Chemical Society, for support of this research. V.S.J.d.M. acknowledges a Rumble Fellowship provided by Wayne State University for support of his graduate studies.

Supplementary Material Available: Listings of anisotropic thermal parameters for the heavy atoms, hydrogen atom positional parameters, torsion angles, and least-squares planes and deviations (7 pages); a complete listing of the observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

Organorhenium Imido Complexes: Syntheses, Structure, and Reactivity[1]

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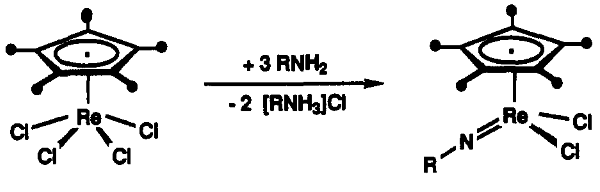
Imido complexes of heptavalent rhenium have been synthesized by three different routes: (i) aminolysis of the half-sandwich complex (η^5-C_5Me_5)$ReCl_4$ (**1**) (Me = CH_3) with primary amines gives the imido derivatives (η^5-C_5Me_5)Re(N^tBu)Cl_2 (**2a**, ^{t}Bu = *tert*-butyl) and (η^5-C_5Me_5)Re(NCH_3)Cl_2 (**2b**). The rhenium–nitrogen distance in compound **2a** (1.709 (3) Å) corresponds to a triple bond (single-crystal X-ray diffraction), while the analogous oxo congener (η^5-C_5Me_5)$ReOCl_2$ has relatively little rhenium–oxygen triple-bond character. (ii) Sequential deoxygenation of methyltrioxorhenium(VII) (**6**) via decarboxylation upon treatment with 2,6-diisopropylphenyl isocyanate yields mono- and dinuclear methylrhenium(VII) imido complexes **7–9** in good yields; imido bridging occurs when the mononuclear compounds of types $CH_3ReO(NR)_2$ (**8a**) and $CH_3Re(NR)_3$ (**9a**) are dissolved in polar solvents such as typically 1,2-dimethoxyethane. (iii) Nucleophilic substitution of Me_3SiO–Re(N^tBu)$_3$ (**10**) by organolithium or Grignard reagents was used to synthesize the new methyl-, allyl-, ethyl-, and phenylalkynyl derivatives R′–Re(N^tBu)$_3$ (R′ = CH_3, **11a**; C_3H_5, **11b**; C_2H_5, **11c**; $C_6H_5C{\equiv}C$, **11d**). These compounds are thermally very robust even though **11b,c** exhibit alkyl groups with β-hydrogen atoms. σ- instead of π-coordination of the allyl ligand of **11b** underlies the strong electron-releasing character of the three imido ligands; this suggests that even π-ligands R′ in compounds of type R′–Re(NR)$_3$ will be only σ-coordinated, in contrast to the oxo congeners R′–ReO_3. [2 + 2] Cycloaddition intermediates can be trapped in the reaction of the oxorhenium(III) alkyne complexes of type (η^5-C_5Me_5)ReO(η^2-RC≡CR) (**3a**, R = CH_3; **3b**, C_6H_5) with phenyl isocyanate to give phenyl carbamidato-*N*,*O* complexes **4a,b** that undergo consecutive decarboxylations and isocyanate addition to yield finally ureato-*N*,*N*′ compounds **5a,b**.

Introduction

We have previously reported on the synthesis, reactivity, and catalytic properties of high-valent rhenium oxo complexes of types R–ReO_3 (R = CH_3,[3] mesityl[4]), Cp^*ReO_3,[5-7] and Cp^*ReOX_2 (X = alkyl, halide).[6,7] To better understand the behavior of multiply bonded ligands in these systems, we have examined synthetic pathways to analogous imido complexes, R–Re(NR′)$_3$, Cp^*Re(NR)$_3$, and Cp^*Re(NR)X_2. In this context, the synthesis of the half-sandwich complex Cp^*Re(N^tBu)Cl_2 (**2a**) via aminolysis of the tetrachloro precursor compound **1** (Scheme I) has recently been communicated in a review article.[7a] Imido complexes of rhenium in high oxidation states are important models and possible catalysts of oxyamination reactions known for osmium(VIII) imido systems.[8] Since related rhenium oxo complexes are effective catalysts in

Scheme I



1 **2a,b**

• = CH_3

a: R = $^tC_4H_9$
b: R = CH_3

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Table I. Selected Bond Distances (picometers) and Bond Angles (degrees) of the Imido Complex **2a**[a]

bond dist		bond angles	
Re–Cl1	238.50 (8)	Cl1–Re–Cl2	124.5
Re–Cl2	237.72 (8)	Cl1–Re–N	102.72 (7)
Re–N	170.9 (3)	Cl1–Re–Cp*	112.5
Re–C11	245.8 (3)	Cl1–Re–Cp	124.5
Re–C12	247.5 (3)	Cl2–Re–N	100.33 (7)
Re–C13	222.3 (3)	Cl2–Re–Cp*	110.5
Re–C14	216.9 (3)	Cl2–Re–Cp	122.9
Re–C15	222.3 (3)	N–Re–Cp*	134.6
Re–Cp*	196.6	N–Re–Cp	114.6
Re–Cp	194.9	Re–N–C1	170.5 (2)
C1–N	146.1 (3)		

[a] Cp* indicates the center of the $C_5(CH_3)_5$ ligand. Cp indicates the center of the allyl ligand.

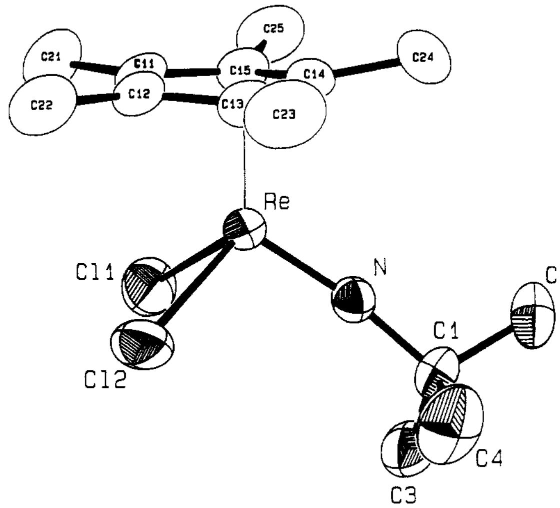


Figure 1. ORTEP drawing of the imidorhenium(V) complex **2a** in the crystal. Thermal ellipsoids are drawn to 50% probability. Hydrogen atoms are omitted for clarity.

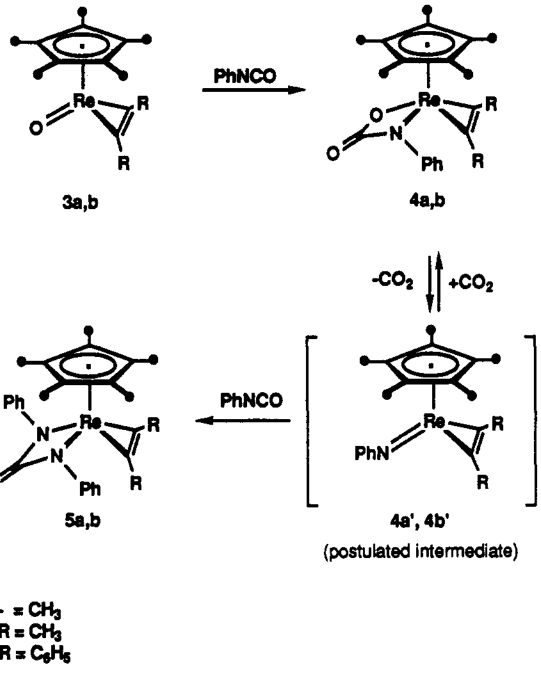
olefin metathesis (functionalized olefins)[3b] as well as for olefin epoxidation,[3b] we have entered the chemistry of the imido congeners. First results are reported in this paper.

Results and Discussion

I. Structure of the Imidorhenium(V) Complex (η^5-C_5Me_5)Re(N^{t}Bu)Cl_2 (2a). As a significant distortion in the η^5-bonded π-ligand η^5-C_5Me_5 is observed in the oxo complex Cp*ReOCl_2,[7a] i.e., an allyl/alkene structure, a more detailed investigation of the structure of the analogous imido complex Cp*Re(N^{t}Bu)Cl_2 was deemed necessary. It proved possible to obtain crystals and perform a single-crystal X-ray diffraction study. This compound crystallizes from tetrahydrofuran/*n*-hexane at −30 °C in the space group *P*2(1)/*n* (*International Tables*, No. 14, cf. Experimental Part). Selected bonding parameters are compiled in Table I.

The triply bonded nature of the imido ligand in this formally 16e$^-$ complex (d^2 Re^V) can clearly been seen in the approximate linearity of Re–N–C unit (Figure 1). It is also apparent in the short Re–N distance (1.709 (3) Å), which can be compared to a Re–O distance of 1.700 (4) Å in Cp*ReOCl_2. In this latter case, like in most other oxorhenium species derived thereof, the rhenium-to-oxygen bond has less triple-bond contribution compared with CH_3ReO_3[9] because the π-bonded C_5Me_5 ligand releases electron density to the metal, thus preferring form A over B. According to ^{17}O NMR and IR results, the σ-alkyl complex CH_3ReO_3 rather approaches form B.[9]

Scheme II



$$L_xM{=}\overline{\underline{O}} \longleftrightarrow L_x\overset{-}{M}{\equiv}\overset{+}{O}|$$

A B

It would be expected that in the structurally similar complexes Cp*ReOCl_2 and Cp*Re(NR)Cl_2, metal–imido bonds would be at least 0.03 Å, the difference in covalent bond lengths between N and O,[10] *longer* than the analogous oxo bonds. A higher bond order close to three is therefore suggested. For comparison, the Re–O distance in Re(O)Cl_3(PEt$_2$Ph)$_2$ of 1.660 (9) Å[11] can be compared to the Re–N distances in Re(NMe)Cl_3(PEtPh$_2$)$_2$ (1.685 (11) Å)[12] and Re(NC_6H_4X)Cl_3(PEt$_2$Ph)$_2$ (X = OMe, 1.709 (4) Å; X = C(O)Me, 1.690 (5) Å).[13]

The shift of the Cp* ring centroid is almost the same as that observed for the analogous oxo complex Cp*ReOCl_2. However, the distances between the metal and the ring (ring centroid, ring normal, center of allyl substructure) in the oxo complex are consistently 0.01 Å longer (Table I). The allyl/alkene structure in the imido complex can be seen in the bending away of the alkene section from what would be the normal ring plane (8.3°). The distortion can also be seen in the unequal bond lengths within the ring (alkene 1.387 (4), allyl 1.448 (4), 1.444 (4) Å). This contrasts with a fold of 9.3° and comparable C–C bond lengths within the ring ligand in the above-mentioned oxo complex.[7a]

Imido groups appear to be better π-donating ligands than oxo groups in complexes with similar structures, e.g., by comparison of infrared stretching frequencies in a series of *trans*-carbonyltungsten complexes,[14] but appear to be

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poorer trans-influencing ligands, e.g., by comparison of bond lengths in trans-configurated chlororhenium complexes.[15] The better π-donating ability appears to manifest itself in the short Re–N bond of Cp*Re(N^{t}Bu)Cl$_2$ (**2a**), while the effect of the trans influence on the metal–ring bonding appears to be less than that observed in the oxo complex.[7a] Reaction of **1** with dimethylamine yields the corresponding imido product (η^5-C$_5$Me$_5$)Re(NCH$_3$)Cl$_2$ (**2b**).

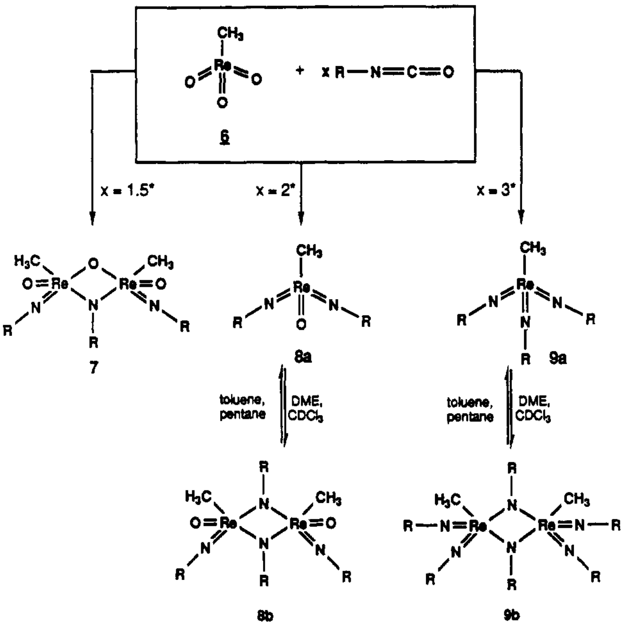
II. (Carbamidato)- and (Ureato)rhenium(III) Complexes. All attempts to cleanly prepare complexes of the form Cp*ReO$_x$(NR)$_{3-x}$ by substitution of oxo ligands utilizing isocyanates, amines, or silylamines have proved fruitless to date. An observation that is perhaps relevant in this context is that reaction of the alkyne complexes Cp*ReO(η^2-RC≡CR) (**3a,b**) with phenyl isocyanate leads first to formation of [2 + 2] cycloaddition products and then to apparent formation of transient imido complexes that are quickly trapped under the reaction conditions (Scheme II).

If R = CH$_3$, then under the reaction conditions (refluxing toluene) separable mixtures of the carbamidato-*N,O* complex **4a** and ureato-*N,N′* complex **5a** are obtained. Heating the carbamidato complex **4a** in the *absence* of excess isocyanate leads to decomposition at much higher temperatures (ca. 180 °C). This reactivity implies that the postulated imido intermediate must react with CO$_2$ in reverse of its formation very efficiently. It is, perhaps, an indication that the ability of the imido ligand for forming a triple bond is reduced, and its reactivity correspondingly enhanced, by the highly electron donating ligand set at rhenium. The alkynes are 4e$^-$ ligands in the (formally Re^{III}) oxo starting compounds **3a,b**. Invocation of imido intermediates **4a′,b′** assumes a dissociative mechanism, which is difficult to test due to the long reaction times and competing decomposition reactions. An associative mechanism could be occurring, also. However, cycloreversion (retro[2 + 2] addition) would appear the simpler option, one that could potentially be tested by using labeled CO$_2$. Compounds **4** and **5** show rapid rotation of the alkyne ligands that could not be frozen out at the NMR time scale at low temperatures (−80 °C).

Two major pathways to complexes of the form CH$_3$ReO$_x$(NR)$_{3-x}$, i.e., alkyl substitution on a preformed rhenium trisimido fragment or oxo substitution in an alkyl trisoxo complex, have been explored. Oxo substitution via reaction of methyltrioxorhenium(VII) with isocyanates occurs with CO$_2$ loss, presumably via carbamidato complexes of the type isolated upon reaction of phenyl isocyanate with Cp*ReO(η^2-RC≡CR) (**3a,b**, see Scheme II). The nature of the resultant imido complexes is outlined below.

III. Alkylrhenium(VII) Imido Complexes. If an equimolar mixture of **6** and phenyl isocyanate are reacted in refluxing 1,2-dimethoxyethane (DME) for 3 h, a change from colorless to red is observed with concomitant gas evolution. The EI mass spectrum of the isolated product displays a molecular ion at *m/z* 325 and a fragmentation pattern consistent with the new monoimido complex CH$_3$ReO$_2$(NPh). However, further isolation and characterization proved difficult due to the extreme sensitivity of the complex toward hydrolysis. Trace amounts of water cause formation of the aniline adduct CH$_3$ReO$_3$·H$_2$NC$_6$H$_5$. This base adduct can be prepared directly from **6** and aniline and has been isolated and structurally fully characterized.[9a]

Scheme III[a]



[a] R = 2,6-Diisopropylphenyl. Asterisk: 1,2-Dimethoxyethane (DME) as solvent (see text).

(1) Imido Derivatives of Methyltrioxorhenium(VII) (6). In an attempt to prepare more stable complexes by utilizing more sterically demanding ligands, **6** was reacted with 2,6-diisopropylphenyl isocyanate (DIPP–NCO) in differing stoichiometries, as shown in Scheme III.

(a) Reaction of CH$_3$ReO$_3$ (**6**) with 1 equiv of DIPP–NCO in refluxing 1,2-dimethoxyethane (DME) yields a complex with the formula CH$_3$ReO$_2$(N–DIPP). The ^{17}O NMR spectrum of this complex indicates a monomeric structure with two chemically equivalent terminal oxo ligands (δ(^{17}O) 788 in CDCl$_3$). However, it is difficult to isolate the complex analytically pure as more highly substituted products are also present.

(b) If 1.5 equiv of the isocyanate is used under otherwise the same conditions, dimeric complex **7** is obtained. Terminal (ν(ReO) = 948 cm^{-1}) and bridging oxo groups (ν(ReO) = 661 cm^{-1}) are seen in the infrared spectra of this complex. Two rhenium-bonded methyl groups are observed in the ^{1}H NMR spectrum, as well as two sets of isopropyl signals. This dimer *is not* observed to cleave to a mixture of monomers upon standing in polar or nonpolar solvents.

(c) Reaction with 2 equiv of DIPP–NCO in refluxing DME leads to the dinuclear bis(imido) complex **8b** in isolated yields of 85–95%. Bridging and terminal imido ligands can be observed in the ^{1}H NMR spectrum, as well as a terminal oxo band in the infrared spectrum (934 cm^{-1}, KBr). Upon standing in diethyl ether/*n*-pentane mixtures, the dimer cleaves to the monomeric species **8a**.

(d) Finally, reaction with 3 equiv of DIPP–NCO in refluxing DME yields the dinuclear tris(imido) complex **9b**. This purple complex can be isolated in 90% yield. Upon standing in diethyl ether/*n*-pentane mixtures, this complex cleaves to the monomeric species **9a**. The monomer can be directly obtained from CH$_3$ReO$_3$ **6** and the isocyanate in boiling *toluene* as a purple, crystalline complex in 80–90% yield (Scheme III). Interruption of the reaction in boiling DME after short reaction times leads also to isolation of the monomeric species **9a**. These observations come to the (unexpected, tentative) conclusion that *the monomer **9a** converts to dimer **9b** in the more polar sol-*

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[14] Nugent, W. A.; Mayer, J. M. *Metal–Ligand Multiple Bonds*; Wiley: New York, 1988.

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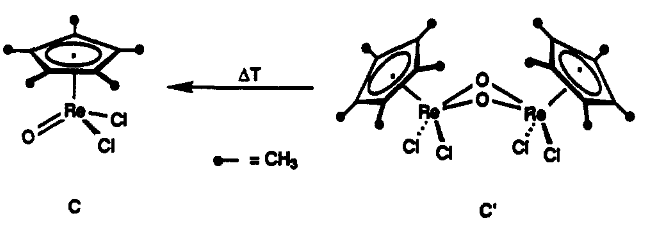
Scheme IV



Scheme V

$$Re_2O_7 + (Me_3Si)_2O \xrightarrow{\Delta} 2\ Me_3SiO\text{-}ReO_3$$

$$\left.\begin{array}{c} Me_3SiO\text{-}ReO_3 \\ + \\ (Me_3Si)NH(^tBu) \end{array}\right\} \xrightarrow{(Me_3Si)_2O} \underset{10}{Me_3SiO\text{-}Re(N^tBu)_3}$$

$$\underset{10}{Me_3SiO\text{-}Re(N^tBu)_3} + R^- \longrightarrow \underset{11a\text{-}d}{R\text{-}Re(N^tBu)_3}$$

vent since other effects (temperature, time) have been ruled out experimentally.

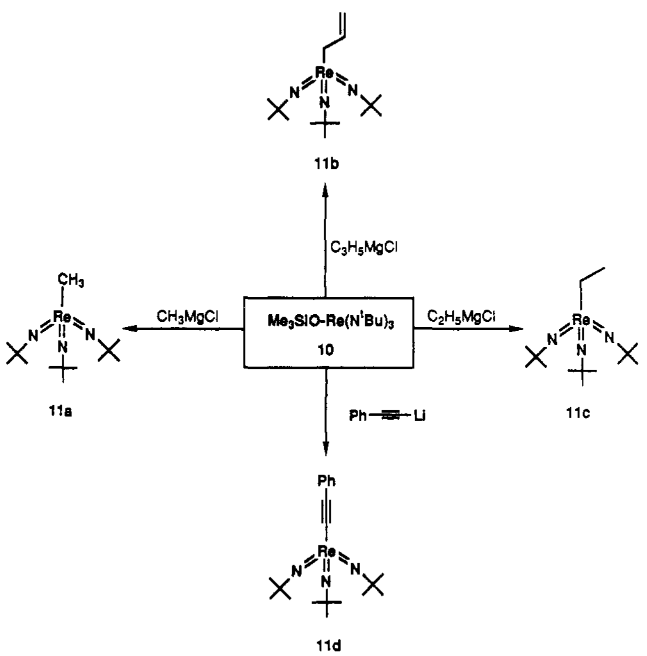
Stepwise substitution of oxo ligands utilizing aryl isocyanates in the silylperrhenate $Me_3SiOReO_3$ has previously been observed.[16] Dimer formation was also observed in this system but was proposed to occur by condensation of the $ReOSiMe_3$ groups to form an oxo bridge and 1 equiv of $(Me_3Si)_2O$. This dimerization process is much different from the apparent dependence of the aggregation state of the resulting imido complexes on the method of preparation in the $CH_3ReO_x(N\text{–}DIPP)_{3-x}$ system.

The factors controlling bridging vs terminal structures comprise a general, fundamentally interesting question in the chemistry of multiply bonded ligands. We have previously observed, for example, that Cp^*ReOCl_2 (C, Scheme IV) prepared by hydrolysis of Cp^*ReCl_4 (1) in the presence of pyridine, is monomeric,[6,7a] while reaction of $[Cp^*ReO_2]_2$ with $MgCl_2$ yields dimeric $[Cp^*ReOCl_2]_2$ (C′), a complex with bridging oxo groups.[17,18,26] Heating of the dinuclear species leads to cleavage of the bridges and formation of the monomeric species. We have also observed this phenomenon with the isocyanate rhenium(V) complex $Cp^*ReO(NCO)_2$ (NCO instead of Cl in formulas C and C′).[1]

The observed solvent dependence in methylrhenium(VII) complexes of the bulky imido ligand used here is obviously due to a relatively low barrier between the monomeric and dimeric forms. In such a case, the equilibrium between them could be shifted rather easily by small effects such as differences in dipole-induced solvent ordering, etc. The dinuclear compounds **7**, **8b**, and **9b** show two methyl resonances in the ^1H NMR spectra since the symmetry is distorted due to conformational requirements of the imido isopropyl groups.

(2) Imido Complexes of Type R–Re(NR′)$_3$. The only monomeric tris(imido)rhenium complexes, R–Re(NR′)$_3$, have been prepared by Schrock et al. (R = CH_2CMe_3;[19] R′ = ^tBu,[19] R′ = DIPP[20]) and Wilkinson et al. (R = aryl, R′ = ^tBu)[21] by a different route: reaction of $Me_3SiORe(NR')_3$ with alkyl- or aryl-transfer reagents of lithium and magnesium. The reaction sequence for the *tert*-butylimido complexes as employed by these authors is illustrated in Scheme V.

Scheme VI



Only *alkyl groups without β-hydrogen atoms* have so far been attached to the rhenium(VII) in these complexes.[21-23] We have used the same reaction sequence to prepare the imido analogue **11a** of CH_3ReO_3 as well as to prepare the other simple alkylrhenium(VII) imides **11b–d**.

Reaction of **10**[22] with Grignard reagent or with methyllithium leads to clean formation of $CH_3Re(N^tBu)_3$ (**11a**, 79% isolated yield), a distillable, golden-yellow liquid at room temperature (Scheme VI).

The proton NMR spectra (1.80 ppm, 3 H; 1.36 ppm, 27 H (C_6D_6)) and the electron impact mass spectra (parent ion at m/z = 415) are consistent with the proposed structure. The ^{13}C NMR shift difference between the α- and β-carbons in the *tert*-butyl groups ($\Delta\delta \approx 36$ ppm) indicates a very high amount of nucleophilic character in the imido ligands. This occurs because not all three imido ligands simultaneously can form formal triple bonds to the metal center.[23] This value can be compared to the ca. 45 ppm shift difference observed in $Cp^*Re(\equiv N^tBu)Cl_2$ (**2**, Experimental Part). A ^{13}C NMR shift difference of less than 50 ppm has been shown to correlate with the reactivity of the imido ligands toward reaction with benzophenone to yield an oxo complex and the corresponding Schiff base.[14] Enhanced nucleophilicity should also enhance the susceptibility to protonation. A practical consequence of this drive to reduce the electron density on the metal center is that all of these alkylimido complexes are *extremely sensitive to hydrolysis*. They are completely stable in the presence of dry oxygen.

These formally $14e^-$ imido complexes appear to be electronically saturated, e.g., they do not react with donor ligands to make base adducts as is observed and thoroughly studied for the parent compound CH_3ReO_3.[24] As a matter

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of fact, electronic saturation at the rhenium in terms of the noble-gas rule may be provided by the electron-donating character (π-bonds) of the imido groups. In addition, reaction with allyl Grignard leads to formation of the new compound (η^1-C_3H_5)Re(N^tBu)$_3$ (**11b**, Scheme VI), which is obtained as a thermally stable, gold-colored oil at room temperature. The *monodentate* nature of the allyl ligand is clearly shown by the observed $ABCM_2$ coupling pattern (J_{A-B} = 1.2, J_{A-C} = 17.1, J_{B-C} = 10.4, J_{M-C} = 7.8 Hz) in ^1H NMR spectrum, as well as in the three ^{13}C NMR shifts of the allyl group (Experimental Part).

Surprising in light of all previous efforts to prepare β-H containing alkyl complexes of high-valent rhenium, reaction of **10** with ethyl Grignard yields the ethyl complex **11c** cleanly and in high yield (Scheme V). The compound is obtained as a light yellow, distillable oil at room temperature. The presence of the ethyl group is given proof by the ^1H and ^{13}C NMR spectra as well as by the mass spectra (m/z = 429; parent ion, ^{187}Re).

Reaction of the siloxy complex **10** with Ph—C≡CLi yields, after sublimation, pure σ-acetylide complex **11d**. This complex could be recrystallized at −40 °C from hexamethyldisiloxane, and the resultant waxy yellow–orange crystals of **11d** handled at room temperature. The lack of an appreciable change in the ^{13}C shift difference between the α- and β-carbons in the *tert*-butyl groups of the imido ligands ($\Delta\delta \approx 38$ ppm) and the ν(C═C) of 2116.3 cm^{-1} (cf. 2120 cm^{-1} in H—C≡C—Ph) in the infrared spectra would appear to indicate that back-bonding into the acetylide ligand is not important in this complex. These data prove also the σ-coordination of the ligand to the metal atom (Scheme V).

An interesting feature in the mass spectra of these imido complexes is that loss of a methyl group from an imido ligand is a very favorable process. Even though an M^+ parent ion is observed, in all cases the base peak is $[M - CH_3]^+$. Surprisingly, no evidence of β-elimination to yield a hydride was observed in the mass spectra of the *ethyl* complex.

Concluding Remarks

All attempts to synthesize a half-sandwich complex via reaction of the easily available siloxy complex **10** with a cyclopentadienyl (Na, Tl, $SnBu_3$) or pentamethylcyclopentadienyl source (K, MgCl, Li) have failed.[35] In most cases no reaction occurs. It may, therefore, be true that the ring-transfer reagents are too bulky for reaction with the highly sterically hindered starting material. However, the observed σ- instead of π-bonding in the allyl complex implies that the ring in such a half-sandwich trisimido complex would not be pentacoordinated. The results using preformed half-sandwich fragments also seem to indicate that it is difficult to reconcile polyhapto ligands with the highly electron-donating imido ligands on these high-valent rhenium centers. A recent theoretical study comes to the conclusion that the ·ReO_3 fragment is isoelectronic with ·CH_3 and suggests that π-bonding to yield half-sandwich complexes is not very favorable.[25] Our experimental results show that the highly electron donating imido ligands accentuate this tendency. This theoretical study also implies that a strong σ-bond should form, consistent with the observed stability of the metal–carbon bond in organorhenium(VII) compounds of type R–Re(═X)$_3$ (X = O, NR). To further verify these statements, we are attempting the synthesis of (allyl)ReO_3 and similar compounds containing potentially π-coordinating ligands.

In summary, we have synthesized and structurally characterized a half-sandwich organorhenium(VII) imide, Cp*Re(≡N^tBu)Cl_2 (**2a**), which compound has allowed a detailed comparison with the analogous oxo complex Cp*Re(═O)Cl_2. The differences between these two closely related compounds appear to be consistent with the differences in π-donating ability and trans influence of the two multiply bonded ligands. Furthermore, methyltrioxorhenium(VII) was reacted with bulky aryl isocyanates, giving rise to *sequential substitution* of the oxo ligands. A surprising solvent dependence of the aggregation state, monomer vs dimer, was observed for these complexes. We have utilized the preformed trisimido species, Me_3SiO–Re(N^tBu)$_3$ (**10**), to synthesize simple trisimido complexes such as $CH_3Re(NR)_3$ (**11a**), the first β-H-containing derivative $C_2H_5Re(NR)_3$ (**11c**), and the σ-allyl complex (η^1-C_3H_5)Re(NR)$_3$ (**11b**, R = $^tC_4H_9$). We rationalize much of the chemistry of these tetrahedral rhenium complexes by invoking a strong metal–carbon σ-bond and by considering the different π-donating abilities of the multiply bonded oxo and imido ligands.

Experimental Part

All manipulations were undertaken utilizing standard Schlenk techniques under N_2. Solvents were dried under N_2 by standard methods and stored over Davison 4-Å molecular sieves. Infrared spectra were recorded as thin films between KBr plates or in KBr pellets with a Nicolet FT-5DX instrument and are reported in cm^{-1}. JEOL-JNM-GX400 and GX-270 spectrometers were used for ^1H and ^{13}C NMR spectroscopy. (If not otherwise noted, the spectra were taken from $CDCl_3$ solutions at room temperature and referenced to internal solvent. All J values are reported in hertz.) Mass spectra were recorded by using a Varian MAT 311-A instrument (EI and FD spectra) and with a Varian MAT FS-90 instrument (CI spectra); m/z values are reported for ^{187}Re, normal $^{185,187}Re$ isotope distributions observed. Microanalysis were obtained from our Microanalytical Laboratory. Starting compounds Cp*$ReCl_4$ (**1**),[26] Cp*ReO(η^2-R—C≡C—R) (**3a,b**),[27] CH_3ReO_3 (**6**),[3,24] and Me_3SiO–Re(N^tBu)$_3$ (**10**)[22] were prepared as reported in the literature. For column chromatography, silylated silica (heated under a high vacuum for several days) was used (Merck no. 7719; 0.063–0.200 mm). Abbreviations are as follows: Me = CH_3, Et = C_2H_5, Ph = C_6H_5, ^tBu = *tert*-butyl, Cp* = $C_5(CH_3)_5$.

(*tert*-Butylimido)dichloro(η^5-pentamethylcyclopentadienyl)rhenium(V) (2a). (η^5-C_5Me_5)$ReCl_4$ (**1**, 225 mg, 0.49 mmol) was added as a solid to a solution of *tert*-butylamine (1.50 g, 20.5 mmol) in 5 cm^3 of toluene at room temperature. A dirty green solution formed from which a colorless solid separated. After filtration, the solvent was removed in vacuo to leave a dark brown oil, which was extracted with *n*-pentane (2 × 3 cm^3). The olive-green residue was then recrystallized repeatedly from tetrahydrofuran/*n*-hexane (1/4) at ca. −30 °C to give blue–green, well-shaped crystals: yield 125 mg (56%); ^1H NMR (270 MHz, C_6D_6, 28 °C) δ 1.83 (s, 15 H, C_5Me_5), 1.18 [s, 9 H, $(CH_3)_3C$]; ^{13}C NMR δ 107.9 (s, C_5Me_5), 76.0 (s, Me_3C), 31.4 (q, Me_3C), 12.7 (q, C_5Me_5); IR (KBr, cm^{-1}) 1249 s (Me_3C), 338 and 332 m (ν(ReCl)); EI-MS (90 °C, 70 eV) M^+ 463 (rel intensity 21), $[M - C_4H_8]^+$ 407 (100), $[M - C_4H_{11}N]^+$ 390 (20%), $[M - C_4H_9 - Cl]^+$ 371 (65), $[M - C_4H_{11}N - Cl]^+$ 354 (24%). Anal. Found: C, 36.3; H, 5.3; Cl, 15.0; N, 3.0; Re, 40.3. Calcd for $C_{14}H_{24}Cl_2NRe$ (463.46): C, 36.3; H, 5.2; Cl, 15.3; N, 3.0; Re, 40.2.

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Dichloro(methylimido)(η^5-pentamethylcyclopentadienyl)rhenium(V) (2b).[36] Methylamine is condensed at -30 °C into a solution of 200 mg (0.43 mmol) of 1 in 10 cm^3 of tetrahydrofuran. The sample is allowed to warm to room temperature. During this period (30 min) a change from violet to dark green is observed. After filtration, the solvent is removed from the filtrate in vacuo, and a brown-green powder is isolated. The compound is purified by column chromatography at -30 °C, whereby **2b** is eluated with diethyl ether/tetrahydrofuran (1 + 1 vol/vol) as a dark-green zone. After removal of the solvent in vacuo, the green residue was recrystallized from *n*-hexane/tetrahydrofuran (1 + 5 vol/vol), yielding 120 mg (65%) of **2b** as green needles: ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 2.08 (s, 15 H), 2.17 (s, 3 H); ^{13}C NMR δ 107.6 (s), 56.18 (q), 12.14 (q); EI-MS (110 °C, 70 eV) M$^+$ 421 (rel. intensity 52), [M - CH_3N - Cl]$^+$ 354 (100). Anal. Found: C, 31.32; H, 4.38; N, 3.17. Calcd for $C_{11}H_{18}Cl_2NRe$ (421.38): C, 31.35; H, 4.31; N, 3.32.

[η^2-Butyne-2](η^5-pentamethylcyclopentadienyl)(*N*-phenylcarbamato-*N*,*O*)rhenium(III) (4a). Cp*Re(η^2-MeC≡CMe)O (**3a**, 200 mg, 0.5 mmol) was dissolved in 1 cm^3 of freshly distilled, dry, degassed phenyl isocyanate. The resultant red-brown solution was diluted with 10 cm^3 of *n*-octane and brought to reflux. The reaction temperature was held between 120 and 130 °C for 12 h, after which time the reaction mixture was cooled to room temperature. All volatiles were then removed in vacuo (oil pump). The oily brown residue was extracted several times at -78 °C with cold *n*-hexane (ca. 25 cm^3). The *n*-hexane extracts were discarded. The resultant residue was dissolved in 5 cm^3 of CH_2Cl_2 and filtered through 2-3 g of silylated SiO_2 (Merck, 0.063-0.200 mm). The solvent was then removed in vacuo. The fine, red-brown powder obtained could be chromatographed on silylated SiO_2 (packed in *n*-hexane; *l* = 40 cm, Φ = 1.5 cm) at -25 °C. A small amount of a yellow, rhenium-free organic product is obtained upon elution with *n*-hexane. Elution with a *n*-hexane/CH_2Cl_2 mixture (10/1 to 10/2) yields a red-orange zone containing the ureato complex **5a** (75 mg, 25%). Elution with hexane/CH_2Cl_2 (2/1) yields an uncharacterized mixture of rhenium-containing products (60 mg). The carbamidato complex **4a** is obtained as a red zone upon elution with *n*-hexane/CH_2Cl_2/$(C_2H_5)_2O$ (1/1/1). **4a** is obtained contaminated with the ureato complex **5a** and must be chromatographed a second time under the above-described conditions. Yield 95 mg (37%) of the analytically pure carbamidato complex **4a** after recrystallization from *n*-hexane/diethyl ether; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 7.05 (m, 2 H, C_6H_5), 6.98 (m, 2 H, C_6H_5), 6.83 (m, 1 H, C_6H_5), 3.12 (s, 6 H, ≡CCH_3), 1.82 (s, 15 H, $C_5(CH_3)_5$); ^{13}C NMR δ 210.1 (q, $^2J_{C-H}$ = 2.5, ≡CCH_3), 175.1 (s, C=O), δ 146.7 (t, $^2J_{C-H}$ = 4, C_6H_5), 128.1 (m, C_6H_5), 123.5 (m, C_6H_5), 121.6 (m, C_6H_5), 105.2 (s, C_5Me_5), 18.8 (q, $^1H_{C-H}$ = 129, ≡CCH_3), 10.7 (q, $^1J_{C-H}$ = 128, $C_5(CH_3)_5$); IR (KBr) ν(C-H) 3066 w, 3020 w, 2964 m, 2911 s, 2862 m; ν(C=C) 1693 vs; ν(CO) = 1670 vs; ν(C=C) 1593 w; δ(C-H) 1487 s, 1453 s; ν(CMe-CMe) 1378 s; ν(CN) 1319 vs; δ(=C—H) 792 s, 758 s, 734 s, 695 s, 672 s; EI-MS (70 eV) M$^+$ 511 (0.1), [M - CO_2]$^+$ 467 (100), [M - CO_2 - C_4H_8]$^+$ 411 (44), [M - C_6H_5NCO]$^+$ 392 (12), [M - CO_2 - C_4H_6 - C_6H_5]$^+$ 336 (7); CI-MS (isobutene) [M + H]$^+$ 512 (9), [M + H - HCO_2]$^+$ 467 (46), [M + H - HCO_2 - C_4H_8]$^+$ 411 (10), [M + H - C_6H_5NCO]$^+$ 393 7 (3). Anal. Found: C, 49.92; H, 5.32; N, 2.99. Calcd for $C_{21}H_{26}NO_2Re$ (510.65): C, 49.39; H, 5.13; N, 2.74. Compound **4b** is synthesized analogously.[28]

(η^2-Diphenylethyne)(η^5-pentamethylcyclopentadienyl)(*N*,*N'*-diphenylureato-*N*,*N'*)rhenium(III) (5b). Cp*Re(η^2-PhC≡CPh)O (**3b**, 260 mg, 0.5 mmol) was dissolved in 2 cm^3 of freshly distilled, dry, degassed phenyl isocyanate. The resultant red-brown solution was diluted with 10 cm^3 of *n*-octane and brought to reflux. The reaction was carried out as described for the carbamidato complex **4a** (see above). The crude product mixture was separated by column chromatography. A yellow zone containing a small amount of a rhenium-free organic compound was first eluted with *n*-hexane. A red-orange zone containing the ureato complex **5b** was obtained upon elution with *n*-hexane/CH_2Cl_2 (10/1 to 10/2). The carbamidato complex **4b** was obtained as a yellow-orange zone (85 mg, 27%) upon elution with *n*-hexane/CH_2Cl_2/$(C_2H_5)_2O$ (1/1/1). The carbamidato complex is obtained contaminated with the ureato complex and must be chromatographed a second time under the above-described conditions; yield 125 mg (35%) of analytically pure **4b** after recrystallization from *n*-hexane/diethyl ether; ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C) δ 7.62 (m, 4 H, C_6H_5), 7.42 (m, 4 H, C_6H_5), 7.36 (m, 6 H, C_6H_5), 7.12 (m, 4 H, C_6H_5), 6.81 (m, 2 H, C_6H_5), 1.74 (s, 15 H, $C_5(CH_3)_5$); ^{13}C NMR δ 205.2 (s, ≡CPh), 160.5 (s, CO), 145.7 (t, $^2J_{C-H}$ = 4, C_6H_5), 128.5 (m, C_6H_5), 124.3 (m, C_6H_5), 122.1 (m, C_6H_5), 101.2 (s, C_5Me_5), 9.8 (q, $^1J_{C-H}$ = 128, $C_5(CH_3)_5$); IR (KBr) ν(CH) 3065 w, 3022 w, 2963 m, 2927 s, 2853 m; ν(CO) 1642 vs; ν(C=C) 1594 vs; ν(CN) 1309 vs; δ (=C—H) 768 sh, 753 s, 693 s; EI-MS (70 eV) M$^+$ 710 (6), [M - C_6H_5NCO]$^+$ 591 (100), [M - C_6H_5NCO - $C_{14}H_{10}$]$^+$ 413 (4), [M - C_6H_5NCO - $C_{14}H_{12}$]$^+$ 411 (10). Anal. Found: C, 62.06; H, 4.95; N, 4.33. Calcd for $C_{37}H_{35}N_2ORe$ (709.91): C, 62.60; H, 4.97; N, 3.95. Compound **5a** is synthesized analogously.[28]

Tris(*tert*-butylimido)methylrhenium(VII) (11a). To a solution of **10** (166 mg, 0.34 mmol) in 5 cm^3 of freshly distilled THF at -78 °C was added dropwise CH_3MgCl as a 3.0 M solution in THF (0.13 mL, 0.38 mmol) with stirring. The solution was allowed to warm to 30 °C and stirred 10 h. Volatile components were then removed in vacuo. The residue was extracted with *n*-pentane. The filtered extract was then concentrated in a high vacuum, and the resultant yellow oil was subsequently short-path distilled under high vacuum. The resultant bright golden oil crystallized upon cooling below ca. 0 °C; yield 111 mg (79%); ^{1}H NMR (400 MHz, 23 °C, C_6D_6) δ 1.80 (s, 3 H, CH_3), 1.36 (s, 27 H, $C(CH_3)_3$); ^{13}C NMR (C_6D_6) δ 68.02 (s, CMe_3), 31.75 (q, $^1J_{C-H}$ = 126, $C(CH_3)_3$), -6.08 (q, $^1J_{C-H}$ = 132, Re-CH_3); IR (thin film, KBr plates) 2968 s, 2921 m, 2896 w, 2862 w, 1452 w, 1357 m, 1230 s, 1212 s, 1133 m, 918 m, 806 m, 669 m, 596 m; EI-MS (70 eV) M$^+$ 415 (14), [M - CH_3]$^+$ 400 (100), [M - C_4H_9]$^+$ 359 (11). Anal. Found: C, 37.28; H, 7.26; N, 10.05. Calcd for $C_{13}H_{30}N_3Re$ (414.2): C, 37.66; H, 7.24; N, 10.14.

Tris(*tert*-butylimido)ethylrhenium(VII) (11c). To a solution of **10** (193 mg, 0.39 mmol) in 5 cm^3 of freshly distilled THF at -78 °C was added dropwise C_2H_5MgCl as a 2.0 M solution in THF (0.22 mL, 0.43 mmol) with stirring. The solution was allowed to warm to 30 °C and stirred for 10 h. Volatile components were then removed in vacuo, and the residue was extracted with *n*-pentane. The filtered extract was then concentrated in vacuo, and the resultant yellow oil short-path distilled under high vacuum. The resultant bright golden oil crystallized upon cooling below ca. -20 °C; yield 120 mg (70%); ^{1}H NMR (400 MHz, 23 °C, C_6D_6) δ 2.92 (q, 2 H, $^3J_{H-H}$ = 7.32, CH_2CH_3), 1.98 (t, 3 H, $^3J_{H-H}$ = 7.32, CH_2CH_3), 1.36 (s, 27 H); ^{13}C NMR (C_6D_6) δ 68.15 (s, CMe_3), 31.82 (q, $^1J_{C-H}$ = 127, $C(CH_3)_3$), 15.35 (t, $^1J_{C-H}$ = 128, CH_2CH_3), δ 24.26 (q, $^1J_{C-H}$ = 125, CH_2CH_3); IR (thin film, KBr plates) 2970 s, 2925 m, 2897 w, 2858 m, 1452 m, 1358 m, 1230 s, 1212 s, 1132 m, 913 m, 841 m, 806 m, 597 m, 490 m; EI-MS (70 eV) M$^+$ 429 (15), [M - CH_3]$^+$ 414 (100), [M - NC_4H_9]$^+$ 358 (11). Anal. Found: C, 38.64; H, 7.48; N, 9.54. Calcd for $C_{14}H_{32}N_3Re$ (428.2): C, 39.23; H, 7.47; N, 9.81. Due to the oil consistency of the material, satisfactory carbon analysis could not be obtained.

Tris(*tert*-butylimido)(η^1-2-propenyl)rhenium(VII) (11b). To a solution of **10** (201 mg, 0.41 mmol) in 10 cm^3 of freshly distilled THF at -78 °C was added dropwise C_3H_5MgCl as a 2.0 M solution in THF (0.23 mL, 0.46 mmol) with stirring. The solution was allowed to warm to 30 °C and stirred for 10 h. Volatile components were then removed in vacuo, and the residue was extracted with *n*-pentane. The filtered extract was then concentrated in vacuo, and the resultant yellow oil short-path distilled under high vacuum. The product is a bright yellow "semisolid" at room temperature; yield 145 mg (80%); ^{1}H NMR (400 MHz, 23 °C, C_6D_6) δ 6.35 (ddt, 1 H, CH_2CH=CH_2) 4.94 (dd, 1 H, $^3J_{H-H}$ = 17.1, $^4J_{H-H}$ = 1.2, CH_2CH=CH_2), δ 4.74 (dd, 1 H, $^2J_{H-H}$ = 10.4, $^4J_{H-H}$ = 1.2, CH_2CH=CH_2), 3.55 (d, 2 H, $^3J_{H-H}$ = 7.9, CH_2CH=CH_2), 1.36 (s, 27 H); ^{13}C NMR (C_6D_6) δ 68.52 (s, CMe_3), 31.56 (q, $^1J_{C-H}$ = 126.7, $C(CH_3)_3$), 24.57 (t, $^1J_{C-H}$ = 133, CH_2CH=CH_2), 145.78 (d, $^1J_{C-H}$ = 151, CH_2CH=CH_2), 111.61 (t, $^1J_{C-H}$ = 155.3, CH_2CH=CH_2); IR (thin film, KBr plates) 2968 s, 2943 w, 2921 m, 2898 w, 2861 w, 1452 m, 1357 m, 1230 s, 1210 s, 1132 m, 1025 w, 914 m, 883 w, 840 m, 805 m, 599 m, 489 m; EI-MS (70 eV) M$^+$ 441 (36), [M - CH_3]$^+$ 426 (100), [M - C_4H_9]$^+$ 385 (7), [M - NC_4H_9]$^+$ 370 (6). Anal. Found: C, 39.38; H, 7.45; N, 9.32. Calcd for $C_{15}H_{32}N_3Re$ (440.2): C, 40.89; H, 7.27; N, 9.54.

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(28) Fischer, R. A. Ph.D. Thesis, Technische Universität München, Germany, 1989; page 156.

Due to the oily consistency of the material, satisfactory carbon analysis could not be obtained.

Tris(*tert*-butylimido)(η^1-phenylacetylenyl)rhenium(VII) (11d). To a mixture of **10** (550 mg, 1.13 mmol) and PhC≡CLi (134 mg, 1.24 mmol) at −78 °C was added 20 cm^3 of freshly distilled THF. The resultant solution was allowed to warm to 30 °C and stirred for 10 h. Volatile components were then removed in vacuo, and the residue was extracted with *n*-pentane. The filtered extract was then evaporated in vacuo to dryness. The resultant orange wax was sublimed to a liquid nitrogen cooled probe under high vacuum. The orange sublimate was recrystallized from 3–4 cm^3 of $(Me_3Si)_2O$ at −40 °C to yield waxy orange crystals stable at room temperature; yield 491 mg (87%); ^{1}H NMR (400 MHz, 23 °C, C_6D_6) δ 7.44 (m, 2 H, C_6H_6), 6.84 (m, 3 H, C_6H_6), 1.39 (s, 27 H); ^{13}C NMR (100 MHz, 23 °C, THF-d_8) δ 70.02 (CMe_3), 31.72 (q, $^1J_{C\text{-}H}$ = 127, $C(CH_3)_3$), 106.28 (s, br, ReC≡CPh), 125.59 (t, $^3J_{C\text{-}H}$ = 4.6, ReC≡CPh), 124.11 (m, $^2J_{C\text{-}H}$ = 7.3, *C*-1 in C_6H_5), δ 132.03 (d of mult, $^1J_{C\text{-}H}$ = 162.5, C_6H_5), 128.59 (d of mult, $^1J_{C\text{-}H}$ = ca. 161), 128.47 (d of mult, $^1J_{C\text{-}H}$ = ca. 161, C_6H_5); IR (KBr) 2962 s, 2921 m, 2852 m, 2116 m, 1357 m, 1230 s, 1204 s, 1125 m, 1026 m, 916 m, 801 m, 761 s, 696 m; EI-MS (70 eV) $[M + H]^+$ 502 (39), $[M - CH_3]^+$ 486 (100), $[M - C_4H_9]^+$ 444 (1), $[M - NC_4H_9]^+$ 430 (10). Anal. Found: C, 47.84; H, 6.64; N, 8.19. Calcd for $C_{20}H_{32}N_3Re$ (500.2): C, 47.98; H, 6.40; N, 8.40.

(μ-(2,6-Diisopropylphenyl)imido)(μ-oxo)bis[((2,6-diisopropylphenyl)imido)methyloxorhenium(VII)] (7). A solution of 70 mg (0.28 mmol) of **6** and 90 μL (0.86 mg, 0.42 mmol) of 2,6-(diisopropyl)phenyl isocyanate in 15 cm^3 of 1,2-dimethoxyethane (DME) was refluxed over 24 h. A color change from yellow to deep red was observed. After cooling and evaporation of the solvent, the residue was dried at 10^{-3} Pa for 24 h. Recrystallization from *n*-pentane at −30 °C yielded 120 mg (77%) of **7** as brown crystals; ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$) δ 1.13 (d, $^3J_{H\text{-}H}$ = 6.87, 12 H), 1.15 (d, $^3J_{H\text{-}H}$ = 6.87, 12 H), 1.24 (d, $^3J_{H\text{-}H}$ = 6.87, 6 H), 1.26 (d, $^3J_{H\text{-}H}$ = 6.87, 6 H), 2.426 (s, 3 H), 2.429 (s, 3 H), 3.41 (sept, $^3J_{H\text{-}H}$ = 6.87, 4 H), 3.64 (sept, $^3J_{H\text{-}H}$ = 6.87, 2 H), 7.34 (m, 9 H); IR (KBr) ν(Re═O) 948 vs; ν(Re–O–Re) 661 vs; ν(Re═N) 1289 m, 1332 m; ν(C–H) 2962 s, 2925 s, 2868 m, 1359 s, 747 s, 704 vs. Anal. Found: C, 46.68; H, 5.82; N, 4.21; O, 5.09; Re, 38.19. Calcd for $C_{38}H_{57}N_3O_3Re_2$ (976.30): C, 46.74; H, 5.88; N, 4.30; O, 4.91; Re, 38.15.

Bis[(μ-(2,6-diisopropylphenyl)imido)((2,6-diisopropylphenyl)imido)methyloxorhenium(VII)] (8b). Compare the procedure for **7**. Amounts of reactants: 100 mg (0.4 mmol) of **6** and 195 μL (185 mg, 0.8 mmol) of 2,6-diisopropylphenyl isocyanate. After drying at a pressure of 10^{-3} Pa, recrystallization from *n*-pentane/diethyl ether (1 + 1 vol/vol) at −30 °C yielded 190 mg (84%) of analytically pure **8b** as orange cubes; ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$) δ 1.16 (d, $^3J_{H\text{-}H}$ = 6.71, 12 H), 1.19 (d, $^3J_{H\text{-}H}$ = 6.71, 12 H), 1.28 (d, $^3J_{H\text{-}H}$ = 6.71, 12 H), 1.30 (d, $^3J_{H\text{-}H}$ = 6.71, 12 H), 2.454 (s, 3 H), 2.46 (s, 3 H), 2.94 (sept, $^3J_{H\text{-}H}$ = 6.71, 2 H), 3.44 (sept, $^3J_{H\text{-}H}$ = 6.71, 4 H), 3.67 (sept, $^3J_{H\text{-}H}$ = 6.71, 2 H), 6.82–7.37 (m, 12 H). Monomeric form **8a**: ^{1}H NMR δ 1.13 (d, $^3J_{H\text{-}H}$ = 6.71, 12 H), 1.16 (d, $^3J_{H\text{-}H}$ = 6.71, 12 H), 2.44 (s, 3 H), 3.42 (sept, $^3J_{H\text{-}H}$ = 6.71, 4 H), 7.15 (s (br), 6 H); ^{13}C NMR (100 MHz, C_6D_6) (monomeric form **8a**) δ 23.0 (q, $^1J_{C\text{-}H}$ = 125.7), 23.6 (q, $^1J_{H\text{-}H}$ = 125.7), 28.9 (d, $^1J_{C\text{-}H}$ = 127.9), 122.8 (d, $^1J_{C\text{-}H}$ = 159.0), 128.3 (d, $^1J_{C\text{-}H}$ = 160.1), 143 (s), 152.5 (s); IR (KBr) ν(Re═O) 934 s; ν(Re═N) 1290 s, 1332 s; ν(C–H) 2962 vs, 2925 s, 1359 s, 749 vs, 680 vs; FD MS (monomeric form **8a**) M$^+$ 568 (100); molecular weight (osmometric, toluene as solvent) 562. Anal. Found: C, 53.27; H, 6.63; N, 4.89; O, 3.25; Re, 32.36. Calcd for $C_{50}H_{74}N_4O_2Re_2$ (1135.58): C, 52.89; H, 6.57; N, 4.93; O, 2.82; Re, 32.80.

Bis[(μ-(2,6-diisopropylphenyl)imido)bis((2,6-diisopropylphenyl)imido)methylrhenium(VII)] (9b). A solution of 80 mg (0.32 mmol) of **6** and 206 mL (196 mg 0.96 mmol) of 2,6-diisopropylphenyl isocyanate was refluxed for 5 h. During this period the color changed from colorless to purple. After cooling and evaporation of the solvent in vacuo, the resulting purple adhesive powder was liberated from unreacted isocyanate at a pressure of 1 mPa, yielding 220 mg (94%) of **9b** as a purple powder; ^{1}H NMR (400 MHz, 23 °C, $CDCl_3$) δ 1.08 (d, $^3J_{H\text{-}H}$ = 6.83, 48 H), 1.13 (d, $^3J_{H\text{-}H}$ = 6.83 Hz, 12 H), 1.16 (d, $^3J_{H\text{-}H}$ = 6.83, 12 H), 2.44 (s, 3 H), 2.46 (s, 3 H), 3.43 (m, 12 H), 7.0–7.2 (m, 18 H). Monomeric form **9b** ^{1}H NMR ($CDCl_3$) δ 1.08 (d, $^3J_{H\text{-}H}$ = 6.71, 36 H), 2.46 (s, 3 H), 3.46 (sept, $^3J_{H\text{-}H}$ = 6.71, 6 H), 7.03–7.15 (m, 9 H); ^{13}C NMR (C_6D_6, monomeric form **9a**) δ 8.2 (q, $^1J_{C\text{-}H}$ = 133.2), 23.3 (q, $^1J_{C\text{-}H}$ = 125.7), 28.9 (d, $^1J_{C\text{-}H}$ = 127.8), 122.5 (d, $^1J_{C\text{-}H}$ = 150.7), 126.2 (d, $^1J_{C\text{-}H}$ = 159.0), 142.9 (s), 153.4 (s); IR (KBr) ν(Re═N) 1290 s, 1330 s; ν(C–H) 2962 vs, 2932 s, 2869 m, 749 vs; CI MS (dimeric form **9b**) 727 $[M/2]^+$ (2) and higher peaks, which indicate through their isotopic pattern clearly the occurrence of binuclear species containing two rhenium atoms; FD-MS (for monomeric form **9b**) M$^+$ 727 (100). Anal. Found: C, 60.28; H, 7.50; N, 5.58. Calcd for $C_{74}H_{108}N_6Re_2$ (1454.12): C, 61.12; H, 7.49; N, 5.78. The free isocyanate cannot be removed completely, so unsatisfactory carbon analyses were obtained in spite of many attempts.

Table II. Summary of Crystal Data and Details of Intensity Collection for Compound 2a

	Crystal Parameters
empirical formula	$C_{14}H_{24}Cl_2NRe$
formula weight, amu	463.5
color of cryst/shape	blue-green/columns
cryst dimens, mm	0.10 × 0.10 × 0.40
radiation	Mo Kα (λ = 71.073 pm)
temp, °C	23±1
space group	$P2_1/n$ (ref 32, no. 14)
a, pm	905.7 (<1)
b, pm	1667.6 (1)
c, pm	1229.7 (<1)
β, deg	111.45 (<1)
V, pm^3	1729 × 10^6
Z, mol/cell	4
ρ(calcd), g·cm^{-3}	1.781
μ(Mo Kα), cm^{-1}	74.2
	Data Collection
diffractometer	CAD4 Enraf-Nonius
monochromator	graphite, incident beam
scan type	ω scan
scan time, s	max 90
scan width, deg	(1.00 + 0.25 tan θ) ± 25% for bkgd corr
max 2θ, deg	50
no. of reflcns measd	3277 (h:±10;k:+19,1:+14)
no. of indep reflctns	2811
corrctns	Lorentz-polarization, empirical abs [*T*: 0.9489–1.0000]
standard reflctns	3 every 3600 s, intensity check; 3 every 200 orientation check
	Refinement
solution	Patterson method
hydrogen atoms	19 from 24 found, calcd, included but not refined
refinement	full-matrix least-squares
minimization function	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
weighting scheme	$w = 1/\sigma(F_o)^2$
anomalous dispersion	all non-hydrogen atoms
no. of reflcns included	2811, $I \geq 0.0$
no. of parameters refined	163
R	0.026[a]
R_w	0.019[b]
goodness of fit	2.202[c]
shift/err	<0.001
max e_0/Å^3	+0.60
min e_0/Å^3	−0.81

[a] $R = \sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \sum \lvert F_o\rvert$. [b] $R_w = [\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2 / \sum w F_o^2]^{1/2}$. [c] GOF = $[\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(NO - NV)]^{1/2}$.

X-ray Structural Analysis of the Imido Complex 2a. Crystal data of compound **2a** together with details of the X-ray diffraction experiment are reported in Table II. The data collection was performed on an Enraf-Nonius CAD4 four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation. Orientation matrix and cell dimensions were obtained from a least-squares refinement[29] using a set of 66 reflections up to 2θ ≤45.2°. During data collection deorientation of the crystal was controlled every 200 reflections. The intensity data were

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(29) XRAY76-SYSTEM, program PARAM, computer adaption by M. Birkhahn and E. Herdtweck, Universität Marburg, 1979, Technische Universität München, 1986.

Table III. Fractional Atomic Coordinates and Equivalent Temperature Factors for Non-Hydrogen Atoms in Compound 2a with Estimated Standard Deviations in Parentheses

atom	x	y	z	B_{eq}, Å^2
Re	0.07931 (2)	0.11400 (1)	0.29469 (1)	2.862 (3)
Cl1	−0.1746 (1)	0.0522 (1)	0.2091 (1)	5.35 (3)
Cl2	0.0194 (1)	0.1800 (1)	0.1122 (1)	5.59 (3)
N	0.0438 (3)	0.1898 (2)	0.3754 (2)	3.04 (7)
C1	0.0055 (4)	0.2623 (2)	0.4265 (3)	3.28 (9)
C2	0.0854 (5)	0.2578 (3)	0.5594 (3)	4.8 (1)
C3	−0.1755 (5)	0.2653 (3)	0.3892 (4)	5.4 (1)
C4	0.0694 (6)	0.3333 (3)	0.3796 (4)	6.6 (1)
C11	0.1799 (4)	−0.0180 (2)	0.2655 (3)	3.7 (1)
C12	0.2611 (4)	0.0375 (2)	0.2244 (3)	3.5 (1)
C13	0.3317 (4)	0.0966 (2)	0.3159 (3)	3.6 (1)
C14	0.3028 (4)	0.0696 (2)	0.4183 (3)	3.3 (1)
C15	0.1960 (4)	0.0020 (2)	0.3828 (3)	3.4 (1)
C21	0.0872 (6)	−0.0894 (3)	0.1996 (4)	5.9 (1)
C22	0.2762 (6)	0.0399 (3)	0.1071 (4)	6.1 (1)
C23	0.4451 (5)	0.1620 (3)	0.3119 (4)	6.0 (1)
C24	0.3807 (5)	0.1013 (3)	0.5405 (4)	5.2 (1)
C25	0.1499 (6)	−0.0525 (3)	0.4622 (4)	5.7 (1)

corrected for Lorentzian and polarization effects and a decay of 5.1%. An empirical absorption correction was applied. From Patterson maps the Re position could be determined. All remaining non-hydrogen atoms were located by successive structure factor calculations and difference Fourier maps. The least-squares full-matrix refinement minimized the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. Hydrogen atoms were calculated in ideal positions (C–H = 95 pm) and added to the calculations with collective isotropic temperature factors; however, they were not refined. The refinement converged with unweighted and weighted agreement factors $R = 0.026$ and $R_w = 0.019$, respectively. For a satisfactory, complete analysis, the criterion was the absence of significant features in the final difference map. All calculations were performed by VAX-11/730 and VAX-8200 computers using the STRUX-II program system.[30-34] Selected bond lengths and bond angles are given in Table I. Tables II and III list the atomic and thermal parameters.*

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Supplementary Material Available: Tables of the anisotropic thermal parameters of the non-hydrogen atoms, of the fractional coordinates including the calculated H atoms, of the rms amplitudes, and of general displacement parameters U_{ij}, a full listing of bond lengths and angles, and a cell plot for compound **2a** (11 pages); a listing of observed and calculated structure factors for **2a** (14 pages). Ordering information is given on any current masthead page. Further details of the crystal structure determination can be obtained from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, by quoting the depository number CSD 53989, the name of the authors, and the journal citation.

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(30) Schmidt, R. E.; Birkhahn, M.; Massa, W.; Kiprof, P.; Herdtweck, E. STRUX-II, Programmsystem zur Verarbeitung von Röntgendaten, Universität Marburg, 1980, Technische Universität München, 1985/87.

(31) Frenz, B. A. The ENRAF Nonius CAD4 SDP System; *Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; p 64–71.

(32) Cromer, D. T.; Waber, J. T. *International Crystallography Tables*; Kynoch Press: Birmingham, England, 1974; Vol. IV. Table 2.2B.

(33) Cromer, K. T. Reference 32, Table 2.3.1.

(34) Johnson, C. K. ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations; Oak Ridge National Laboratories; Oak Ridge, TN. 1965.

(35) However, organylzinc compounds have been used successfully, e.g. formation of (η^5-C_5Me_5)ReO_3 from Me_3SiO–ReO_3 (**10**) and $Zn(C_5Me_5)_2$ in >40% isolated yield (Herrmann, W. A.; Ludwig, M.; Filippou, A. C. Unpublished results, 1989). In contrast, Me_3SnO–ReO_3 is unreactive, very likely due to its *polymeric structure*; cf.: Herdtweck, E.; Kiprof, P.; Herrmann, W. A.; Degnan, I.; Kuchler, J. G. *Z. Naturforsch., B*, in press.

(36) This compound is also available from (η^5-C_5Me_5)$ReCl_4$ and CH_3–$N[Si(CH_3)_3]_2$; cf.: Herrmann, W. A.; Marz, D. W. Unpublished results, 1989.