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ARTICLE

Oxidorhenium(V) and Rhenium(III) Complexes with *m*-Terphenyl Isocyanides

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Dedicated to Prof. Manfred Scheer on the Occasion of his 65th Birthday

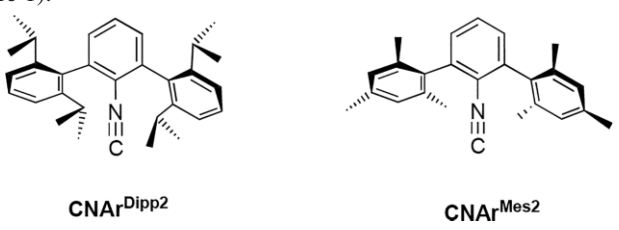
Abstract. Reactions of the sterically encumbered *m*-terphenyl isocyanides $CNAr^{Dipp2}$ (Dipp = 2,6-diisopropylphenyl) and $CNAr^{Mes2}$ (Mes = 2,4,6-trimethylphenyl) with $(NBu_4)[ReOCl_4]$ in CH_2Cl_2 form stable complexes of the composition $(NBu_4)[ReOCl_3(CNAr^R)]$ or $[ReOCl_3(CNAr^R)_2]$ depending on the amount of isocyanide added. In the $[ReOCl_3(CNAr^R)_2]$ complexes, *cis* coordination of the two isocyanides is observed for $CNAr^{Mes2}$, while the sterically more demanding $CNAr^{DIPP2}$ ligands are found in *trans* positions. The rhenium(III) species $[ReCl_3(PPh_3)(CNAr^{Mes2})_2]$ was obtained from the reaction of $[ReOCl_3(PPh_3)_2]$ and $CNAr^{Mes2}$. The ν(CN) IR frequencies measured for the Re^V complexes appear at higher wavenumbers than for the uncoordinated isocyanides, which suggests a low degree of backdonation into *anti*-bonding orbitals of these ligands.

Introduction

m-Terphenyl isocyanides have been shown to be useful ancillary ligands for the isolation of unusual and highly reactive transition metal complexes.[1–21] These encumbering ligands stabilize transition metal centers featuring high degrees of coordinative and electronic unsaturation. In addition, the kinetic protection afforded by *m*-terphenyl isocyanides has also allowed for the isolation of transition metal complexes featuring unusual ligands such as boron monofluoride (BF) and nitrous oxide (N_2O).[11,12] Such isocyanide ligands function as both strong σ-donors and π-acids.[13,14] This dual property allows isocyanides to bind well to transition metals in a range of formal oxidation states. It has been previously reported that *m*-terphenyl isocyanides can stabilize unusual low-valent complexes of both manganese and molybdenum,[7,15–18] but also some medium to high valent *m*-terphenyl isocyanide complexes of Mn and Mo have been isolated via chemical oxidation of low-valent precursors,[15,19–21] thereby demonstrating the utility of these encumbering ligands across a range of metal-based redox states. Very recently, we studied reactions of *m*-terphenyl isocyanides with technetium complexes of various oxidation states and found that even technetium(V) complexes with these ligands are stabilized when strong donors such as nitrido or phenylimido ligands are present.[22] Remarkably, we did not succeed to isolate corresponding oxidotechnetium(V) complexes. Corresponding reactions with $(NBu_4)[TcOCl_4]$ resulted in an oxygen-transfer and the formation of considerable amounts of isocyanates.

There are only a few examples of structurally characterized oxidorhenium(V) complexes with isocyanides. Most of them possess $\{ReO_2\}^+$ or $\{Re_2O_3\}^{4+}$ cores,[23–26] which is a common structural feature of such complexes with neutral ligands and is also frequently found with related amines, imines or chelating phosphines.[27] To the best of our knowledge, there are only two reports about monooxidorhenium(V) complexes with isocyanide ligands: $[ReOCl_3(CNCMe_3)_2]$ and $[ReOCl_3\{CN\text{-}C_6H_3\text{-}(2,6\text{-}Me)_2\}_2]$.[26,28]

Herein, we report an initial survey of reactions between *m*-terphenyl isocyanides and oxorhenium(V) complexes. To assess the role of steric factors, we have employed the *m*-terphenyl isocyanide ligand $CNAr^{Dipp2}$ [Ar^{Dipp2} = 2,6-(2,6-$(i\text{Pr})_2C_6H_3)_2C_6H_3$] and its less sterically encumbering derivative $CNAr^{Mes2}$ (Ar^{Mes2} = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$) (Figure 1).[13,15,29]



$CNAr^{Dipp2}$ $CNAr^{Mes2}$

Figure 1. Ligands used.

Results and Discussion

Reactions between the bulky isocyanides $CNAr^{Mes2}$ or $CNAr^{Dipp2}$ and the common oxidorhenium(V) precursor

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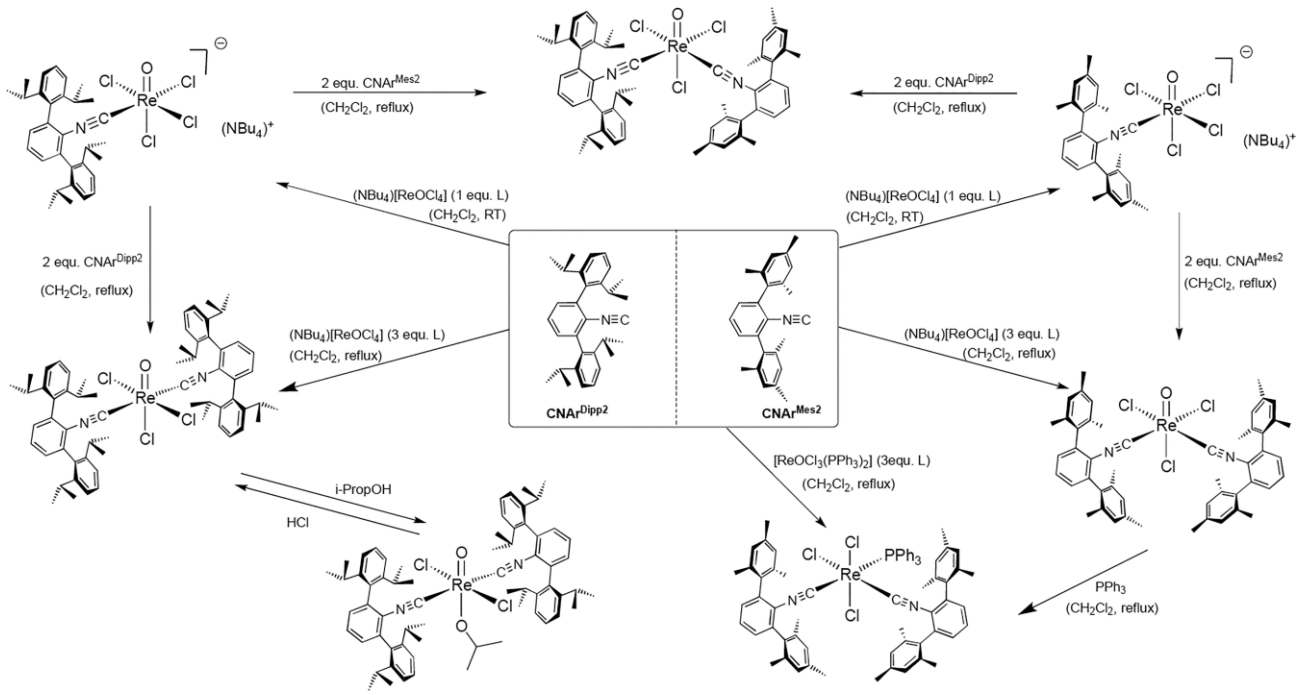

Scheme 1. Reactions of $CNAr^{Mes2}$ and $CNAr^{Dipp2}$ with oxidorhenium(V) complexes.

$(NBu_4)[ReOCl_4]$ in dichloromethane result in the formation of anionic compounds of the composition $[ReOCl_4(CNAr^R)]^-$ or neutral $[ReOCl_3(CNAr^R)_2]$ complexes depending on the amount of isocyanide added and the reaction conditions applied. A summary of the performed reactions and obtained products is shown in Scheme 1.

The anionic $[ReOCl_4(CNAr^R)]^-$ complexes precipitate as their tetrabutylammonium salts directly from the reaction mixtures after the addition of toluene. The blue-green crystalline solids are readily soluble in polar organic solvents such as CH_2Cl_2 or acetonitrile. Their IR spectra show the ν(ReO) bands at 966 cm^{-1} for $(NBu_4)[ReOCl_4(CNAr^{Mes2})]$ and 978 cm^{-1} for the $CNAr^{Dipp2}$ complex, respectively. This is in the normal range for rhenium(V) oxido complexes,[24] and similar absorptions have also been found for $[ReOCl_3(CNCMe_3)_2]$ and $[ReOCl_3\{CN\text{-}C_6H_3\text{-}(2,6\text{-}Me)_2\}_2]$.[26,28]

The *m*-terphenyl isocyanides in the $(NBu_4)[ReOCl_4(CNAr^R)]$ complexes are bonded in the equatorial coordination spheres *cis* to the oxido ligands as has been found by single-crystal X-ray diffraction. Figure 2 depicts the molecular structures of the complex anions. Ellipsoid plots of the structures and more details of the structure determinations are contained in the Supporting Information. The Re-C1 bonds are slightly shorter than in other rhenium(V) complexes with aliphatic isocyanides,[24,25] but similar to those in the dimeric complex $[Re_2O_3Cl_3\{CN\text{-}C_6H_3\text{-}(2,6\text{-}Me)\}_4]$.[26]

Reactions of the $(NBu_4)[ReOCl_4(CNAr^R)]$ complexes or of $(NBu_4)[ReOCl_4]$ with an excess of the isocyanides in boiling CH_2Cl_2 enforce the exchange of a second chlorido ligand and the formation of neutral $[ReOCl_3(CNAr^R)_2]$ complexes. However, some side reactions have also been observed and considerable amounts of the corresponding *m*-terphenyl isocyanates, $ONCAr^R$, were present in the final reaction mixtures. Obviously, oxygen transfer to the isocyanides becomes important with prolonged reaction times and higher temperatures. This finding is in a line with our first experience with technetium complexes of $CNAr^{Mes2}$ and $CNAr^{Dipp2}$, where stable techne-

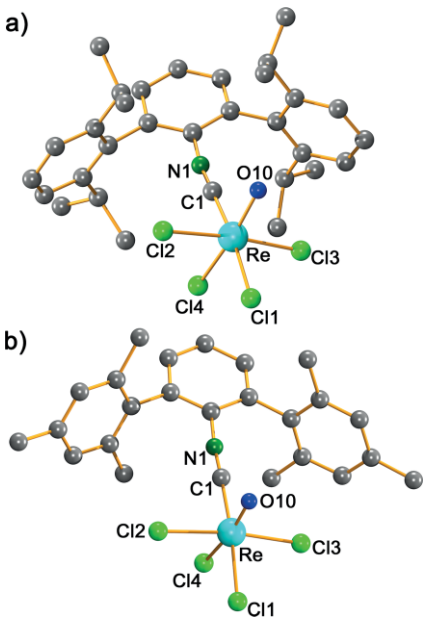

Figure 2. Structures of the complex anions of (a) $(NBu_4)[ReOCl_4(CNAr^{Dipp2})]$ (Selected bond lengths: Re–O10 1.813(7), Re–C1 2.06(1), C1–N1 1.15(1) Å] and (b) $(NBu_4)[ReOCl_4(CNAr^{Mes2})]$ (Selected bond lengths: Re–O10 1.701(5), Re–C1 2.053(6), C1–N1 1.145(7) Å].

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tium(V) complexes were formed with nitrido and phenylimido co-ligands, while we were hitherto unable to isolate corresponding oxidotechnetium(V) compounds.[22] In contrast, the isolated $[ReOCl_3(CNAr^R)_2]$ complexes are indefinitely stable as solids and in solution with non-coordinating solvents. The blue, crystalline compounds are readily soluble in CH_2Cl_2, $CHCl_3$ or acetonitrile, sparingly soluble in diethyl ether or toluene and insoluble in hexane. Single crystals of sufficient size and quality for X-ray diffraction were grown from CH_2Cl_2/toluene mixtures.

The molecular structures of $[ReOCl_3(CNAr^{Dipp2})_2]$ and $[ReOCl_3(CNAr^{Mes2})_2]$ are shown in Figure 3. Interestingly, the two products represent two isomers. The isocyanide ligands in $[ReOCl_3(CNAr^{Mes2})_2]$ are in *cis*-arrangement, which is in accordance with the bonding situation in $[ReOCl_3(CNCMe_3)_2]$,[26] while the $CNAr^{Dipp2}$ ligands in $[ReOCl_3(CNAr^{Dipp2})_2]$ are *trans* to each other. Such a result is not completely surprising and it has been shown before for a number of examples that the formation of the individual isomers is the result of a complex interplay of electronic and steric factors.[13,15,29] Two illustrative examples for this fact are given with low-valent carbonyl complexes of rhenium and molybdenum: (i) The reaction of $[Re(CO)_5Br]$ with an excess of $CNAr^{Dipp2}$ gives under mild conditions *cis*-$[Re(CO)_3Br(CNAr^{Dipp2})_2]$ with the common facial tricarbonylrhenium(I) core, while from the same reaction after 5 h reflux in toluene the *trans*-isomer with the less favored meridional arrangement of the carbonyls can be isolated.[30] (ii) Treatment of the molybdenum(0) complex *trans*-$[Mo(CO)_3(NCCH_3)(CNAr^{Dipp2})_2]$ with the strong σ-donor pyridine results in a *trans*/*cis* rearrangement of the isocyanide ligands and *cis*-$[Mo(CO)_3(py)(CNAr^{Dipp2})_2]$ can be isolated from such reactions in good yields.[15]

Both above mentioned reactions show that a *cis* arrangement of two of the sterically encumbered $CNAr^{Dipp2}$ ligands on octahedrally coordinated metal ions is possible, but it was not observed with the oxidorhenium(V) complexes of the present study. However, a mixed-isocyanide complex of the composition *cis*-$[ReOCl_3(CNAr^{Dipp2})(CNAr^{Mes2})]$ could be isolated from reactions of $(NBu_4)[ReOCl_4(CNAr^{Dipp2})]$ with $CNAr^{Mes2}$ or $(NBu_4)[ReOCl_4(CNAr^{Mes2})]$ with $CNAr^{Dipp2}$ (Scheme 1). It should be noted that no exchange of the already coordinated isocyanides of the starting complexes has been observed. The *cis* coordination of the isocyanides in $[ReOCl_3(CNAr^{Dipp2})(CNAr^{Mes2})]$ has been proven unambiguously by a crystal structure determination (Figure 3c). NMR spectra have not been taken from this compound.

In spite of the steric bulk of the *m*-terphenyl isocyanides, the metal ions are not completely shielded (not even in *trans*-$[ReOCl_3(CNAr^{Dipp2})_2]$) and some exchange reactions of the chlorido ligands can be observed. For example, the dissolution of the blue complex in alcohols results in a color change to pale purple. This is the result of the exchange of one of the Cl^- ligands by an alkoxy ligand. The reaction is reversible and the blue starting compound can be recovered upon complete evaporation of the alcohol. Pale purple single crystals of *trans*-$[ReOCl_2(iso\text{-}PropO)(NCAr^{Dipp2})_2]$ were obtained from a concentrated CH_2Cl_2/*i*PropOH solution and studied by X-ray diffraction. The molecular structure of the product is shown in Figure 3d and confirms the replacement of the Cl^- *trans* to the oxido ligand. This coordination position is weakened by the *trans* influence of the multiple-bonded oxygen atom. The replacement of Cl^- ligands by RO^- ligands has been observed previously when reactions starting from $[ReOCl_3(PPh_3)_2]$ are performed in alcohols. In such cases, $[ReOCl_2(OR)(PPh_3)_2]$ complexes are frequently observed as side-products.[31–34] The formation of a methoxy complex has also been described for the dissolution of $[ReOCl_3(CNCMe_3)_2]$ in methanol on the basis of spectroscopic data.[28]

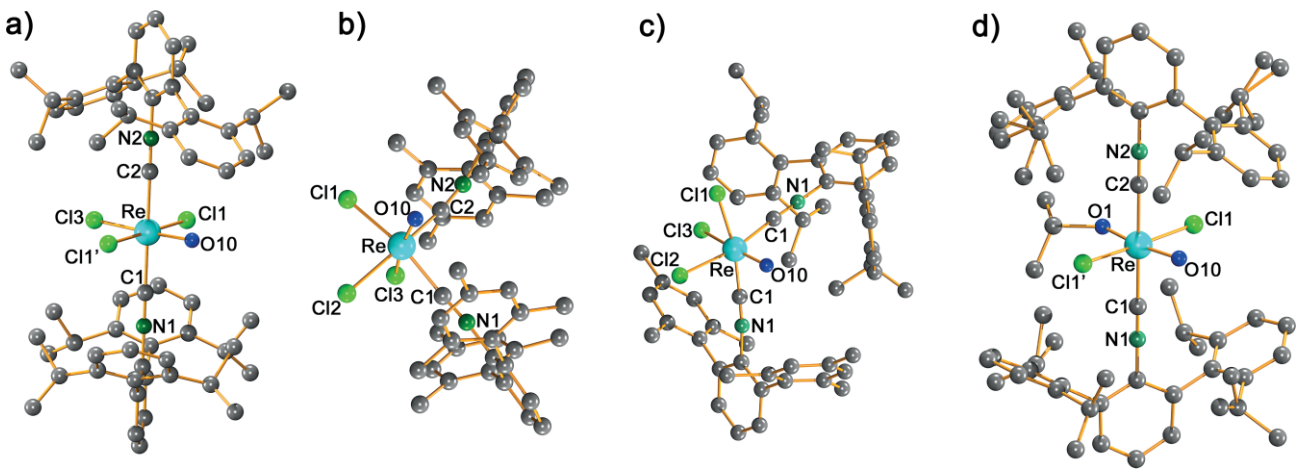

Figure 3. Molecular structures of (a) *trans*-$[ReOCl_3(CNAr^{Dipp2})_2]$ [Selected bond lengths: Re–C1 2.087(7), Re–C2 2.096(6), C1–N1 1.154(8), C2–N2 1.143(8) Å], (b) *cis*-$[ReOCl_3(CNAr^{Mes2})_2]$ [Selected bond lengths: Re–C1 2.058(6), Re–C2 2.03(1), C1–N1 1.152(6), C2–N2 1.18(1) Å], (c) *cis*-$[ReOCl_3(CNAr^{Dipp2})(CNAr^{Mes2})]$ [Selected bond lengths: Re–C1 2.072(8), Re–C2 2.075(8), C1–N1 1.143(8), C2–N2 1.145(8) Å], (d) *trans*-$[ReOCl_2(iso\text{-}PropO)(CNAr^{Dipp2})_2]$ [Selected bond lengths: Re–C1 2.12(1), Re–C2 2.09(1), C1–N1 1.14(1), C2–N2 1.15(1) Å]. Symmetry operation (') 1 –*x*, y, 1.5–z. Hydrogen atoms are omitted for clarity. The Re–O and Re–Cl bond lengths are influenced by positional disorders of the respective atoms and, thus, less indicative for a detailed structural discussion. The shown molecules are related to the major components, details about the disorders are given in the Supporting Information.

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During all reactions described above starting from $(NBu_4)[ReOCl_4]$, the oxidation state "+5" of the rhenium and the central $\{ReO\}^{3+}$ core were maintained. This is not the case when another common Re^V precursor, $[ReOCl_3(PPh_3)_2]$, is used. The released PPh_3 can act as a reductant and rhenium(III) compounds are frequently formed.[27] Very recently, we have studied such reactions more in detail. It has been found that the reducing capacity of the released PPh_3 can be used for a selective reduction of diarylselenides or -tellurides and the isolation of oxidorhenium(V) complexes with the resulting arylselenolates or -tellurolates.[35] When a suspension of the sparingly soluble $[ReOCl_3(PPh_3)_2]$ in CH_2Cl_2 is heated with $CNAr^{Mes2}$, the green solid gradually dissolves and a yellow solution is obtained, from which the paramagnetic rhenium(III) complex *cis*-$[ReCl_3(PPh_3)(CNAr^{Mes2})_2]$ can be isolated in good yields. The compound is extremely soluble in most organic solvents including diethyl ether and has been crystallized from hexane.

An X-ray structural analysis of the bright yellow crystals confirms the formation of a Re(III) complex with two $CNAr^{Mes2}$ ligands in *cis* arrangement (see Figure 4). We assume that released PPh_3 also acts as a reductant in the present reaction. This assumption is supported (i) by the transient observation of the blue color of *cis*-$[ReOCl_3(CNAr^{Mes2})_2]$ during the dissolution process of $[ReOCl_3(PPh_3)_2]$, (ii) the fact that $OCNAr^{Mes2}$ is only formed as a minor side-product during the reaction of $(NBu_4)[ReOCl_4]$ and an excess of $CNAr^{Mes2}$ (*vide supra*), (iii) the ^{31}P NMR detection of $OPPh_3$ in the yellow reaction mixture, and (iv) the successful synthesis of $[ReCl_3(PPh_3)(CNAr^{Mes2})]$ by the addition of PPh_3 to solutions of *cis*-$[ReOCl_3(CNAr^{Mes2})_2]$.

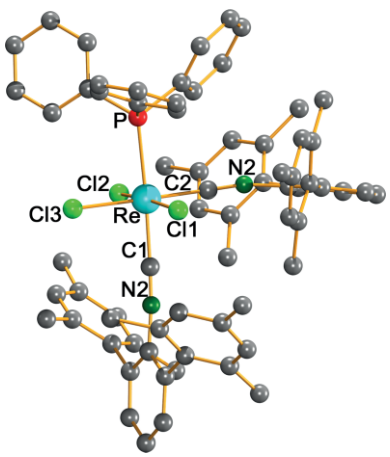

Figure 4. Molecular structure of *cis*-$[ReCl_3(PPh_3)(CNAr^{Mes2})_2]$ [Selected bond lengths: Re–C1 2.051(3), Re–C2 1.999(3), Re–P 2.498(1), Re–Cl1 2.051(3), 2.228(1), Re–Cl3 2.427(1), C1–N1 1.152(3), C2–N2 1.158(3) Å].

The positions of the observed ν(CN) IR frequencies are remarkable in the sense that they do not reflect a considerable degree of backdonation. They are summarized in Table 1 together with the ν(ReO) bands. For the electron-poor rhenium(V) complexes, the binding of the ligands as effective σ-donors is not unexpected and indeed only for the Re(III) compound, *cis*-$[ReCl_3(PPh_3)(NCAr^{Mes2})_2]$, is the lowering of one of the ν(CN) IR frequencies observed. But the example of the Re(III) complex also shows that the corresponding IR frequencies are sensitive to other structural features such as the *trans* ligand (here Cl^- vs. PPh_3). Similar findings have been reported earlier for various complexes with *m*-terphenylisocyanides.[1–22] Thus, the absolute values of these stretches should be regarded with suspicion in the discussion of the bonding situation in such compounds.

Table 1. Selected IR frequencies /cm^{-1}.

	ν(CN)	ν(ReO)
$CNAr^{Dipp2}$	2124	–
$(NBu_4)[ReOCl_4(CNAr^{Dipp2})]$	2185	978
trans-$[ReOCl_3(CNAr^{Dipp2})_2]$	2196	961
trans-$[ReOCl_2(iso\text{-}propO)(CNAr^{Dipp2})_2]$	2175	945
$CNAr^{Mes2}$	2120	–
$(NBu_4)[ReOCl_4(CNAr^{Mes2})]$	2179	966
cis-$[ReOCl_3(CNAr^{Mes2})_2]$	2204	971
cis-$[ReOCl_3(CNAr^{Dipp2})(CNAr^{Mes2})]$	2196	967
cis-$[ReCl_3(PPh_3)(CNAr^{Mes2})_2]$	2138, 2094	–

Conclusions

Reactions of $(NBu_4)[ReOCl_4]$ with the sterically encumbered *m*-terphenyl isocyanides $CNAr^{Dipp2}$ and $CNAr^{Mes2}$ form stable oxidorhenium(V) complexes with one or two isocyanides in their coordination spheres depending on the conditions applied. The formation of a rhenium(III) product was observed when $[ReOCl_3(PPh_3)_2]$ was used as starting material or PPh_3 was added as a reductant.

The steric bulk of the ligands controls the isomerism of the formed $[ReOCl_2(X)(CNAr^R)_2]$ (X = Cl or iso-PropO) complexes: *cis* compounds are formed with two $CNAr^{Mes2}$ or with one CNR^{Mes2} and one $CNAr^{Dipp2}$ ligands, while with two $CNAr^{Dipp2}$ ligands only *trans* isomers were obtained. Needless to say that the transition metal ions in the unequal isomers are differently protected. This is visualized with the space-filling models shown in Figure 5.

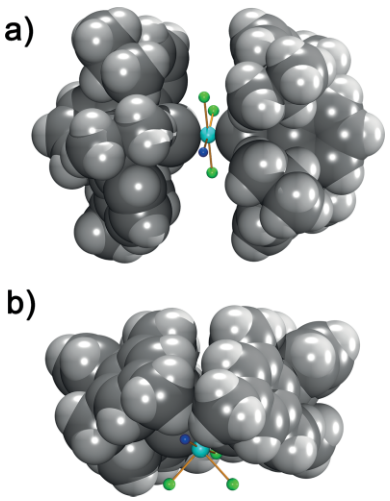

Figure 5. Space-filling models of *trans*-$[ReOCl_3(CNAr^{Dipp2})_2]$ and *cis*-$[ReOCl_3(CNAr^{Mes2})_2]$.

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It is evident that the central {$ReOCl_3$} unit of *trans*-[$ReOCl_3(CNAr^{Dipp2})_2$] is well shielded. Nevertheless, reactions on this side are possible when the incoming unit is small as has been shown by the reversible exchange of the labilized chlorido ligand in *trans* position to the Re=O bond by an isopropoxy ligand. The *cis* coordination of the $CNAr^{Mes2}$ ligands provides a more open coordination sphere, which should also enable the attack of (small) chelating ligands. Corresponding reactions on the protected metal centers are planned for the future.

Experimental Section

General Considerations: Commercially supplied sovents and chemicals were reagent grade and have been used without further purification. The syntheses have been done on air. $(NBu_4)[ReOCl_4]$, $[ReOCl_3(PPh_3)_2]$, $CNAr^{Dipp2}$ and $CNAr^{Mes2}$ were prepared by literature procedures.[16,23,35,36]

Analytical Methods: IR spectra were recorded on a Nicolet iS10 instrument. NMR spectra were recorded at 25 °C on JEOL 400 MHz ECS-400 or JNM-ECA400II spectrometers. Elemental analyses were performed using a vario EL III CHN elemental analyzer (Elementar Analysensysteme GmbH). Some of the compounds show slightly higher carbon values, which is explained by the presence of minor amounts of ligands in the precipitated solids.

X-ray Crystallography: Single crystal X-ray diffraction data were collected on a Bruker D8 Venture or a STOE IPDS II T. Absorption corrections were carried out by multiscan (Bruker D8 Venture) or integration methods (STOE IPDS II T).[37,38] Structure solutions and refinements were done with the SHELX-2008 program packages.[39,40] Hydrogen atoms were placed at calculated positions and refined by a riding model. The visualization of the molecular structures was done using the program DIAMOND 4.2.2.[41]

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1989356, CCDC-1989357, CCDC-1989358, CCDC-1989359, CCDC-1989360, CCDC-1989361, and CCDC-1989362 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

$(NBu_4)[ReOCl_4(CNAr^{Dipp2})]$ and $(NBu_4)[ReOCl_4(CNAr^{Mes2})]$: $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was dissolved in 1 mL CH_2Cl_2 and one equivalent of the $CNAr^R$ ligand dissolved in 2 mL of CH_2Cl_2 was added. The mixture was stirred at room temperature for 30 min and toluene (2 mL) was added. Slow evaporation of the CH_2Cl_2 gave blue-green crystals of the $(NBu_4)[ReOCl_4(CNAr^R)]$ salts, which were filtered off and washed with toluene and a small amount of diethyl ether.

$(NBu_4)[ReOCl_4(CNAr^{Dipp2})]$: Yield 81 mg (80 %). $C_{47}H_{73}Cl_4N_2ORe$ (1010.1): calcd. C 55.9, H 7.3, N 2.8 %; found C 55.3, H 7.5, N 2.9 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2959(s), 2933(m), 2873(m), 2185(vs), 1580(w), 1472(m), 1415(w), 1384(w), 1363(w), 1329(w), 1253(w), 1179(w), 1057(m), 978(s), 903(m), 791(m), 754(vs), 738(m), 584(m) cm^{-1}. **^{1}H NMR** (CH_2Cl_2, ppm): 0.96 (tr., *J* = 7.3 Hz, 12 H, *cation* CH_3), 1.10 (d., *J* = 6.8 Hz, 12 H, CH_3), 1.21 (d., *J* = 6.8 Hz, 12 H, CH_3), 1,36 (h., *J* = 7.5 Hz, 8 H, *cation* CH_2), 1,53 (td., 8 H, *cation* CH_2), 2.55 (hept., *J* = 6.8 Hz, 4 H, *CH*), 3.07 (m., 8 H, *cation* CH_2), 7.19 – 7.44 (m., 9 H, *aryl*).

$(NBu_4)[ReOCl_4(CNAr^{Mes2})]$: Yield 79 mg (85 %). $C_{41}H_{61}Cl_4N_2ORe$ (925.9): calcd. C 53.2, H 6.6, N 3.0 %; found C 52.5 H 6.5, N 2.8 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2960(s), 2933(m), 2873(m), 2179(vs), 1614(w), 1458(m), 1378(w), 1239(m), 1149(w), 1031(w), 966(vs), 905(m), 879(m), 852(w), 842(w), 819(m), 785(w), 760(m), 736(m), 602(w) cm^{-1}. **^{1}H NMR** (CH_2Cl_2, ppm): 0.73 (tr., *J* = 7.1 Hz,12 H, *cation* CH_3), 1.15 (m., 8 H, *cation* CH_2), 1.33 (m., 8 H, *cation* CH_2), 1,85 (s., 12 H, CH_3), 2,02 (s., 6 H, CH_3), 2.86 (m., 8 H, *cation* CH_2), 6.69 (s., 4 H, *aryl*), 7.14 – 7.23 (m., 3 H, *aryl*).

$[ReOCl_3(CNAr^{Dipp2})_2]$ and $[ReOCl_3(CNAr^{Mes2})_2]$: $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was dissolved in 5 mL CH_2Cl_2 and three equivalents of the $CNAr^R$ ligand dissolved in 5 mL of CH_2Cl_2 were added. The mixture was heated under reflux for 30 min and toluene (2 mL) was added. Slow evaporation of the CH_2Cl_2 gave blue crystals of the $[ReOCl_3(CNAr^R)2]$ complexes. They were filtered off and washed with cold diethyl ether.

$[ReOCl_3(CNAr^{Dipp2})_2]$: Yield 91 mg (79 %). $C_{62}H_{74}Cl_3N_2ORe$ (1155.8): calcd. C 64.4, H 6.5, N 2.4 %; found C 65.0, H 6.5, N 2.7 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2958(s), 2915(m), 2849(m), 2196(vs), 1579(w), 1471(m), 1383(w), 1361(w), 1329(w), 1055(m), 961(s), 941(w), 825(w) 797(m), 752(s), 581(s) cm^{-1}. **^{1}H NMR** (CH_2Cl_2, ppm): 1.06 (d., *J* = 6.8 Hz, 24 H, CH_3), 1.12 (d., *J* = 6.8 Hz, 24 H, CH_3), 2.44 (qq., *J* = 6.8 Hz, 8 H,*CH*), 7.22–7.39 (m., 18 H, *aryl*).

$[ReOCl_3(CNAr^{Mes2})_2]$: Yield 73 mg (74 %). $C_{50}H_{50}Cl_3N_2ORe$ (987.5): calcd. C 64.4, H 6.5, N 2.8 %; found C 66.1, H 6.2, N 2.7 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2951(w), 2204(vs), 1613(m), 1457(m), 1380(w), 1236(s), 1186(m), 1126(m), 984(w), 911(vs), 851(s) 808(s), 787(m), 754(s), 736(m), 608(w) cm^{-1}. **^{1}H NMR** (CH_2Cl_2, ppm): 2.00 (s., 24 H, CH_3), 2.23 (s., 12 H, CH_3), 6.85 (s., 8 H, *aryl*), 7.37–7.54 (m., 6 H, *aryl*).

$[ReOCl_2(iso\text{-}PropO)(CNAr^{Dipp2})_2]$: $(NBu_4)[ReOCl_4]$ (58 mg, 0.1 mmol) was dissolved in 5 mL CH_2Cl_2 and three equivalents of $CNAr^{Dipp2}$ dissolved in 5 mL of CH_2Cl_2 were added. The mixture was heated under reflux for 30 min. iso-Propanol (3 mL) was added and the mixture was heated under reflux for an additional period of 1 h. During this time, the color of the mixture turned to pale purple. Pale purple single crystals deposited by slow evaporation of the solvent. They were filtered off and washed with diethyl ether. Yield 41 mg (35 %). $C_{65}H_{81}Cl_2N_2O_2Re$ (1179.4): calcd. C 66.2, H 6.9, N 2.4 %; found C 66.1, H 6.2, N 2.7 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2958(s), 2866(m), 2175(vs), 1579(w), 1461(m), 1410(w), 1383(m), 1361(m), 1329(w), 1252(w), 1164(w), 1119(m), 1056(m), 1006(w), 945(vs), 862(m), 825(m) 798(s), 753(s), 725(w), 688(w), 583(m)) cm^{-1}.

$[ReOCl_3(CNAr^{Mes2})(CNAr^{Dipp2})]$: $(NBu_4)[ReOCl_4(CNAr^{Dipp2})$ (55 mg, 0.05 mmol) was dissolved in 3 mL CH_2Cl_2 and two equivalents of $CNAr^{Mes2}$ dissolved in 1 mL of CH_2Cl_2 were added. The mixture was heated under reflux for 30 min. Toluene (2 mL) was added and the mixtures was kept in a refrigerator (~4 °C) for crystallization. Blue crystals deposited within 1 week. They were filtered off and washed with cold diethyl ether. Yield 24 mg (45 %). b) The same compound is formed from $(NBu_4)[ReOCl_4(CNAr^{Mes2})$ and $CNAr^{Dipp2}$ following the procedure described above. Yield 19 mg (35 %). $C_{56}H_{62}Cl_3N_2ORe$ (1071.6): calcd. C 62.8, H 5.8, N 2.6 %; found C 63.1, H 5.9, N 2.4 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2955(m), 2866(m), 2196(vs), 1611(w), 1578(m), 1500(w), 1461(m), 1444(m), 1380(m), 1363(w), 1346(m), 1320(m), 1287(m), 1275(m), 1161(m), 1149(m), 967(s), 898(m), 851(m), 802(s), 792(s), 751(vs), 729(m), 703.(w) cm^{-1}.

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$[ReCl_3(PPh_3)(CNAr^{Mes2})_2]$: $[ReOCl_3(PPh_3)_2]$ (58 mg, 0.1 mmol) was suspended in 2 mL CH_2Cl_2 and three equivalents of $CNAr^{Mes2}$ dissolved in 1 mL of CH_2Cl_2 were added. The mixture was heated under reflux for 10 min. During this time, the sparingly starting material dissolved and the color of the initially blue solution turned to bright yellow. Hexane (3 mL) was added and the mixtures were kept in a refrigerator for crystallization. Yellow crystals deposited overnight. They were filtered off and washed with hexane. Yield 78 mg (75 %). $C_{68}H_{65}Cl_3N_2PRe$ (1233.7): calcd. C 66.2, H 5.3, N 2.3 %; found C 66.1, H 5.3, N 2.6 %. **IR** (KBr): $\tilde{\nu}_{max}$ = 2915(w), 2138(s), 2094 (s), 1590(m), 1572(w), 1456(w), 1436(m), 1419(m), 1377(w), 1357(w), 1339(w), 1308(w), 1281(w), 1271(w), 1253(w), 1184(w), 1117(m), 1076(m), 1010(w), 888(w), 861(m), 852(s), 807(s) 787(s), 738(s), 721(m), 694(s) cm^{-1}.

Supporting Information (see footnote on the first page of this article): Details of structure determinations, ellipsoid plots, selected bond lengths and angles.

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Keywords: Isocyanides; Rhenium; Oxido complexes; Bulky ligands

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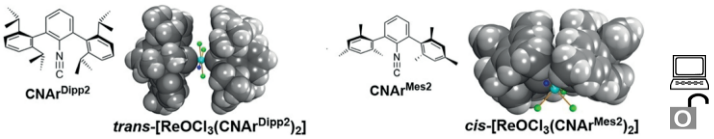

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