

Reactions of 2-(Trimethylsiloxy)phenyl Isocyanide with Complexes of Rhenium in the +1, +3, and +5 Oxidation States

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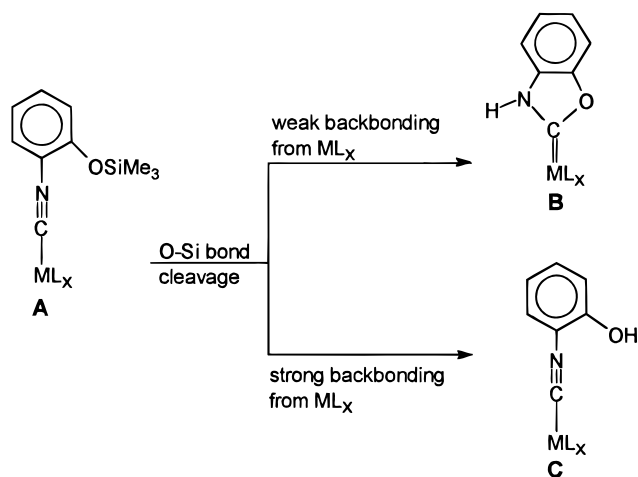
Received October 24, 1995[®]

2-(Trimethylsiloxy)phenyl isocyanide (**1**) reacts with *trans*-[ReCl(N₂)(dppe)₂] (dppe = 1,2-bis(diphenylphosphino)ethane) in boiling THF to give *trans*-[Re(Cl)(CNC₆H₄-2-OSiMe₃)(dppe)₂] (**3**). In boiling CH₂Cl₂ the same reaction proceeds with Si–O bond cleavage to yield *trans*-[Re(Cl)(CNC₆H₄-2-OH)(dppe)₂] (**4**). Si–O bond cleavage was also observed in the reaction of 2,6-bis(trimethylsiloxy)phenyl isocyanide (**2**) with *trans*-[ReCl(N₂)(dppe)₂] in boiling CH₂Cl₂, which yields *trans*-{Re(Cl)[CNC₆H₃(OH)₂-2,6](dppe)₂} (**5**). The Re(II) complex *trans*-[ReCl₂(dppe)₂] (**6**) was isolated as a side product in the above reactions. The complex *mer*-[ReCl₃(NCCH₃)(PPh₃)₂] reacts with **1** in CH₂Cl₂ to give the isocyanide complex *mer*-[ReCl₃(CNC₆H₄-2-OH)(PPh₃)₂] (**7**). Complex **7** was shown by X-ray crystallography to crystallize with two molecules of chloroform per asymmetric unit. Reaction of *fac*-[Re(O)Cl₃(SMe₂)(OPPh₃)] with 2 equiv of **1** leads to a Re(V) diisocyanide complex which upon Si–O bond cleavage gives the dicarbene complex *fac*-{Re(O)Cl₃[CN(H)C₆H₄-2-O]₂} (**9**). The crystal structure of complex **9**, which crystallizes with one molecule of hydrogen-bonded OPPh₃ per asymmetric unit, is reported.

Introduction

2-(Trimethylsiloxy)phenyl isocyanide (**1**) has been shown to be an excellent precursor for the preparation of transition-metal N,O-heterocarbene complexes (Scheme 1). Complexes with coordinated **1** (**A**) react after hydrolysis of the Si–O bond in an intramolecular cyclization reaction to give complexes with the 1,2-dihydrobenzoxazol-2-ylidene ligand (**B**).¹ The cyclization reaction can be suppressed, if the isocyanide carbon atom is deactivated for nucleophilic attack by (d→p)π backbonding from the metal center. In such cases hydrolysis of the Si–O bond yields complexes with the 2-hydroxyphenyl isocyanide ligand (**C**). We have shown that the substitution pattern of a metal center can determine the subsequent reactivity of coordinated **1**. For example, [W(CO)₅(**1**)] reacts after cleavage of the Si–O bond to give (1,2-dihydrobenzoxazol-2-ylidene)pentacarbonyl-tungsten, while *cis*-[W(CO)₄(PPh₃)(**1**)] yields under the same reaction conditions the isocyanide complex *cis*-[W(CO)₄(PPh₃)(CN-C₆H₄-2-OH)].² Substitution of the π-acceptor CO by the σ-donor PPh₃ enhances the backbonding and stabilizes the coordinated isocyanide. Similar behavior was observed for iron complexes upon intramolecular conversion of π-acceptors into σ-donors.³ In most of the investigated cases, the force constant for the CN bond (*k*(CN)) in coordinated **1** allows the prediction of the course of the reaction after Si–O bond cleavage.² An alternate method for the stabilization of coordinated hydroxyphenyl isocyanides (**C**) against intramolecular carbene formation is the engagement of

Scheme 1



the hydroxy group in hydrogen bonds, thereby reducing their nucleophilicity. This strategy was successfully employed for the stabilization of 2,6-dihydroxyphenyl isocyanide coordinated to Cr(CO)₅.⁴

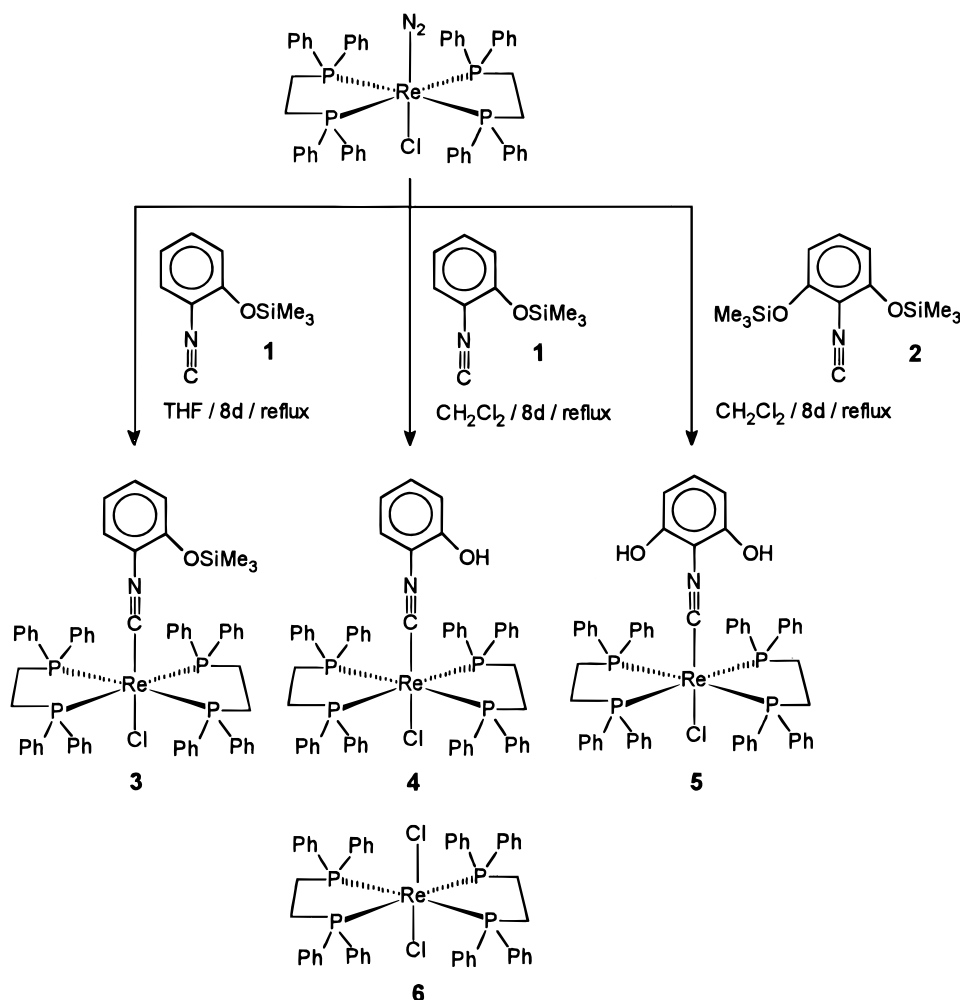
In general, the tendency for carbene formation by intramolecular nucleophilic attack at the isocyanide carbon atom is much higher with 2-hydroxyphenyl isocyanide than that observed for coordinated 2-hydroxyethyl isocyanide⁵ or for an intermolecular attack of a nucleophile on a coordinated isocyanide. This is caused by the relatively high acidity of the hydroxy group in 2-hydroxyphenyl isocyanide, by the orientation of the isocyanide and the hydroxyl group in one plane,

[®] Abstract published in *Advance ACS Abstracts*, February 1, 1997.

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Scheme 2. Reaction of *trans*-[ReCl(N₂)(dppe)] with Isocyanides **1 and **2****

and by the high stability of the formed cyclic N,O-carbene, which possesses some aromatic character.¹ Currently we are investigating the scope of this reaction for the preparation of unusual N,O-heterocarbene complexes. In this contribution we present the reactions of 2-(trimethylsilyloxy)phenyl isocyanide (**1**) and 2,6-bis(trimethylsilyloxy)phenyl isocyanide (**2**) with complexes of rhenium in the +1, +3, and +5 oxidation states together with the products obtained after Si–O bond cleavage, including the first rhenium(V) complex with a cyclic N,O-heterocarbene ligand.

Results and Discussion

Reactions of **1 and **2** with Re(I) Complexes.** The complex *trans*-[ReCl(N₂)(dppe)₂]⁶ reacts with **1** in boiling dry THF to yield the isocyanide complex *trans*-[ReCl(CN(C₆H₄-2-OSiMe₃))(dppe)₂] (**3**) (Scheme 2). Complex **3** was isolated as a yellow, air-stable powder. It takes up to 8 days for an appreciable amount of **3** to form in this reaction. A similarly long reaction time in boiling THF has been noted by Pombeiro et al. for the displacement of dinitrogen from *trans*-[ReCl(N₂)(dppe)₂] by aliphatic^{7a} and aromatic^{7b} isocyanides. The Re(I) complexes are much

more inert toward dinitrogen substitution by isocyanides than the complexes of the type *trans*-[M(N₂)(dppe)₂] (M = Mo, W),⁸ where complete dinitrogen substitution by CNCH₃ occurs in THF within hours at 20 °C (M = Mo) or under reflux (M = W).^{7a,9} The IR spectrum of **3** exhibits an intense absorption at ν 1858 cm⁻¹ assigned to the CN stretching vibration. This value falls in the range observed for complexes of the type *trans*-[ReCl(CNR)(dppe)₂] (1880 cm⁻¹, R = C₆H₄-4-CH₃; 1770 cm⁻¹, R = C₆H₃Cl₂-2,6)^{7b} and is much lower than the ν (CN) value for free **1** (2120 cm⁻¹),¹⁰ illustrating the strong (d→p) π -back-bonding from the electron-rich Re(I) center.

If the reaction of *trans*-[ReCl(N₂)(dppe)₂] with **1** is carried out in boiling dichloromethane under otherwise identical reaction conditions (8 days reaction time), a different isocyanide complex, namely *trans*-[ReCl(CN(C₆H₄-2-OH))(dppe)₂] (**4**) can be isolated (Scheme 2). Since no benzoxazole¹⁰ was detected in the reaction mixture, cleavage of the Si–O bond could only have occurred after coordination of **1** to the rhenium atom. We have reported on the cleavage of the Si–O bond in coordinated **1** in methanol with catalytic amounts of KF.^{1–4} Apparently, dichloromethane itself is acidic

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enough or liberates enough HCl for Si–O bond hydrolysis if the reaction time is sufficiently long. The mechanism of Si–O bond hydrolysis is currently not known. However, the slow protonation of tertiary amines by previously dried dichloromethane has been reported,^{11a} and dichloromethane is known to liberate HCl.^{11b} The slow cleavage of the Si–O bond is perfectly suited for the synthesis of **4**. Addition of water would lead to faster Si–O bond hydrolysis which is undesirable since the substitution of N₂ by the isocyanide in *trans*-[ReCl(N₂)(dppe)₂] is a slow process and a fast Si–O hydrolysis would lead to conversion of **1** to benzoxazole before coordination to the Re(I) center.

The IR absorption for the CN stretching vibration in **4** was again found at a very low wavenumber (ν 1855 cm⁻¹). This precludes intramolecular nucleophilic attack of the liberated hydroxy oxygen atom at the isocyanide carbon atom. The force constant for the CN bond in **4** was calculated to be $k(\text{CN}) = 1315 \text{ N m}^{-1}$, a value much lower than required (approximately $k(\text{CN}) = 1730 \text{ N m}^{-1}$)² for intramolecular carbene formation. Similar results were obtained if *trans*-[ReCl(N₂)(dppe)₂] was reacted with ligand **2** in boiling dichloromethane (Scheme 2). Dinitrogen was substituted by the isocyanide, and both Si–O bonds were cleaved over the reaction time of 8 days, giving the complex *trans*-{ReCl[CNC₆H₄(OH)₂-2,6](dppe)₂} (**5**). No 4-hydroxybenzoxazole was detected, indicating Si–O bond cleavage after coordination of the ligand. The isocyanide carbon atom in **5** is also strongly deactivated for nucleophilic attack ($\nu(\text{CN})$ 1862 cm⁻¹, $k(\text{CN}) = 1320 \text{ N m}^{-1}$).

Isocyanides which are coordinated to strongly electron releasing sites as in **3–5** cannot be attacked by nucleophiles at the isocyanide carbon but instead are susceptible to electrophilic attack at the isocyanide nitrogen atoms as was demonstrated by Pombeiro et al.^{7a} However, no external electrophile was present. Dichloromethane or the coordinated hydroxyphenyl isocyanides are not acidic enough to deliver protons for an electrophilic attack at the isocyanide nitrogen atom.

In all substitution reactions of *trans*-[ReCl(N₂)(dppe)₂] with isocyanides we noted a yellow crystalline byproduct which was characterized as the neutral Re(II) complex *trans*-[ReCl₂(dppe)₂]·CH₂Cl₂ (**6**·CH₂Cl₂) by X-ray crystallography. This complex had previously been obtained in reactions of *trans*-[ReCl(N₂)(dppe)₂] with nitriles and was characterized crystallographically as the solvates *trans*-[ReCl₂(dppe)₂]·CD₂Cl₂ and *trans*-[ReCl₂(dppe)₂]·2THF.¹² The molecular parameters calculated for **6**·CH₂Cl₂ match those reported¹² and will therefore not be presented here. We assume that HCl liberated from the solvent CH₂Cl₂ is responsible for the oxidation Re(I) → Re(II).

Reaction of 1 with *mer*-[ReCl₃(NCCH₃)(PPh₃)₂]. Reaction of *mer*-[ReCl₃(NCCH₃)(PPh₃)₂]¹³ with isocyanides proceeds with acetonitrile substitution to yield the complexes *mer*-ReCl₃(CNR)(PPh₃)₂ (R = C(CH₃)₃, *c*-C₆H₁₁, C₆H₄, CH₂COOCH₃, CH₂CH₂N(CH₂CH₂)₂O).¹⁴

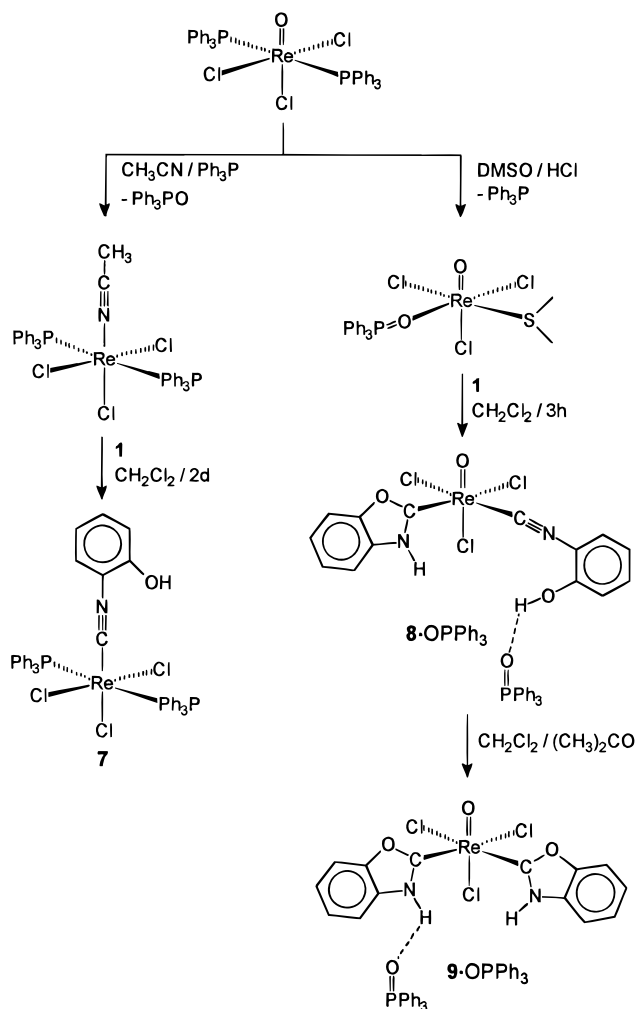
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Scheme 3. Preparation of the Re(III) Isocyanide Complex **7** and of the Re(V) Complex **9-OPPh₃**



The same reaction with the isocyanide **1** (in CH₂Cl₂, 48 h) yields *mer*-[ReCl₃(CNC₆H₄-2-OH)(PPh₃)₂] (**7**) in 70% yield (Scheme 3). The isocyanide has substituted the acetonitrile molecule, and the Si–O bond in the ligand was cleaved under these conditions. The rhenium(III) atom in **7** is much less electron releasing than in the Re(I) complexes **3–5**, and consequently, the IR absorption for the CN stretch appears at a much higher wavenumber (ν 2107 cm⁻¹, $k(\text{CN}) = 1690 \text{ N m}^{-1}$). However, the back-bonding is still strong enough for complete deactivation of the coordinated ligand against intramolecular nucleophilic attack. The metal fragments in **7** as well as in **3–5** act practically as protection groups for the isocyanide ligand, which in the uncoordinated state would immediately cyclize to form benzoxazole.¹⁰

Complex **7** can be crystallized from chloroform as the orange solvate **7**·2CHCl₃, which was characterized by single-crystal X-ray structure analysis (Figure 1). The structure analysis confirms the complex stabilization of hydroxyphenyl isocyanide, a ligand which does not exist in the uncoordinated state. The molecular parameters of **7** (Table 1) resemble equivalent values in *mer*-[ReCl₃(CN-*t*-C₄H₉)(PPh₃)₂].¹⁴ The angle C1–N–C2 (170(1)°) and the distance Re–C1 (2.03(1) Å) in **7** compare well to the equivalent values in *mer*-[ReCl₃(CN-*t*-C₄H₉)(PPh₃)₂] (C1–N–C2 = 170.1(9)°, Re–C1 = 2.004(7) Å).¹⁴ The observed increase in $\nu(\text{CN})$ as one goes from Re(I)

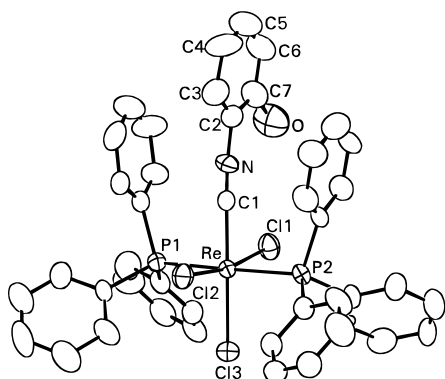


Figure 1. Molecular structure of complex **7** in $7 \cdot 2\text{CHCl}_3$. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for $7 \cdot 2\text{CHCl}_3^a$

Re–C1	2.347(3)	N–C2	1.38(2)
Re–Cl2	2.331(3)	C2–C3	1.38(2)
Re–Cl3	2.429(3)	C2–C7	1.38(2)
Re–P1	2.487(3)	C3–C4	1.36(2)
Re–P2	2.491(3)	C4–C5	1.34(3)
Re–C1	2.03(1)	C5–C6	1.39(3)
O–C3	1.42(2)	C6–C7	1.33(2)
N–C1	1.10(1)		
Cl1–Re–Cl2	168.9(1)	P2–Re–C1	89.0(3)
Cl1–Re–Cl3	98.2(1)	C1–N–C2	170(1)
Cl1–Re–P1	87.45(9)	Re–C1–N	178(1)
Cl1–Re–P2	88.36(9)	N–C2–C3	120(1)
Cl1–Re–C1	83.1(3)	N–C2–C7	120(1)
Cl2–Re–Cl3	92.6(1)	C3–C2–C7	119(1)
Cl2–Re–P1	90.46(9)	O–C3–C2	119(1)
Cl2–Re–P2	93.67(9)	O–C3–C4	121(2)
Cl2–Re–C1	86.1(3)	C2–C3–C4	120(2)
Cl3–Re–P1	89.85(9)	C3–C4–C5	120(2)
Cl3–Re–P2	90.68(9)	C4–C5–C6	121(2)
Cl3–Re–C1	178.6(3)	C5–C6–C7	120(2)
P1–Re–P2	175.81(9)	C2–C7–C6	119(2)
P1–Re–C1	90.6(3)		

^a Estimated standard deviations are given in parentheses.

to Re(III) isocyanide complexes also has consequences for their molecular structures.

While **3–5** were not investigated by X-ray diffraction, the molecular structure of the complex *trans*-[ReCl(CNCH₃)(dppe)₂], which should be very similar to the presumed molecular structures of **3–5**, has recently been described.¹⁵ In the Re(I) complex the isocyanide angle C–N–C is 139.4(10)° and the Re–C(isocyanide) distance is 1.8761(12) Å. In comparison to **7** the Re(I) isocyanide complex exhibits stronger (d→p)π back-bonding, which results in a lower ν(CN) value, a shorter Re–C distance, and a much smaller C–N–C angle for the coordinated isocyanide. In this situation the isocyanide nitrogen can be considered as almost sp²-hybridized. However, even in the Re(III) isocyanide complex **7** there exists enough (d→p)π back-bonding to prevent nucleophilic attack of the hydroxy group at the isocyanide nitrogen. To facilitate this attack, we have prepared isocyanide complexes of rhenium in the +5 oxidation state.

Reaction of 1 with *fac*-[Re(O)Cl₃(SMe₂)(OPPh₃)]. *fac*-[Re(O)Cl₃(PPh₃)₂]¹⁶ reacts with DMSO in the presence of HCl to give the substitution-labile complex *fac*-

[Re(O)Cl₃(SMe₂)(OPPh₃)].¹⁷ Reaction of this complex with 2 equiv of **1** in CH₂Cl₂ leads to substitution of the organic ligands and gives initially the greenish blue carbene–isocyanide complex **8** (Scheme 3). The molecular structure of **8** was assigned on the basis of microanalytical and IR spectroscopic data.

Initially two ligands **1** must have been coordinated to the Re(V) center. The Si–O bonds were cleaved in both ligands. One hydroxyphenyl isocyanide ligand has reacted *via* intramolecular nucleophilic attack to give the cyclic carbene ligand 1,2-dihydrobenzoxazol-2-ylidene (identified by ν(NH) 3230 cm⁻¹ for the carbene), while the second ligand coordinates as hydroxyphenyl isocyanide (ν(CN) 2207 cm⁻¹, ν(OH) 3437 cm⁻¹). No resonance for an Si–O bond was found in the IR spectrum between ν 900 and 980 cm⁻¹. At first glance it is surprising that two different ligands are coordinated to Re(V), particularly since the force constant for the hydroxyphenyl isocyanide (*k*(CN) = 1855 N m⁻¹) falls in the range where normally intramolecular carbene formation occurs.² We have described an iron complex where a 1,2-dihydrobenzoxazol-2-ylidene and a hydroxyphenyl isocyanide ligand are coordinated to the same metal center.³ However, the force constant for the hydroxyphenyl isocyanide ligand in this iron complex (*k*(CN) = 1659 N m⁻¹) is far too low for carbene formation, and thus, the cyclization is prevented for electronic reasons. Different reasons must exist for the presence of the hydroxyphenyl isocyanide ligand in **8**, which is strongly activated for intramolecular carbene formation.

The microanalytical data show the presence of one molecule of OPPh₃ per molecule of **8**. We assume that this phosphineoxide engages in a hydrogen bond to the hydroxy proton as depicted in Scheme 3, thereby stabilizing the hydroxyphenyl isocyanide. Similar behavior was observed for a chromium complex of 2,6-dihydroxyphenyl isocyanide that can be stabilized in the presence of amines, which form two R₃N···H–O hydrogen bonds, while the absence of amines leads immediately to formation of the carbene complex.⁴ Complex **8** was difficult to isolate and decomposes in solution slowly. This prevented further NMR spectroscopic characterization.

Recrystallization of **8** from dichloromethane/acetone leads to the dicarbene complex **9** in 85% yield (relative to *fac*-[Re(O)Cl₃(SMe₂)(OPPh₃)]). Now both hydroxyphenyl isocyanide ligands have cyclized to 1,2-dihydrobenzoxazol-2-ylidene ligands. No ν(CN) was observed any longer in the IR spectrum, and the typical absorption for the NH group of the carbene ligand was found at ν(NH) = 3233 cm⁻¹.

Complex **9** was characterized by an X-ray structure analysis (Figure 2). This analysis confirmed the identity of **9** as a *cis*-dicarbene complex which crystallized with one molecule of OPPh₃ hydrogen-bonded (N1–O4 = 2.678(4) Å) to one carbene N–H proton. Bond distances and angles within the coordinated carbene ligands are identical within statistical limits (Table 2). They differ insignificantly from the values observed for 1,2-dihydrobenzoxazol-2-ylidene coordinated to low-valent transition metals^{1–4} or triphenylboron,¹⁸ indicating little

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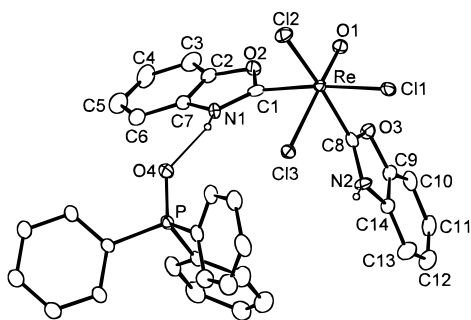


Figure 2. Molecular structure of **9**-OPPh₃. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for 9-OPPh₃^a

Re—Cl1	2.405(1)	N2—C14	1.397(5)
Re—Cl2	2.382(1)	C2—C3	1.373(6)
Re—Cl3	2.3929(9)	C2—C7	1.378(6)
Re—O1	1.686(3)	C3—C4	1.374(6)
Re—C1	2.095(4)	C4—C5	1.408(7)
Re—C8	2.097(4)	C5—C6	1.393(6)
P—O4	1.496(3)	C6—C7	1.388(6)
O2—C1	1.361(5)	C9—C10	1.373(6)
O2—C2	1.391(5)	C9—C14	1.386(6)
O3—C8	1.360(5)	C10—C11	1.390(6)
O3—C9	1.394(5)	C11—C12	1.398(7)
N1—C1	1.322(5)	C12—C13	1.398(6)
N1—C7	1.402(5)	C13—C14	1.378(6)
N2—C8	1.317(5)		
Cl1—Re—Cl2	87.79(4)	O2—C2—C7	107.9(3)
Cl1—Re—Cl3	87.94(3)	C3—C2—C7	123.6(4)
Cl1—Re—O1	99.42(9)	C2—C3—C4	115.7(4)
Cl1—Re—C1	171.2(1)	C3—C4—C5	121.7(4)
Cl1—Re—C8	87.2(1)	C4—C5—C6	122.0(4)
Cl2—Re—Cl3	88.62(3)	C5—C6—C7	115.3(4)
Cl2—Re—O1	101.1(1)	N1—C7—C2	105.2(3)
Cl2—Re—C1	90.4(1)	N1—C7—C6	133.1(4)
Cl2—Re—C8	169.4(1)	C2—C7—C6	121.7(4)
Cl3—Re—O1	168.0(1)	Re—C8—O3	120.4(3)
Cl3—Re—C1	83.4(1)	Re—C8—N2	130.9(3)
Cl3—Re—C8	81.9(1)	O3—C8—N2	108.5(3)
O1—Re—C1	89.4(1)	O3—C9—C10	128.0(4)
O1—Re—C8	88.9(1)	O3—C9—C14	108.6(3)
C1—Re—C8	93.2(1)	C10—C9—C14	123.3(4)
C1—O2—C2	108.2(3)	C9—C10—C11	115.6(4)
C8—O3—C9	107.3(3)	C10—C11—C12	121.5(4)
C1—N1—C7	110.5(3)	C11—C12—C13	122.2(4)
C8—N2—C14	111.4(3)	C12—C13—C14	115.5(4)
Re—C1—O2	117.4(3)	N2—C14—C9	104.1(3)
Re—C1—N1	134.3(3)	N2—C14—C13	134.0(4)
O2—C1—N1	108.2(3)	C9—C14—C13	121.9(4)
O2—C2—C3	128.5(4)		

^a Estimated standard deviations are given in parentheses.

sensitivity of these parameters toward the Lewis acid coordinated by the carbene carbon atom.

Carbene complexes of high-valent rhenium are rare, and to our knowledge the complex **9**-OPPh₃ constitutes the only example of a crystallographically characterized Re(V) N,O-heterocarbene complex. Various Fischer-type carbene complexes have been reported for Re(0)¹⁹ and Re(I).²⁰ In addition, protonation of isocyanides coordinated to electron-rich Re(I) centers leading to aminocarbyne complexes has been demonstrated by Pombeiro.^{7a} In the Re(0) carbonyl complexes of type $\{(\text{CO})_5\text{Re}-\text{Re}(\text{CO})_4[\text{C}(\text{OR})(\text{SiPh}_3)]\}$ Re(0)—C(carbene) dis-

tances of 2.08(5)–2.10(4) Å have been observed for carbenes *trans* to the Re—Re bond. Similar Re—C(carbene) distances are observed in Re(I) complexes in which the carbene ligand is located *trans* to a carbonyl (2.125–

(9) Å for $[(\text{CO})_5\text{ReCOCH}_2\text{CH}_2\text{CH}_2]^+$ ^{20a}). A significant shortening of the Re(I)—C(carbene) bond distance was observed in cyclopentadienyl-substituted complexes with the carbene ligand *cis* to a carbonyl ligand (1.990(5) Å for $\{(\text{C}_5\text{H}_5)\text{Re}(\text{CO})_2[\text{C}(\text{OEt})(\text{Ph})]\}$ ^{20b}).

The two observed Re^V—C(carbene) distances in **9**-OPPh₃ (2.095(4) and 2.097(4) Å; Table 2) fall in the range observed for Fischer carbenes of Re(0) and Re(I). The short Re^V—C distances in **9**-OPPh₃ can be attributed to the smaller atomic radius of the Re(V) center compared to Re(0) and Re(I) and to the previously noted ability of the doubly heteroatom substituted 1,2-dihydrobenzoxazol-2-ylidene ligands in **9**-OPPh₃ not only to act as σ -donors but also to attract some back-bonding from the metal center.²¹

Experimental Section

All operations were performed under an atmosphere of dry argon by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. NMR spectra were recorded on a Bruker AM 250 (250 MHz) instrument. Infrared spectra were taken on a Perkin-Elmer 983 spectrometer. Elemental analyses (C,H,N) were performed at the Freie Universität Berlin on a Vario elemental analyzer. Mass spectra (FAB) were recorded on Finnigan MAT 112 or MAT 711 instruments. 2-(Trimethylsilyloxy)phenyl isocyanide (**1**),¹⁰ 2,6-bis(trimethylsilyloxy)phenyl isocyanide (**2**),⁴ and the rhenium complexes *trans*-[ReCl(N₂)(dppe)₂],⁶ *fac*-[Re(O)Cl₃(PPh₃)₂],¹⁶ *mer*-[ReCl₃(NCCCH₃)(PPh₃)₂],¹³ and *fac*-[Re(O)Cl₃(SMe₂)(OPPh₃)]¹⁷ were synthesized as described in the literature.

trans-[ReCl(1)(dppe)₂] (**3**). A suspension was prepared under argon from *trans*-[ReCl(N₂)(dppe)₂] (0.480 g, 0.460 mmol) and 60 mL of THF. To this was added 0.78 g (4.08 mmol) of **1**. The mixture was heated to reflux under argon, and after 2 days most of the solid had dissolved. Heating was continued for another 6 days, after which a clear greenish yellow solution was obtained. The solvent was removed, yielding a yellow powder. Recrystallization from CHCl₃/THF gave **3** as a microcrystalline yellow powder (0.20 g, 36%). Anal. Calcd for C₆₂H₆₁CINOP₄ReSi (*M_r* = 1209.81): C, 61.55; H, 5.08; N, 1.16. Found: C, 61.38; H, 4.99; N, 1.40. ¹H NMR (250 MHz, C₆D₆): δ 7.4–7.2 (m, 4 H, Ar *H* of **1**), 7.2–6.9 (m, 40 H, Ar *H* of dppe), 2.8–2.5 (m, br, 8 H, CH₂), 1.45 (s, 9 H, SiCH₃). IR (CH₂Cl₂; cm⁻¹): ν 1858 (s, CN). MS (FAB, positive ions; *m/z*, relative intensity): 1209 (M⁺, 3.45), 1018 (M⁺ - 1, 0.85), 811 (M⁺ - dppe, 0.31), 620 (M⁺ - 1 - dppe, 3.94).

trans-[ReCl(CNC₆H₄-2-OH)(dppe)₂] (**4**). Complex **4** was synthesized from 0.480 g of *trans*-[ReCl(N₂)(dppe)₂] and 0.78 g of **1** under conditions identical with those employed for the preparation of **3**, with the exception that dichloromethane was used as solvent. Yield: 0.18 g, 34%. Anal. Calcd for C₅₉H₅₃-CINOP₄Re (*M_r* = 1137.63): C, 62.29; H, 4.70; N, 1.23. Found: C, 62.01; H, 4.59; N, 1.43. ¹H NMR (250 MHz, CDCl₃): δ 7.45–7.25 (m, 4 H, Ar *H* of isocyanide), 7.2–9.9 (m, 40 H, Ar *H* of dppe), 2.8–2.4 (m, br, 8 H, CH₂). IR (CH₂Cl₂; cm⁻¹): ν 1855 (s, CN). MS (FAB, positive ions; *m/z*, relative intensity): 1137 (M⁺, 0.27), 1018 (M⁺ - isocyanide, 2.83), 620 (M⁺ - isocyanide - dppe, 0.80).

trans-[ReCl(CNC₆H₄(OH)₂-2,6)(dppe)₂] (**5**). The synthesis of **5** was carried out in analogy to the preparation of **4** by substituting **1** for 1.1 g (3.9 mmol) of **2**. Yield: 0.14 g, 26%.

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Table 3. Summary of Crystal Structure Data^a

	7·2CHCl ₃	9·OPPh ₃
cryst size, mm	0.80 × 0.52 × 0.15	0.30 × 0.20 × 0.11
formula	C ₄₅ H ₃₇ Cl ₉ NO ₂ Re	C ₃₂ H ₂₅ Cl ₃ N ₂ O ₄ Pre
fw	1175.03	825.10
space group	<i>P</i> 2 ₁ (No. 4)	<i>P</i> 1̄ (No. 2)
<i>a</i> , Å	12.076(5)	11.374(4)
<i>b</i> , Å	16.207(5)	12.497(2)
<i>c</i> , Å	12.385(3)	12.608(3)
α, deg	90.0	66.594(14)
β, deg	101.23(2)	71.37(2)
γ, deg	90.0	80.31(2)
<i>V</i> , Å ³	2378(2)	1556.7(8)
<i>Z</i>	2	2
<i>d</i> _c , g/cm ³	1.641	1.760
<i>d</i> _o , g/cm ³	1.66	1.78
μ _c , cm ⁻¹	32.0	43.0
radiation (λ, Å)		Mo Kα (0.710 73)
data collec temp, °C	-120(2)	-120(2)
2θ range, deg	2 ≤ 2θ ≤ 45	5.0 ≤ 2θ ≤ 50
<i>hkl</i> range	0 ≤ <i>h</i> ≤ 12, 0 ≤ <i>k</i> ≤ 17, -13 ≤ <i>l</i> ≤ 13	0 ≤ <i>h</i> ≤ 13, -14 ≤ <i>k</i> ≤ 14, -12 ≤ <i>l</i> ≤ 13
no. of unique data	3229	5473
no. of obsd data, <i>F</i> _o ² ≥ 3σ(<i>F</i> _o ²)	3111	4547
<i>R</i> , % ^b	3.84	2.19
<i>R</i> _w , % ^b	4.60	2.57
<i>ρ</i> factor ^b	0.08	0.03
GOF ^b	1.150	1.010
no. of variables	531	388
max shift/error	<0.01	<0.01
resid electron dens, e/Å ³	-0.19, 1.86 (near Re)	-0.18, 0.76
abs cor	4 ψ-scans	7 ψ-scans
max, min cor	0.788, 0.999	0.889, 0.999

^a Estimated standard deviations are given in parentheses. ^b See ref 25.

Anal. Calcd for C₅₉H₅₃ClNO₂P₄Re (*M*_r = 1153.63): C, 61.43; H, 4.63; N, 1.21. Found: C, 60.33; H, 4.78; N, 1.73. ¹H NMR (250 MHz, CDCl₃): δ 7.49–6.75 (m, br, 43 H, Ar *H*), 2.65–2.35 (m, br, 8 H, *CH*₂). ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 134.3, 132.6, 128.6, 128.5, 127.6, 127.2 (Ar *C*; only six of the expected resonances were observed, but two of these appeared split), 30.9 (*CH*₂). IR (CH₂Cl₂; cm⁻¹): ν 1862 (s, CN). MS (FAB, positive ions; *m/z*, relative intensity): 1154 (M⁺, 1.65), 1119 (M⁺ – Cl, 2.35), 1020 (M⁺ – isocyanide, 2.51).

trans-[ReCl₂(dppe)₂] (6). After crystallization of complexes 3–5 an additional yellow complex could be isolated from the mother liquor as a THF or CH₂Cl₂ solvate (depending on the solvent used for crystallization) in 5–10% yield relative to *trans*-[ReCl(N₂(dppe)₂]. The CH₂Cl₂ solvate was shown by X-ray crystallography to be the known complex *trans*-[ReCl₂(dppe)₂] (6).¹² Analytical data are for solvent-free 6. Anal. Calcd for C₅₂H₄₈Cl₂P₄Re (*M*_r = 1054): C, 59.20; H, 4.55. Found: C, 60.33; H, 4.88. MS (FAB, positive ions; *m/z*, relative intensity): 1054 (M⁺, 3.45), 1018 (M⁺ – Cl, 4.55), 983 (M⁺ – 2 Cl, 1.33).

fac-[ReCl₃(CNC₆H₄-2-OH)(PPh₃)₂]·2CHCl₃ (7·2CHCl₃). A 250 mL Schlenk flask equipped with a dropping funnel was charged with 0.50 g (0.58 mmol) of *mer*-[ReCl₃(PPh₃)₂-(NCCCH₃)]¹³. Dichloromethane (100 mL) was added under argon. A solution of 0.11 g (0.58 mmol) of 1 in 20 mL of dichloromethane was added slowly *via* the dropping funnel. The reaction mixture was stirred at room temperature for 48 h. After removal of the solvent in vacuo the residue was washed four times with hexane (25 mL each) and dried under vacuum. The product was recrystallized from chloroform, giving the solvate 7·2CHCl₃ as orange-red crystals (0.43 g, 63%). Anal. Calcd for C₄₅H₃₇Cl₉NO₂Re (*M*_r = 1175.03): C, 46.00; H, 3.17; N, 1.19. Found: C, 46.71; H, 3.27; N, 1.31. ¹H NMR (250 MHz, CDCl₃): δ 15.75 (m, Ar *H* of PPh₃), 8.75 (m, Ar *H* of PPh₃), 7.6 (m, 4 H, Ar *H* of isocyanide); OH was not detected. ¹³C{¹H} NMR (62.9 MHz, CDCl₃): δ 138.04, 135.67, 134.75, 133.23, 131.65, 131.32, 128.06, 127.56, 126.53, 124.52 (Ar *C*); the resonance for isocyanide carbon was not detected. IR (KBr; cm⁻¹): ν 3434 (s, OH), 2107 (s, CN). MS (FAB, positive ions; *m/z*, relative intensity): 935 (M⁺, 3.6), 900 (M⁺ – Cl, 4.07), 816 (M⁺ – isocyanide, 1.50).

fac-[Re(O)Cl₃(CNC₆H₄-2-OH)[CN(H)(C₆H₄-2-O)]·OPPh₃ (8·OPPh₃). A 0.23 g (1.2 mmol) amount of 1 was added with a syringe to a suspension of 0.40 g (0.6 mmol) of *fac*-[Re(O)Cl₃(SMe₂)(OPPh₃)]¹⁷ in 50 mL of dichloromethane. The mixture was stirred at room temperature for 3 h, giving a clear blue solution. The solvent was stripped in vacuo, and the greenish blue residue was analyzed. Anal. Calcd for C₃₂H₂₅Cl₃N₂O₄Pre (*M*_r = 825.10): C, 46.58; H, 3.05; N, 3.40. Found: C, 46.41; H, 3.02; N, 3.82. IR (KBr; cm⁻¹): ν 3437 (s, OH), 3230 (s, NH), 2207 (s, CN).

fac-[Re(O)Cl₃[CN(H)C₆H₄-2-O]₂]·OPPh₃ (9·OPPh₃). The entire solid residue from the previous reaction was dissolved in dichloromethane/acetone. Crystallization gave 9·OPPh₃ as bright blue crystals (0.43 g, 85%). Anal. Calcd for C₃₂H₂₅Cl₃N₂O₄Pre (*M*_r = 825.10): C, 46.58; H, 3.05; N, 3.40. Found: C, 46.48; H, 3.11; N, 3.54. ¹H NMR (250 MHz, CDCl₃): δ 8.05 (s, 2 H, *NH*), 7.8 (d, 2 H, Ar *H*), 7.65 (d, 2 H, Ar *H*), 7.55–7.2 (m, 19 H, Ar *H*). IR (KBr; cm⁻¹): ν 3233 (NH). MS (FAB, positive ions; *m/z*, relative intensity): 547 (M⁺, 0.33), 531 (M⁺ – O, 0.12), 511 (M⁺ – Cl, 3.74), 475 (M⁺ – 2 Cl, 2.38), 392 (M⁺ – Cl – isocyanide, 1.14), 356 (M⁺ – 2 Cl – isocyanide, 3.17), 279 (OPPh₃⁺, 100).

Crystal Structure Analyses. Crystals of 7·2CHCl₃ are air-sensitive (loss of solvent), while 9·OPPh₃ is air-stable. A suitable specimen of 7·2CHCl₃ was selected at -120 °C using a device similar to that described by Veith²² and mounted in the cold stream (-120(2) °C) of an Enraf-Nonius CAD-4 diffractometer. A crystal of 9·OPPh₃ was selected in air and mounted at -120(2) °C on an Enraf-Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table 3. Data for both compounds were collected using ω-2θ scans. Raw data were reduced to structure factors²³ (and their esd's) by correcting for scan speed and Lorentz and polarization effects. No crystal decay was detected, and

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absorption corrections based on ψ -scans were applied to the raw data. The space group was found to be $P2_1$ for $7 \cdot 2\text{CHCl}_3$ and $P\bar{1}$ for $9 \cdot \text{OPPh}_3$. Both structures were solved by Patterson methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed almost all hydrogen positions. However, hydrogen atoms were added to the structure models at calculated positions ($d(\text{C}-\text{H}) = 0.95 \text{ \AA}$, $d(\text{N}-\text{H}) = 0.87 \text{ \AA}$)²⁴ and are unrefined. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the B_{eq} value of the parent atom. The positional parameters for the hydrogen atom bound to O in $7 \cdot 2\text{CHCl}_3$ were not determined and could not be calculated. The correct crystallographic enantiomer for $7 \cdot 2\text{CHCl}_3$ was determined by refinement of both possible crystallographic enantiomers and selection of the model giving the better R value as the correct choice. All calculations were carried out with the MolEN package.²⁵ ORTEP²⁶ was used for all molecular drawings.

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Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of positional parameters, all bond distances and angles, and anisotropic thermal parameters and additional ORTEP drawings for **7** and **9** (14 pages). Ordering information is given on any current masthead page.

OM950846P

(25) MolEN: Molecular Structure Solution Procedures. Program Descriptions; Enraf-Nonius, Delft, The Netherlands, 1990. Definition of residuals: $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, $R_w = [\sum w||F_o| - |F_c||^2 / \sum w|F_o|^2]^{1/2}$, and $\text{GOF} = [\sum w|F_o|^2 - |F_c|^2 / (n_o - n_p)]^{1/2}$ with n_o = number of structure factors, n_p = number of parameters, $w = 1/(\sigma_F)^2$, $\sigma_F = \sigma_{F^2}/2F$, and $\sigma_{F^2} = \{[\sigma_j]^2 + [\rho F^2]^2\}^{1/2}$.

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