	2.02	2.14
Weighting scheme	$w = 1/\sigma^2(F_0)$		units weights
Final maximum shift/esd	0.001 (0.000)	0.154 (0.008)	0.010 (-0.001)
Max./Min. residual electron density [eÅ ⁻³]	2.04/-1.45	0.63/-1.14	1.21/-1.09

¹⁾ Crystal structure basis and solution have been deposited at the Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England.

From Fig. 1, it can be seen, that the metal atoms in **5c** and **6a** have a strongly distorted coordination geometry. The most prominent distortion arises from the leaning over of the P nuclei towards the Re-bound H-atoms (P–Re–P angles of $163.5(1)^\circ$ in **5c** and of $160.0(2)^\circ$ in **6a**, respectively), as commonly observed in transition-metal-hydride chemistry.

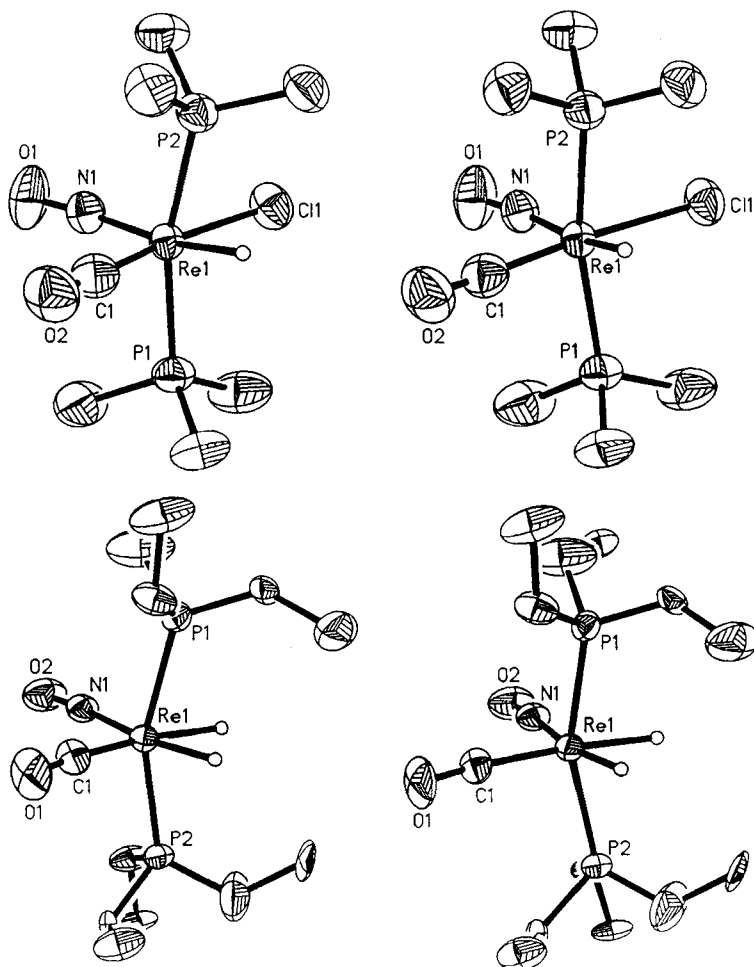
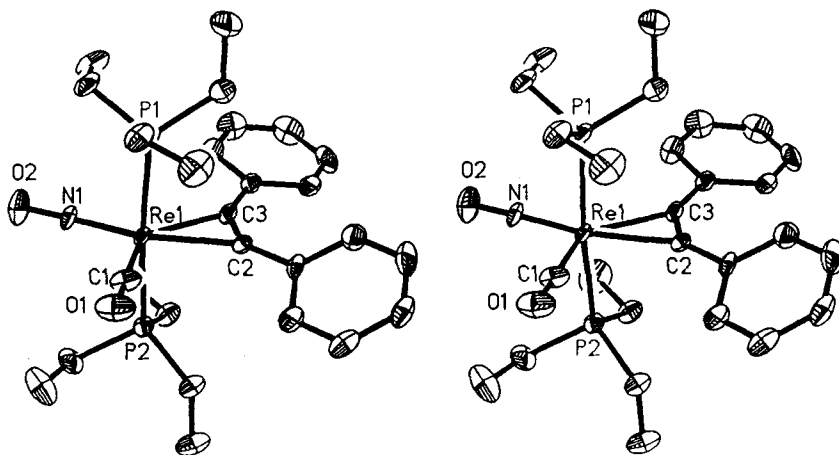


Fig. 1. Stereoview ORTEP plots of **5c** (top) and **6a** (bottom). Thermal ellipsoids are drawn with 50% probability. Selected bond lengths and angles of **5c**: Re(1)–C(1) 1.921(8), Re(1)–N(1) 1.921(8), Re(1)–Cl(1) 2.432(2), Re(1)–P(1) 2.432(2), Re(1)–P(2) 2.422(2) Å. P(1)–Re(1)–P(2) $163.5(1)^\circ$, Cl(1)–Re(1)–N(1) $98.3(2)^\circ$, Cl(1)–Re(1)–C(1) $169.4(3)^\circ$. Selected bond lengths and angles of **6a**: Re(1)–C(1) 1.96(1), Re(1)–N(1) 1.78(1), Re(1)–P(1) 2.375(5), Re(1)–P(2) 2.342(5) Å. C(1)–Re(1)–N(1) $102.5(6)^\circ$, P(1)–Re(1)–P(2) $160.0(2)^\circ$.

Otherwise the structural parameters, such as the bond distances and the non-phosphorus-ligand related angles around the metal center, in these compounds correspond quite closely to those of other low oxidation state octahedral Re complexes [9]. In **5c**, the H ligand is positioned *trans* to the NO group, which could not be unambiguously established from its spectroscopic data and was not supported by literature evidence [3d].

The trigonal bipyramidal complex **8d** bears the σ donors in the axial positions and the acceptor ligands in the equatorial plane. The tolane ligand is bound to the Re-atom in quite unusual asymmetric fashion, a distortion which obviously originates from the $\sqrt{3}/OC$ substitutional asymmetry of the $[\text{Re}(\text{CO})(\text{NO})\text{L}_2]$ fragment. The deviation from trigonal bipyramidal coordination geometry may be envisaged as a 17° rotation of the stylenic moiety around the Re center towards the CO ligand. A similar situation was found in $[\text{W}(\text{BH}_4)(\text{CO})(\text{NO})\text{L}_2]$ complexes, where the distortion was explained in terms of strong polarization of the 'two above three valence orbitals' of the $[\text{W}(\text{CO})(\text{NO})\text{L}_2]$ fragment [10].



2. Stereoview ORTEP plot of **8d**. Thermal ellipsoids are drawn with 50% probability. Selected bond lengths and angles: Re(1)–C(1) 1.949(6), Re(1)–N(1) 1.796(4), Re(1)–C(2) 2.186(5), Re(1)–C(3) 2.132(5), Re(1)–P(1) 2.452(5), Re(1)–P(2) 2.445(2), C(1)–O(1) 1.148(8), N(1)–O(2) 1.207(6), C(2)–C(3) 1.300(8) Å. P(1)–Re(1)–P(2) 81.1, C(1)–Re(1)–N(1) 104.2(2), C(1)–Re(1)–C(2) 92.9(2), N(1)–Re(1)–C(3) 127.9(2), C(2)–C(3)–C(10) 145.8(5), C(3)–C(2)–C(4) 143.8(5)°.

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Experimental Part

General. All reactions and manipulations were carried out under dry N_2 using solvents purified by standard methods. All reactions were monitored by IR spectroscopy. Unless stated otherwise, chromatographic workup was carried out at ambient temp. on silica 60 (Merck, 230–400 mesh ASTM) as a stationary phase, and solvents were used without further purification. M.p. (uncorrected): Büchi 530. IR: Biorad FTS-45, wave numbers $[\text{cm}^{-1}]$. ^1H - ^{13}C -NMR: Varian Gemini-200, chemical shifts δ [ppm] relative TMS, only first-order P coupling constants are given [11]. ^{31}P -NMR: Varian XL-200 rel. external H_3PO_4 . MS: Finnigan MAT-8240; m/z relative to the highest peak based on the natural isotope distribution.

$[\text{Re}_2\text{Cl}_4(\text{CO})_4(\text{NO})_2]$ (**1**). $[\text{Re}(\text{CO})_5\text{Cl}]$ (5.0 g, 13.83 mmol) and 2.3 g (13.9 mmol) of $[\text{NEt}_4]\text{Cl}$ were heated to reflux in 150 ml of Bu_2O . During the warming up, a short period of homogeneity of the reaction mixture was observed. Then, under vigorous evolution of CO gas, a white precipitate of $[\text{Et}_4\text{N}]_2[\text{Re}_2\text{Cl}_2(\mu\text{-Cl})_2(\text{CO})_4]$ formed. Refluxing was continued for 4 h. After cooling the mixture to r.t., the supernatant Bu_2O was decanted (may be used in further reactions) from the white precipitate. The residual solvent was removed *in vacuo* and replaced by CH_2Cl_2

(ca. 150 ml). Addition of 1.62 g (13.8 mmol) of $[\text{NO}][\text{BF}_4]$ caused an immediate color change of the mixture to yellow with further evolution of CO. Depending on the amount of added CH_2Cl_2 , the soln. became clear, before a bright yellow precipitate began to form. After ca. 12 h, the $[\text{Re}_2\text{Cl}_4(\text{CO})_6]^{2-}$ anion could no longer be detected by IR. The solvent was then removed on a rotary evaporator. All further operations were conducted in air, since **1** was found to be air-stable. Compound **1** was washed 4 times with 25-ml portions of H_2O , until the rinsing was colorless. Drying *in vacuo* afforded 4.3 g (90% yield) of **1**, which was pure enough for most synthetic purposes. A purer product was obtained by chromatography on silica with toluene/MeCN 1:1 as eluent. Compound **1** was identified using the spectroscopic data published in [4] [5].

$[\text{ReCl}_2(\text{CO})(\text{NO})\{(i\text{-MeO})_3\text{P}\}_2]$ (**2a**). $[\text{Re}_2\text{Cl}_4(\text{CO})_4(\text{NO})_2]$ (**1**; 2.0 g, 2.91 mmol) was dissolved in 50 ml of MeCN and heated to reflux for 1/2 h. After cooling in an ice-bath to 0°, 1.2 ml (11.7 mmol) of $(\text{MeO})_3\text{P}$ (r.t.) were added, and the mixture was allowed to warm up to r.t. The mixture was heated to reflux for 2 h and then taken to dryness *in vacuo*. The residue was chromatographed with CH_2Cl_2 , and a yellow fraction was collected. Removal of the solvent yielded 2.73 g of **2a** (83%). M.p. 148–150°. IR (CH_2Cl_2): 2027s (CO), 1755s (NO). $^1\text{H-NMR}$ (C_6D_6): 3.59 (t, $J(\text{P,H}) = 11.0$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 53.4 (s, $(\text{CH}_3\text{O})_3\text{P}$); 194.1 (t, $J(\text{P,C}) = 10.7$, ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 100.9 (s). MS: 563 (4, M^+), 535 (46, $[\text{M} - \text{CO}]^+$), 505 (8, $[\text{M} - \text{CO} - \text{NO}]^+$), 411 (28, $[\text{M} - \text{CO} - \text{P}(\text{OMe})_3]^+$), 93 (100, $[\text{P}(\text{OMe})_2]^+$). Anal. calc. for $\text{C}_7\text{H}_{18}\text{Cl}_2\text{NO}_8\text{P}_2\text{Re}$: C 14.92, H 3.22, N 2.48; found: C 14.86, H 2.97, N 2.30.

$[\text{ReCl}_2(\text{CO})(\text{NO})\{(i\text{-PrO})_3\text{P}\}_2]$ (**2b**) was prepared as described for **2a** using 2.0 g (2.91 mmol) of **1** and 3.0 ml (11.7 mmol) of $(i\text{-PrO})_3\text{P}$. The crude product was chromatographed with toluene. The yellow fraction was collected and evaporated to dryness: 3.3 g of **2b** (77%). M.p. 129–130°. IR (hexane): 2024s (CO), 1750s (NO). $^1\text{H-NMR}$ (C_6D_6): 1.27 (d, $\text{P}(\text{OCH}(\text{CH}_3(\text{a}))(\text{CH}_3(\text{b})))_3$, $J(\text{H,H}) = 6.0$); 1.28 (d, $J(\text{H,H}) = 6.2$, $\text{P}(\text{OCH}(\text{CH}_3(\text{a}))(\text{CH}_3(\text{b})))_3$); 5.22 (m, $\text{P}(\text{OCH}(\text{CH}_3)_2)_3$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 23.8 (br., $\text{P}(\text{OCH}(\text{CH}_3)_2)_3$); 71.5 (t, $J(\text{P,C}) = 5.9$, $\text{P}(\text{OCH}(\text{CH}_3)_2)_3$); 195.4 (t, $J(\text{P,C}) = 10.7$, ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): 93.4 (s). MS: 731 (27, M^+), 703 (100, $[\text{M} - \text{CO}]^+$), 673 (19, $[\text{M} - \text{CO} - \text{NO}]^+$). Anal. calc. for $\text{C}_{19}\text{H}_{42}\text{Cl}_2\text{NO}_8\text{P}_2\text{Re}$: C 31.19, H 5.79, N 1.91; found: C 30.97, H 5.78, N 2.13.

$[\text{ReCl}_2(\text{CO})(\text{NO})(\text{Me}_3\text{P})_2]$ (**2c**) was prepared as described for **2a** using 2.0 g (2.91 mmol) of **1** and 1.2 ml (11.7 mmol) of Me_3P . The mixture was stirred at r.t. The crude product was chromatographed with CH_2Cl_2 over silica. A yellow fraction was collected. Evaporation to dryness yielded 1.94 g of **2c** (71%). M.p. 193–195° (dec.). IR (CH_2Cl_2): 1996s (CO), 1733s (NO). $^1\text{H-NMR}$ (C_6D_6): 1.27 (t, $J(\text{P,H}) = 8.7$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 12.7 (t, $J(\text{P,C}) = 34.0$, $(\text{CH}_3)_3\text{P}$); 202.6 (t, $J(\text{P,C}) = 6.8$, ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): -27.9 (s). MS: 467 (13, M^+), 439 (100, $[\text{M} - \text{CO}]^+$), 409 (27, $[\text{M} - \text{CO} - \text{NO}]^+$), 363 (49, $[\text{M} - \text{CO} - \text{Me}_3\text{P}]^+$). Anal. calc. for $\text{C}_7\text{H}_{18}\text{Cl}_2\text{NO}_2\text{P}_2\text{Re}$: C 17.99, H 3.88, N 2.99; found: C 18.13, H 3.74, N 2.88.

$[\text{ReCl}_2(\text{CO})(\text{NO})(\text{Et}_3\text{P})_2]$ (**2d**) was prepared as described for **2a** using 2.0 g (2.91 mmol) of **1** and 1.64 ml (11.7 mmol) of Et_3P . The crude product was chromatographed with toluene. A yellow fraction resulted which was evaporated to dryness: 2.24 g of **2d** (70%). M.p. 96–98°. IR (hexane): 1982s (CO), 1716s (NO). $^1\text{H-NMR}$ (C_6D_6): 0.93 (t, $J(\text{H,H}) = 7.6$, $J(\text{P,H}) = 15.2$, $\text{P}(\text{CH}_2\text{CH}_3)_3$); 1.88 (m, $\text{P}(\text{CH}_2\text{CH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 7.1 (s, $\text{P}(\text{CH}_2\text{CH}_3)_3$); 15.2 (t, $J(\text{P,C}) = 29.5$, $\text{P}(\text{CH}_2\text{CH}_3)_3$); 204.0 (t, $J(\text{P,C}) = 7.2$, ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CDCl_3): -3.0 (s). MS: 551 (14, M^+), 523 (100, $[\text{M} - \text{CO}]^+$), 493 (18, $[\text{M} - \text{CO} - \text{NO}]^+$), 405 (86, $[\text{M} - \text{CO} - \text{Et}_3\text{P}]^+$). Anal. calc. for $\text{C}_{13}\text{H}_{30}\text{Cl}_2\text{NO}_2\text{P}_2\text{Re}$: C 28.32, H 5.48, N 2.54; found: C 28.33, H 5.41, N 2.72.

$[\text{ReCl}_2(\text{CO})(\text{NO})\{(i\text{-Pr})_3\text{P}\}_2]$ (**2e**) was prepared as described for **2a** using 1.0 g (1.45 mmol) of **1** and 1.1 ml (5.8 mmol) of $(i\text{-Pr})_3\text{P}$, but the mixture was heated to 60° for 1 h. The crude product was chromatographed with toluene, and a yellow fraction was collected. Evaporation to dryness yielded 1.53 g of **2e** (83%). M.p. 243–245° (dec.). IR (hexane): 1982s (CO), 1716s (NO). $^1\text{H-NMR}$ (C_6D_6): 1.16 (dt, $J(\text{H,H}) = 6.0$, $J(\text{P,H}) = 14.3$, $\text{P}(\text{CH}(\text{CH}_3(\text{a}))(\text{CH}_3(\text{b})))_3$); 1.31 (dt, $J(\text{H,H}) = 6.8$, $J(\text{P,H}) = 14.3$, $\text{P}(\text{CH}(\text{CH}_3(\text{a}))(\text{CH}_3(\text{b})))_3$); 2.77 (m, $\text{P}(\text{CH}(\text{CH}_3)_2)_3$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 18.9 (s, $\text{P}(\text{CH}(\text{CH}_3(\text{a}))(\text{CH}_3(\text{b})))_3$); 19.5 (s, $\text{P}(\text{CH}(\text{CH}_3(\text{a}))(\text{CH}_3(\text{b})))_3$); 23.7 (t, $J(\text{P,C}) = 22.8$, $\text{P}(\text{CH}(\text{CH}_3)_2)_3$); 205.8 (br., ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 14.2 (s). Anal. calc. for $\text{C}_{19}\text{H}_{42}\text{Cl}_2\text{NO}_2\text{P}_2\text{Re}$: C 35.9, H 6.66, N 2.20; found: C 36.6, H 6.73, N 2.13.

$[\text{ReCl}_2(\text{CO})(\text{NO})(\text{Cy}_3\text{P})_2]$ (**2f**) was prepared as described for **2e** using 1.0 g (1.45 mmol) of **1** and 1.63 g (5.8 mmol) of Cy_3P . The residue was chromatographed with CH_2Cl_2 /hexane 1:2, and a yellow fraction was collected. Evaporation to dryness yielded 1.94 g of **2f** (76%). Dec. without melting. IR (CH_2Cl_2): 1979s (CO), 1717s (NO). $^1\text{H-NMR}$ (C_6D_6): 1.23; 1.58; 1.72; 2.21; 2.44; 2.75 (all signals are br.). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 26.3 (s); 27.6 (t, $J(\text{P,C}) = 9.7$); 29.2 (s), 29.5 (s); 34.0 (t, $J(\text{P,C}) = 21.2$); 207.0 (t, $J(\text{P,C}) = 6.8$, ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 3.4 (s). MS: 875 (11, M^+), 847 (71, $[\text{M} - \text{CO}]^+$), 567 (100, $[\text{M} - \text{CO} - \text{Cy}_3\text{P}]^+$), 280 (53, $[\text{Cy}_3\text{P}]$), 198 (96, $[\text{Cy}_2\text{PH}]$). Anal. calc. for $\text{C}_{37}\text{H}_{66}\text{Cl}_2\text{NO}_2\text{P}_2\text{Re}$: C 50.73, H 7.59, N 1.6; found: C 51.14, H 7.29, N 1.75.

$[\text{ReCl}_2(\text{NO})\{(i\text{-MeO})_3\text{P}\}_3]$ (**3**). Complex **1** (2.0 g, 2.91 mmol) was dissolved in 100 ml of MeCN and heated shortly to reflux. After cooling to r.t., 4.2 ml (35 mmol) of $(\text{MeO})_3\text{P}$ were added, and the reaction mixture was again

2 d. After cooling to r.t., the solvent was removed under reduced pressure. The oily yellow 1 in toluene and filtered over a short column of silica (ca. 10 cm). By repeatedly washing with $\text{P}(\text{OMe})_3$ was removed. Elution with Et_2O afforded a mixture of **2a** and **3**, which, after ent, were separated by chromatography with CH_2Cl_2 on a water-cooled column of silica. eluted first as a yellow band (1.4 g, 42% yield after evaporation of CH_2Cl_2). Compound **3** id faintly yellow colored band. Yield: 1.9 g (42%). IR (CH_2Cl_2): 2027s (CO), 1755s (NO), .59 (t, $J(\text{P},\text{H}) = 11.0$, $\text{P}(\text{OCH}_3)_3$). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): 53.4 (s, $\text{P}(\text{OCH}_3)_3$); 194.1 (t, O). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 106.7 (d, $J(\text{P},\text{P}) = 34.7$, $P_{\text{ax}}-\text{OCH}_3$); 110.0 (t, $J(\text{P},\text{P}) = 34.7$, 3 (4, M^+), 535 (46, $[\text{M} - \text{CO}]^+$), 505 (8, $[\text{M} - \text{CO}, \text{NO}]^+$), 411 (28, $[\text{M} - \text{CO}, (\text{MeO})_3\text{P}]^+$), 93 al. calc. for $\text{C}_7\text{H}_{18}\text{Cl}_2\text{NO}_8\text{P}_2\text{Re}$: C 14.92, H 3.22, N 2.48; found: C 14.86, H 2.97, N 2.30.

$\text{VO}\{(\text{MeO})_3\text{P}\}_2$ (**4a**). A soln. of 2.0 g (3.55 mmol) of **2a** in 150 ml of Et_2O was mixed with in Et_2O . After completion of the reaction, which was assured by IR by the absence of the he solvent was removed under reduced pressure and the residue extracted with CH_2Cl_2 and n silica. Crystallization from hexane/ Et_2O yielded impure **4a** (ca. 32%). Due to this, no il analysis of **4a** could be obtained. IR (CH_2Cl_2): 1979s (CO), 1675s (NO). ^1H -NMR (C_6D_6): 3, ReCH_3 (b); 0.99 (t, $J(\text{P},\text{H}) = 9.5$, ReCH_3 (a)); 3.4 (t, $J(\text{P},\text{H}) = 11.1$, POCH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR ($\text{P},\text{C}) = 13.3$, ReCH_3 (b)); -8.8 (t, $J(\text{P},\text{C}) = 12$, ReCH_3 (a)); 51.8 (s, $\text{P}(\text{OCH}_3)_3$); 200.9 (t,). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): 114.8 (s).

$\text{VO}\{(i\text{-PrO})_3\text{P}\}_2$ (**4b**) was prepared as described for **4a**. Compound **2b** (2.0 g, 2.73 mmol) in -ml of 1.6M MeLi in Et_2O were used. Extraction with hexane was followed by chromatography a at -30° . Yield 1.1 g (59%) of crude **4b**. Due to some impurities, no satisfactory elemental i. IR (hexane): 1981s (CO), 1674s (NO). ^1H -NMR (C_6D_6): 0.15 (t, $J(\text{P},\text{H}) = 9.7$, ReCH_3 (b)); i, ReCH_3 (a)); 1.6 (d, $J(\text{H},\text{H}) = 6.1$, POCHCH_3); 4.77 (m, $\text{POCH}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ -NMR ($\text{P},\text{C}) = 13$, ReCH_3 (b)); -3.7 (t, $J(\text{P},\text{C}) = 11.6$, ReCH_3 (a)); 23.8 (s, $\text{PO}-\text{CH}(\text{CH}_3)_2$); 69.5 (s, ($\text{P},\text{C}) = 8.7$, ReCO).

$\text{VO}(\text{Me}_3\text{P})_2$ (**4c**) was prepared as described for **4a**. Complex **2c** (2.0 g, 4.28 mmol) in 150 ml 1.6M MeLi in Et_2O were used. Compound **4c** was chromatographed with CH_2Cl_2 on silica gel g (45%). M.p. 135° (dec.). IR (CH_2Cl_2): 1949s (CO), 1652s (NO). ^1H -NMR (C_6D_6): -0.57 (t, I_3 (b)); 0.49 (t, $J(\text{P},\text{H}) = 9.5$, ReCH_3 (a)); 1.15 (t, $J(\text{P},\text{H}) = 7.6$, PCH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): .5, ReCH_3 (b)); -6.3 (t, $J(\text{P},\text{C}) = 9$, ReCH_3 (a)); 14.1 (t, $J(\text{P},\text{C}) = 41$, PCH_3); 207.6 (t,). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): -38.6 (s). MS: 427 (11, M^+), 412 (21, $[\text{M} - \text{CH}_3]^+$), 399 (100, $[\text{M} - \text{CO}, \text{CH}_3]^+$), 366 (91, $[\text{M} - \text{PMe}_2]^+$). Anal. calc. for $\text{C}_9\text{H}_{24}\text{NO}_2\text{P}_2\text{Re}$: C 25.35, H 5.67, 45, H 5.77, N 3.21.

$\text{VO}(\text{Et}_3\text{P})_2$ (**4d**) was prepared as described for **4a**. Complex **2d** (2.0 g, 3.63 mmol) in 100 ml of 1.6M MeLi in Et_2O were used. Compound **4d** was extracted with hexane and chro-luene on silica at -30° . Yield: 1.32 g (71%). M.p. 82° (dec.). IR (hexane): 1950s (CO), 1662s (C_6D_6): -0.41 (t, $J(\text{P},\text{H}) = 8.7$, ReCH_3 (b)); 0.67 (t, $J(\text{P},\text{H}) = 8.6$, ReCH_3 (a)); 0.9 (dt,) = 14.5, $\text{P}-\text{CH}-\text{CH}_3$); 1.67 (m, PCH_2CH_3). $^{13}\text{C}\{^1\text{H}\}$ -NMR (C_6D_6): -11.4 (t, $J(\text{P},\text{C}) = 9.5$, $J(\text{P},\text{C}) = 8.5$, ReCH_3 (a)); 7.2 (s, PCHCH_3); 16.0 (t, $J(\text{P},\text{C}) = 28$, PCH_2CH_3); 209.7 (t,). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6): -12.2 (s). MS: 511 (5, M^+), 496 (26, $[\text{M} - \text{CH}_3]^+$), 483 (100, $[\text{M} - \text{CO}, \text{Et}_3\text{P}]^+$). Anal. calc. for $\text{C}_{15}\text{H}_{36}\text{NO}_2\text{P}_2\text{Re}$: C 35.28, H 7.11, N 2.74; found: C 35.13,

$\text{VO}\{(i\text{-Pr})_3\text{P}\}_2$ (**4e**) was prepared as described for **4a**. Complex **2e** (2.0 g, 3.15 mmol) in 3.9 ml of 1.6M MeLi in Et_2O were used. Compound **4e** was extracted with toluene and th the same solvent on silica gel at -30° . Yield: 1.3 g (70%) of crude **4e**. Due to the impurity of mental analysis was obtained. IR (hexane): 1947s (CO), 1660s (NO). ^1H -NMR (C_6D_6): -0.92 CH_3 (b)); 0.91 (t, $J(\text{P},\text{H}) = 8.0$, ReCH_3 (a)); 1.17 (m, $\text{PCH}(\text{CH}_3)_2$); 2.45 (m, $\text{PCH}(\text{CH}_3)_2$,) = 8.5 (br., ReCH_3 (b)); -4.3 (t, $J(\text{P},\text{C}) = 7.7$, ReCH_3 (a)); 18.9 (s, PCHCH_3 (b)); 19.6 (s, , $J(\text{P},\text{C}) = 21.7$, $\text{PCH}(\text{CH}_3)_2$); 212.5 (t, $J(\text{P},\text{C}) = 6.6$, ReCO).

$\text{VO}\{(\text{MeO})_3\text{P}\}_2$ (**5a**). Complex **2a** (1 g, 1.77 mmol) was dissolved in 50 ml of THF, cooled i 2.15 ml (2.15 mmol) of 1M $\text{Li}[\text{BHET}_3]$ in THF. Stirring at 0° was continued until the starting toring of the $\nu(\text{CO})$ absorptions) had disappeared. The mixture was evaporated to dryness in e residue was chromatographed immediately with CH_2Cl_2 at -20° . An orange fraction was n of the solvent under reduced pressure yielded 0.67 g of **5a** (72%). M.p. $57-58^\circ$. IR (hexane): $\nu(\text{O})$, 1844w (ReH). ^1H -NMR (C_6D_6): 1.75 (t, $J(\text{P},\text{H}) = 28.8$, ReH); 3.50 (t, $J(\text{P},\text{H}) = 11.9$, -NMR (C_6D_6): 52.7 (s, $\text{P}(\text{OCH}_3)_3$); 198.0 (t, $J(\text{P},\text{C}) = 10.1$, ReCO). $^{31}\text{P}\{^1\text{H}\}$ -NMR (C_6D_6):

120.4 (s). MS: 501 (31, $[M - CO]^+$), 467 (9, $[M - 2 OCH_3]^+$), 125 (30, $[HP(OMe)_3]^+$), 93 (100, $[P(OMe)_2]$). Anal. calc. for $C_7H_{19}ClNO_8P_2Re$: C 15.9, H 3.62, N 2.65; found: C 15.98, H 3.58, N 2.6.

$[ReCl(CO)H(NO)\{(i-PrO)_3P\}_2]$ (**5b**) was prepared as described for **5a** using 1 g of **2b** (1.37 mmol) and 1.4 ml of 1M $Li[BHET_3]$ in THF (1.4 mmol). The residue was chromatographed with toluene at -20° . An orange fraction was collected. Evaporation to dryness *in vacuo* yielded 0.8 g of **5b** (84%). M.p. 73° . IR (hexane): 2012s (CO), 1693s (NO), 1845w (ReH). 1H -NMR (C_6D_6): 1.26 (d, $J(H,H) = 6.0$, $P(OCH(CH_3(a))(CH_3(b)))_3$); 1.28 (d, $P(OCH(CH_3(a))(CH_3(b)))_3$); 2.22 (t, $J(P,H) = 28.6$, $J(H,H) = 6.0$, ReH); 5.08 (m, $P(OCH(CH_3)_2)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 23.7 (s, $P(OCH(CH_3(a))(CH_3(b)))_3$); 23.9 (s, $P(OCH(CH_3(a))(CH_3(b)))_3$); 71.0 (s, $P(OCH(CH_3)_2)_3$); 199.2 (t, $J(P,C) = 10.1$, ReCO). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): 109.6 (s). Anal. calc. for $C_{19}H_{43}ClNO_8P_2Re$: C 32.73, H 6.22, N 2.01; found: C 32.76, H 6.30, N 1.83.

$[ReCl(CO)H(NO)(Me_2P)_2]$ (**5c**) was prepared as described for **5a** using 1 g of **2c** (2.14 mmol) and 1.8 ml of 1M $Li[BHET_3]$ in THF (1.8 mmol). The residue was chromatographed with CH_2Cl_2 at -20° and an orange fraction was collected. Evaporation to dryness yielded 0.72 g of **5c** (78%). M.p. $123-124^\circ$. IR (CH_2Cl_2): 1967s (CO), 1668s (NO), 1811w (ReH). 1H -NMR (C_6D_6): 1.3 (t, $J(P,H) = 8.7$); 1.68 (t, $J(P,H) = 24.4$, ReH). $^{13}C\{^1H\}$ -NMR (C_6D_6): 16.6 (t, $J(P,C) = 35.2$, $P(CH_3)_3$); 207.2 (t, $J(P,C) = 6.0$, ReCO). $^{31}P\{^1H\}$ -NMR (C_6D_6): -30.4 (s). MS: 433 (4, M^+), 405 (100, $[M - CO]^+$), 373 (32, $[M - NO - 2 CH_3]^+$), 76 (33, Me_2P). Anal. calc. for $C_7H_{19}ClNO_2P_2Re$: C 19.42, H 4.42, N 3.23; found: C 19.52, H 4.42, N 3.08.

$[ReCl(CO)H(NO)(Et_3P)_2]$ (**5d**) was prepared as described for **5a** using 1 g of **2d** (1.81 mmol) and 1.82 ml of 1M $Li[BHET_3]$ in THF (1.82 mmol). The crude product was chromatographed with toluene at 0° , and an orange fraction was collected. Evaporation to dryness *in vacuo* yielded 0.69 g of **5d** (74%). M.p. $50-51^\circ$. IR (hexane): 1960s (CO), 1669s (NO), 1827w (ReH). 1H -NMR (C_6D_6): 0.93 (t, $J(H,H) = 7.5$, $J(P,H) = 15.6$, $P(CH_2CH_3)_3$); 1.50 (t, $J(P,H) = 22.3$, ReH); 1.74 (m, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 7.6 (s, $P(CH_2CH_3)_3$); 17.9 (t, $J(P,C) = 31.2$, $P(CH_2CH_3)_3$); 208.4 (t, $J(P,C) = 6.8$, ReCO). $^{31}P\{^1H\}$ -NMR (C_6D_6): 6.4 (s). MS: 517 (5, M^+), 489 (100, $[M - CO]^+$), 459 (23, $[M - CO - NO]^+$), 119 (88, $[HPEt_3]$). Anal. calc. for $C_{13}H_{31}ClNO_2P_2Re$: C 30.2, H 6.04, N 2.71; found: C 30.06, H 5.95, N 2.54.

$[ReCl(CO)H(NO)\{(i-Pr)_3P\}_2]$ (**5e**) was prepared as described for **5a** using 1 g of **2e** (1.57 mmol) and 1.6 ml of 1M $Li[BHET_3]$ in THF (1.6 mmol). The residue was chromatographed with toluene at -20° , and an orange fraction was collected. Evaporation to dryness *in vacuo* yielded 0.74 g of **5e** (83%). Dec. without melting. IR (hexane): 1953s (CO), 1671s (NO), $\nu(ReH)$ not observed. 1H -NMR (C_6D_6): 1.15 (dt, $J(H,H) = 6.4$, $J(P,H) = 14.3$, $P(CH(CH_3(a))(CH_3(b)))_3$); 1.19 (dt, $J(H,H) = 6.8$, $J(P,H) = 14.3$, $P(CH(CH_3(a))(CH_3(b)))_3$); 1.57 (t, $J(P,H) = 22.2$, ReH); 2.57 (m, $P(CH(CH_3)_2)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 18.6 (s, $P(CH(CH_3(a))(CH_3(b)))_3$); 19.1 (s, $P(CH(CH_3(a))(CH_3(b)))_3$); 25.0 (t, $J(P,C) = 25.1$, $P(CH(CH_3)_2)_3$); 210.5 (t, $J(P,C) = 6.8$, ReCO). $^{31}P\{^1H\}$ -NMR (C_6D_6): 31.5 (s). MS: 573 (100, $[M - CO]^+$), 161 (97, $[HP(i-Pr)_3]$). Anal. calc. for $C_{19}H_{43}ClNO_2P_2Re$: C 37.96, H 7.21, N 2.33; found: C 38.48, H 7.23, N 1.96.

$[Re(CO)H_2(NO)\{(MeO)_3P\}_2]$ (**6a**). At r.t., 3.6 ml of 1M *Red Al* in toluene were added to a stirred soln. of **2a** (1.0 g, 1.78 mmol) in toluene. After disappearance of the starting material (IR monitoring), the mixture was cooled in an ice-bath, and 0.5 g crushed ice were added carefully. After stirring at 0° for another $\frac{1}{2}$ h, the mixture was filtered through *Celite*, and the filtrate was taken to dryness under reduced pressure. The dark reddish residue was extracted with Et_2O and filtered through silica. The filtrate was again taken to dryness *in vacuo*, and the crude product was chromatographed with CH_2Cl_2 at -20° . A pale yellow fraction was collected, and after evaporation to dryness *in vacuo*, pale yellow crystals of **6a** were isolated. Yield: 0.36 g (41%). M.p. $51-52^\circ$. IR (hexane): 2005s (CO), 1681s (NO), 1840w (ReH). 1H -NMR (C_6D_6): -5.26 (dt, $J(H,H) = 6.7$, $J(P,H) = 32.9$, ReH_b); -2.04 (dt, $J(H,H) = 6.7$, $J(P,H) = 30.9$, ReH_a); 3.38 (t, $J(P,H) = 12.3$, $P(OCH_3)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 52.3 (s, $P(OCH_3)_3$); 201.3 (t, $J(P,C) = 7.3$, ReCO). $^{31}P\{^1H\}$ -NMR (C_6D_6): 137.8 (s). MS: 493 (82, $[M - 2 H]^+$), 465 (67, $[M - \{2 H, CO\}/NO]^+$), 450 (32, $[M - CH_3 - \{2 H, CO\}/NO]^+$), 435 (22, $[M - 2 H - CO - NO]^+$), 93 (100, $(MeO)_2P$). Anal. calc. for $C_7H_{20}NO_8P_2Re$: C 17.01, H 4.08, N 2.83; found: C 17.03, H 4.05, N 2.69.

$[Re(CO)H_2(NO)\{(i-PrO)_3P\}_2]$ (**6b**) was prepared as described for **6a** using 1 g of **2b** (1.37 mmol) and 2.8 ml 1M *Red Al* in toluene (2.8 mmol). The crude product was chromatographed with toluene at -20° , and a pale yellow fraction was collected. Evaporation to dryness and crystallization from hexane at -80° yielded 0.5 g of **6b** (55%) as yellow crystals. M.p. $59-60^\circ$. IR (hexane): 1997s (CO), 1671s (NO), 1850w (ReH). 1H -NMR (C_6D_6): -4.78 (dt, $J(H,H) = 6.5$, $J(P,H) = 31.7$, ReH_b); -1.51 (dt, $J(H,H) = 6.5$, $J(P,H) = 30.2$, ReH_a); 1.24 (d, $J(H,H) = 6.1$, $P(OCH(CH_3(a))(CH_3(b)))_3$); 1.26 (d, $J(H,H) = 6.1$, $P(OCH(CH_3(a))(CH_3(b)))_3$); 4.82 (m, $P(OCH(CH_3)_2)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 23.7 (s, $P(OCH(CH_3)_2)_3$); 70.2 (s, $P(OCH(CH_3)_2)_3$); 203.5 (t, $J(P,C) = 7.6$, ReCO). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): 126.4 (s). Anal. calc. for $C_{19}H_{44}NO_8P_2Re$: C 34.44, H 6.69, N 2.11; found: C 34.42, H 6.74, N 1.91.

$[Re(CO)H_2(NO)(Me_3P)_2]$ (**6c**) was prepared as described for **6a** using 2 g of **2c** (4.28 mmol) and 8.5 ml of 1M *Red Al* in toluene (8.5 mmol). The crude product was chromatographed with CH_2Cl_2 at -20° , and a pale yellow fraction was collected. Evaporation to dryness produced a yellow oil which was crystallized from Et_2O at -80° . Yield: 0.9 g of **6c** (53%). M.p. $73-74^\circ$. IR (hexane): 1966s (CO), 1655s (NO), 1803w (ReH). 1H -NMR (C_6D_6): -4.24 (dt, $J(H,H) = 6.8$, $J(P,H) = 28.1$, ReH_b); -0.81 (dt, $J(H,H) = 6.8$, $J(P,H) = 27.0$, ReH_a); 1.37 (t, $J(P,H) = 8.1$, $P(CH_3)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 23.0 (t, $J(P,C) = 35.9$, $P(CH_3)_3$); 210.4 (t, $J(P,C) = 5.8$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): -37.7 (s). MS: 397 (100, $[M - 2 H]^+$), 367 (67, $[M - 2 H - NO]^+$), 337 (55, $[M - 2 H - NO - 2 CH_3]^+$). Anal. calc. for $C_7H_{20}NO_2P_2Re$: C 21.1, H 5.06, N 3.52; found: C 20.94, H 5.03, N 3.31.

$[Re(CO)H_2(NO)(Et_3P)_2]$ (**6d**) was prepared as described for **6a** using 2.0 g of **2d** (3.63 mmol) and 7.25 ml of 1M *Red Al* in toluene (7.25 mmol). The crude product was chromatographed with toluene at 0° , and a pale yellow fraction was collected. Evaporation to dryness *in vacuo* yielded 1.44 g of **6d** (82%) as a yellow oil with a m.p. below 0° . IR (hexane): 1961s (CO), 1652s (NO), 1809w (ReH). 1H -NMR (C_6D_6): -5.1 (dt, $J(H,H) = 6.8$, $J(P,H) = 26.1$, ReH_b); -1.42 (dt, $J(H,H) = 6.8$, $J(P,H) = 26.4$, ReH_a); 0.95 (tt, $J(H,H) = 7.6$, $J(P,H) = 16.0$, $P(CH_2CH_3)_3$); 1.60 (m, $P(CH_2CH_3)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 8.1 (s, $P(CH_2CH_3)_3$); 23.5 (t, $J(P,C) = 32.3$, $P(CH_2CH_3)_3$); 211.8 (t, $J(P,C) = 5.5$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): 8.3 (s). MS: 481 (100, $[M - 2 H]^+$), 451 (62, $[M - 2 H - NO]^+$), 423 (59, $[M - 2 H - CO - NO]^+$). Anal. calc. for $C_{13}H_{32}NO_2P_2Re$: C 32.26, H 6.68, N 2.9; found: C 32.54, H 6.48, N 2.75.

$[Re(CO)H_2(NO)\{(i-Pr)_3P\}_2]$ (**6e**) was prepared as described for **6a** using 1 g of **2e** (1.6 mmol) and 3.2 ml of 1M *Red Al* in toluene (3.2 mmol). The crude product was chromatographed with toluene at 0° , and a pale yellow fraction was collected. Evaporation to dryness *in vacuo* yielded 0.57 g of **6e** (63%). M.p. 113° . IR (hexane): 1957s (CO), 1650s (NO), $\nu(ReH)$ not observed. 1H -NMR (C_6D_6): -5.37 (dt, $J(H,H) = 6.7$, $J(P,H) = 23.8$, ReH_b); -1.35 (dt, $J(H,H) = 6.7$, $J(P,H) = 26.2$, ReH_a); 1.49 (dt, $J(H,H) = 6.8$, $J(P,H) = 14.0$, $P(CH(CH_3)_2)_3$); 2.07 (m, $P(CH(CH_3)_2)_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 19.7 (s, $P(CH(CH_3(a))(CH_3(b)))_3$); 19.8 (s, $P(CH(CH_3(a))(CH_3(b)))_3$); 28.2 (t, $J(P,C) = 26.5$, $P(CH(CH_3)_2)_3$); 214.1 (t, $J(P,C) = 5.0$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): 45.2 (s). MS: 565 (100, $[M - 2 H]^+$), 535 (12, $[M - 2 H - NO]^+$), 493 (40, $[M - 2 H - NO - C_3H_6]^+$). Anal. calc. for $C_{19}H_{44}NO_2P_2Re$: C 40.27, H 7.83, N 2.47; found: C 40.17, H 7.88, N 2.51.

$[Re(CO)H_2(NO)(Cy_3P)_2]$ (**6f**) was prepared as described for **6a** using 1 g of **2f** (1.14 mmol) and 2.3 ml of 1M *Red Al* in toluene (2.3 mmol). The crude product was chromatographed with CH_2Cl_2 /hexane 1:3 at 0° , and a pale yellow fraction was collected. Evaporation to dryness *in vacuo* yielded 0.54 g of **6f** (58%). Dec. before melting. IR (CH_2Cl_2): 1945s (CO), 1623s (NO), $\nu(ReH)$ not observed. 1H -NMR (C_6D_6): -4.9 (dt, $J(H,H) = 6.6$, $J(P,H) = 24.0$, ReH_b); -1.0 (dt, $J(H,H) = 6.6$, $J(P,H) = 26.0$, ReH_a); 1.22, 1.6, 1.75, 2.11, 2.17 (very br., $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 26.7 (s); 27.6 (t, $J(P,C) = 9.5$); 27.7 (t, $J(P,C) = 10.0$); 30.2 (s); 30.0 (s); 38.4 (t, $J(P,C) = 25.2$); 214.9 (t, $J(P,C) = 5.2$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): 34.9 (s). MS: 805 (100, $[M - 2 H]^+$). Anal. calc. for $C_{37}H_{68}NO_2P_2Re$: C 55.06, H 8.49, N 1.74; found: C 55.09, H 8.6, N 1.57.

$[Re(CO)_2(NO)\{(i-PrO)_3P\}_2]$ (**7b**). A soln. of 2.0 g (2.73 mmol) of **2b** in 200 ml of Et_2O was reduced at r.t. with ca. 2 g of Na sand under 1 atm of CO. After stirring for 3 d, the color changed from yellow to red-brown. Completion of the reaction was assured by IR spectroscopy monitoring the $\nu(CO)$ band of **2b**. The reaction time depends strongly on the quality of the used Na. The mixture was filtered over *Celite* (10 cm), and the solvent of the filtrate was removed under reduced pressure. Chromatography of the residue on silica gel with toluene at 0° led under careful exclusion of O_2 to the isolation of 1.34 g (71%) of **7b**. M.p. 63° (dec.). IR (CH_2Cl_2): 1961s, 1877vs (CO); 1612s (NO). 1H -NMR (C_6D_6): 1.24 (d, $J(H,H) = 7.2$, $POCH(CH_3)_2$); 4.78 (m, $POCH(CH_3)_2$). $^{13}C\{^1H\}$ -NMR (C_6D_6): 23.6 (s, $POCH(CH_3)_2$); 70.96 (s, $POCH(CH_3)_2$); 209.8 (t, $J(P,C) = 15.5$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): 121.2 (s). MS: 689 (100, M^+), 661 (18, $[M - CO]^+$), 630 (28, $[M - OC_3H_7]^+$), 576 (33, $[M - NO, C_3H_7, C_3H_6]^+$), 549 (64, $[M - 2 CO, 2 C_3H_6]^+$), 43 (29, $C_3H_7^+$). Anal. calc. for $C_{20}H_{42}NO_3P_2Re$: C 34.88, H 6.15, N 2.03; found: C 35.15, H 5.93, N 2.15.

$[Re(CO)_2(NO)(Me_3P)_2]$ (**7c**) was prepared as described for **7b**. Complex **2c** (2.0 g, 2.14 mmol) in 200 ml of Et_2O and ca. 2 g of Na sand were used. Chromatography with CH_2Cl_2 on silica at -30° . Yield: 0.62 g (68%) of **7c**. Dec. before melting. IR (Et_2O): 1935s, 1852vs (CO); 1604s (NO). 1H -NMR (C_6D_6): 1.25 (t, $J(P,H) = 8.3$, PCH_3). $^{13}C\{^1H\}$ -NMR (C_6D_6): 20.5 (t, $J(P,C) = 34.2$, PCH_3); 215.6 (t, $J(P,C) = 10$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): -43.4 (s). Anal. calc. for $C_8H_{18}NO_3P_2Re$: C 22.64, H 4.27, N 3.30; found: C 23.02, H 4.41, N 3.12.

$[Re(CO)_2(NO)(Et_3P)_2]$ (**7d**) was prepared as described for **7b**. Complex **2d** (2.0 g, 3.63 mmol) in 200 ml of Et_2O and ca. 2 g of Na sand were used. Chromatography with toluene on silica at 0° yielded 1.4 g (76%) of **7d**. M.p. 60° (dec.). IR (hexane): 1943s, 1856vs (CO); 1609s (NO). 1H -NMR (C_6D_6): 0.92 (dt, $J(H,H) = 7.6$, $J(P,H) = 16.6$, PCH_2CH_3); 1.57 (m, $J(H,H) = 7.6$, $J(P,H) = 15.2$, PCH_2CH_3). $^{13}C\{^1H\}$ -NMR (C_6D_6): 8.1 (s, PCH_2CH_3); 21.3 (t, $J(P,C) = 31.0$, PCH_2CH_3); 215.2 (t, $J(P,C) = 10.2$, $ReCO$). $^{31}P\{^1H\}$ -NMR (C_6D_6): 42.0 (s). MS: 509 (96, M^+), 481 (71, $[M - CO]^+$), 451 (100, $[M - CO, NO]^+$), 423 (75, $[M - 2 CO, NO]^+$). Anal. calc. for $C_{14}H_{30}NO_3P_2Re$: C 33.07, H 5.95, N 2.75; found: C 33.15, H 6.12, N 2.58.

$[Re(CO)(NO)\{i-PrO\}_2(PhC \equiv CPh)]$ (**8b**). Complex **2b** (1.0 g, 1.37 mmol) was dissolved in 50 ml of THF. This soln. was cooled to -40° and 1 ml of 1.4M (1.4 mmol) soln. of *t*-BuLi was added. A color change to deep-red occurred, and, after 10 min of vigorous stirring, 0.29 g (1.64 mmol) of toluene was added. After warming the mixture slowly to r.t. and stirring it for 1 h, the solvent was removed under reduced pressure. Extraction with hexane was followed by filtration and evaporation to dryness. Subsequent chromatography on a column of silica at -30° and elution with toluene afforded an orange-red band. After evaporation of the solvent, **8b** is obtained as an orange powder. Yield: 0.94 g (82%). M.p. 70° . IR (hexane): 1964s (CO), 1640s (NO). 1H -NMR ($CDCl_3$): 1.05 (*d*, $J(H,H) = 6.12$, $POCHCH_3(b)$); 1.13 (*d*, $J(H,H) = 6.13$, $POCHCH_3(a)$); 4.5 (*m*, $POCHCH_3$); 7.2–7.8 (*m*, Ph). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): 23.8 (*s*, $POCHCH_3$); 69.6 (*s*, $POCH_2CH_3$); 127.6, 127.7, 128.0, 129.6, 129.8, 131.4 (*s*, Ph); 136.0 (*t*, $J(P,C) = 6.0$, ReC(*b*)); 137.5 (*t*, $J(P,C) = 2.7$, ReC(*a*)); 214.7 (*t*, $J(P,C) = 8.0$, ReCO). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): 103.8 (*s*). Anal. calc. for $C_{33}H_{22}NO_8P_2Re$: C 47.25, H 6.25, N 1.67; found: C 47.48, H 6.26, N 1.81.

$[Re(CO)(NO)(Me_3P)_2(PhC \equiv CPh)]$ (**8c**). Complex **2c** (1.0 g, 2.14 mmol) and 0.46 g (2.75 mmol) of toluene dissolved in 100 ml of THF were stirred together with 1.0 g granular Mg (30–55 mesh). The greyish-yellow mixture gradually turned red-brown. The reaction time is dependent on the quality of the Mg and may last up to 3 d. The absence of **2c** was assured by IR spectroscopy. After filtration, the solvent is removed *in vacuo*. Chromatography on silica at -20° and elution with CH_2Cl_2 led to separation of an orange-red band. Evaporation to dryness affords **8c** as an orange microcrystalline powder. Yield: 1.0 g (84%) of **8c**. M.p. 136° (dec.). IR (hexane): 1936s (CO), 1623s (NO). 1H -NMR ($CDCl_3$): 1.23 (*t*, $J(P,H) = 7.2$, PCH_3); 7.1–7.87 (*m*, Ph). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): 17.0 (*t*, $J(P,C) = 30.0$, PCH_3); 125.8, 126.7, 126.9, 128.6, 129.3, 132.1, 136.3 (*s*, Ph); 137.6 (*t*, $J(P,C) = 2.8$, ReC(*b*)); 144.9 (*t*, $J(P,C) = 4.6$, ReC(*a*)); 218.4 (*t*, $J(P,C) = 4.6$, ReCO). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): -34.5 (*s*). MS: 575 (23, M^+), 547 (100, $[M - CO]^+$), 471 (82, $[M - CO, PMe_3]^+$), 178 (14, $C_{14}H_{10}^+$), 76 (11, Me_3P^+). Anal. calc. for $C_{33}H_{22}NO_8P_2Re$: C 47.25, H 6.25, N 1.67; found: C 47.48, H 6.26, N 1.81.

$[Re(CO)(NO)(Et_3P)_2(PhC \equiv CPh)]$ (**8d**) was prepared as described for **8c** using 1.0 g (1.81 mmol) of **2d**, 1.0 g of Mg, 0.38 g (2.16 mmol) of toluene, and 100 ml of THF. Chromatography on silica at r.t. and elution with toluene, yielded 0.92 g (77%) of **8d**. M.p. 121° . IR (hexane): 1931s (CO), 1619s (NO). 1H -NMR ($CDCl_3$): 0.83 (*q*, $J(P,H) = 15.2$, $J(H,H) = 6.9$, PCH_2CH_3); 1.28 (*m*, PCH_2CH_3); 7.0–8.01 (*m*, Ph). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): 7.3 (*s*, PCH_2CH_3); 17.1 (*t*, $J(P,C) = 26.8$, PCH_2CH_3); 144.1 (*t*, $J(P,C) = 4.9$, ReC(*a*)); 125.6, 126.3, 126.6, 128.5, 129.4, 131.2, 136.9 (*s*, Ph); 137.6 (*t*, $J(P,C) = 2.7$, ReC(*b*)); 220.5 (*t*, $J(P,C) = 5.0$, ReCO). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): -2.7 (*s*). MS: 659 (4, M^+), 631 (21, $[M - CO]^+$), 541 (21, $[M - Et_3P]^+$), 513 (28, $[M - CO, Et_3P]^+$), 485 (18, $[M - CO, PEt_3, C_2H_4]^+$), 178 (43, $C_{14}H_{10}^+$), 118 (65, Et_3P^+), 90 (96, $HPeEt_2^+$), 62 (100, $[H_2PEt^+]$). Anal. calc. for $C_{27}H_{40}NO_2P_2Re$: C 49.23, H 6.12, N 2.13; found: C 49.46, H 6.21, N 1.97.

$[Re(CO)(NO)\{i-Pr\}_3P\}_2(PhC \equiv CPh)]$ (**8e**) was prepared as described for **8c** using 1.0 g (1.57 mmol) of **2e**, ca. 1.0 g of Mg, 0.33 g (1.85 mmol) of toluene, and 100 ml of THF. Chromatography on silica at -20° , and elution with toluene yielded 0.74 g (63%) of **8e**. M.p. 124° . IR (hexane): 1926s (CO), 1609s (NO). 1H -NMR ($CDCl_3$): 0.97 (*m*, $PCH_2(CH_3)_2$); 2.0 (*m*, $PCH_2(CH_3)_2$); 7.1–7.7 (*m*, Ph). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): 18.8 (*s*, $PCH_2CH_3(b)$); 19.6 (*s*, $PCH_2CH_3(a)$); 24.4 (*br.*, $PCH_2(CH_3)_2$); 125.6, 126.4, 128.2, 129.8, 130.0 (*s*, Ph); 137.8 (*br.*, ReC(*b*)); 146.8 (*br.*, ReC(*a*)); 224.0 (*br.*, ReCO). $^{31}P\{^1H\}$ -NMR ($CDCl_3$): 12.0 (*s*). Anal. calc. for $C_{33}H_{52}NO_2P_2Re$: C 53.35, H 7.05, N 1.88; found: C 53.23, H 7.29, N 1.75.

$[Re(CO)(NO)(Cy_3P)_2(PhC \equiv CPh)]$ (**8f**) was prepared as described for **8c** using 1.0 g (1.14 mmol) of **2f**, ca. 1.0 g of Mg, 0.24 g (1.37 mmol) of toluene, and 250 ml of THF. Purification of **8f** did not require chromatography. Washing of the raw material with hexane and recrystallization from CH_2Cl_2 yielded 0.68 g (61%) of pure **8f**. M.p. 195° (dec.). IR (hexane): 1925s (CO), 1608s (NO). $^{13}C\{^1H\}$ -NMR ($CDCl_3$): 25.9, 27.3, 28.6, 29.4 (*s*, $PCH_2(CH_2)_5$); 34.2 (*br.*, $PCH(CH_2)_5$); 125.7, 126.0, 128.1, 128.3, 130.3, 131.1 (*s*, Ph); 137.3 (*br.*, ReC(*b*)); 146.8 (*br.*, ReC(*a*)); 224.5 (*br.*, ReCO). $^{31}P\{^1H\}$ -NMR (C_6D_6): 6.8 (*s*). Anal. calc. for $C_{51}H_{76}NO_2P_2Re$: C 62.30, H 7.79, N 1.42; found: C 62.05, H 7.77, N 1.29.

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