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Multiple Bonds between Main-Group Elements and Transition Metals. 166.[1] Oxo/Imido Complexes of Heptavalent Rhenium: Structures, Reactivity, and Behavior in Solution[†]

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Mixed imido/oxo rhenium(VII) complexes, formal derivatives of methyltrioxorhenium(VII) (**1**) with (2,6-diisopropylphenyl)imido ligands of general formula $CH_3ReO_{3-x}(NR)_x$ ($x = 1$, and 2; compounds **2** and **3**, respectively), have been synthesized. Their structures and behavior in solution have been studied by dynamic ^1H and ^{17}O NMR spectroscopy. In the solid state, compounds **2** and **3** display dimeric structures, as shown by X-ray crystallography. In solution, monomeric and dimeric forms exist in equilibria. At elevated temperatures, the monomers are dominant. In the solid state, the dimeric compounds are bridged by oxygen ligands, forming Re_2O_2 units, while in solution, nitrogen bridging is also evident. Formal replacement of all three oxo groups in **1** by (2,6-diisopropylphenyl)imido ligands leads to a compound of formula $CH_3Re(NR)_3$ (**4**). Complex **4** is monomeric both in solution, regardless of the temperature, and in the solid state. Ligand exchange processes take place via dimeric intermediates if organorhenium oxides are mixed with organorhenium(VII) imido/oxo species or organorhenium(VII) imides. Reaction of methylbis(imido)monooxorhenium(VII) (**3**) with (methylcyclopentadienyl) trioxorhenium (**5**) leads to a dimer with mixed methyl/cyclopentadienyl and imido/oxo groups (**6**). Reaction of **2**−**4** with water slowly leads to the formation of **1**, perrhenate, and amines.

Introduction

Organorhenium oxides such as methyltrioxorhenium (**1**) have recently been extensively studied. Applications as active, selective catalysts for organic syntheses as well as in material sciences were discovered.[2] A similarly detailed examination of organorhenium(VII) imido complexes has not yet been performed.[2b] Organorhenium(VII) imido and organorhenium(VII) imido/oxo complexes may have catalytic activity in certain organic reactions, such as hydroamination and oxyamination.[3] Imidorhenium(VII) complexes also offer the possibility for chiral modification with chiral organic groups on the nitrogen, which of course is not possible with divalent oxo ligands. On the basis of an earlier report,[4] we examined structural aspects and the dynamic behavior of imidorhenium(VII) complexes to understand the gradual change of behavior between rhenium−oxo and −imido species. Some unexpected and interesting findings from both a structural and synthetic point of view, including an easy synthetic approach to rhenium imido/oxo complexes with mixed organic ligands, resulted from this work.

Results and Discussion

Synthesis and NMR Spectroscopy. To examine the gradual changes in the physical properties and chemical behavior of compounds of the general type $[CH_3ReO_n(NR)_{3-n}]_m$ ($n = 0-3$; $m = 1, 2$; R = 2,6-diisopropylphenyl) (Scheme 1), we first synthesized these complexes according to literature procedures.[2,4] CH_3ReO_3 (**1**) was refluxed with the corresponding amount of 2,6-diisopropylphenyl isocyanate (DIPP-NCO) in 1,2-dimethoxyethane (DME). The products were obtained as orange crystals in the case of $CH_3ReO(NR)_2$ (**3**) and dark red crystals in the case of $CH_3Re(NR)_3$ (**4**) by recrystallization at −30 °C. However, the preparation of **2** by the reaction between **1** and DIPP-NCO turned out to be problematic. Impurities with higher numbers of imido groups were present in all cases. When **3** is mixed with **1** in solution, their oxo and imido groups exchange rapidly. Therefore **2** can be synthe-

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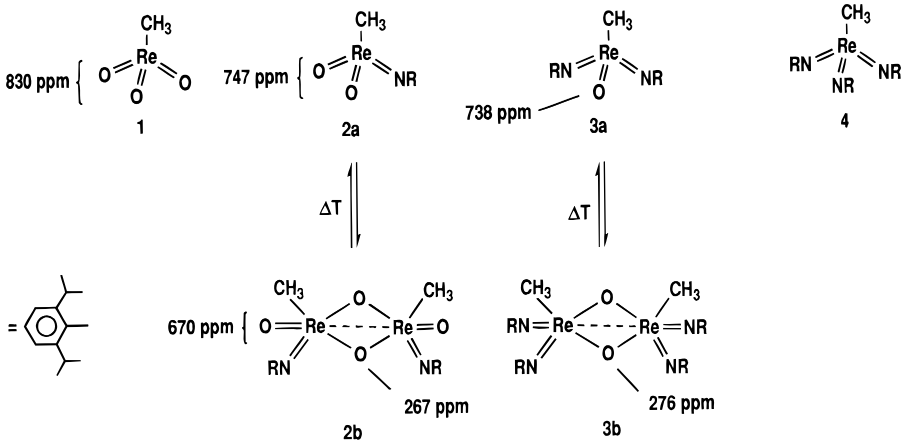
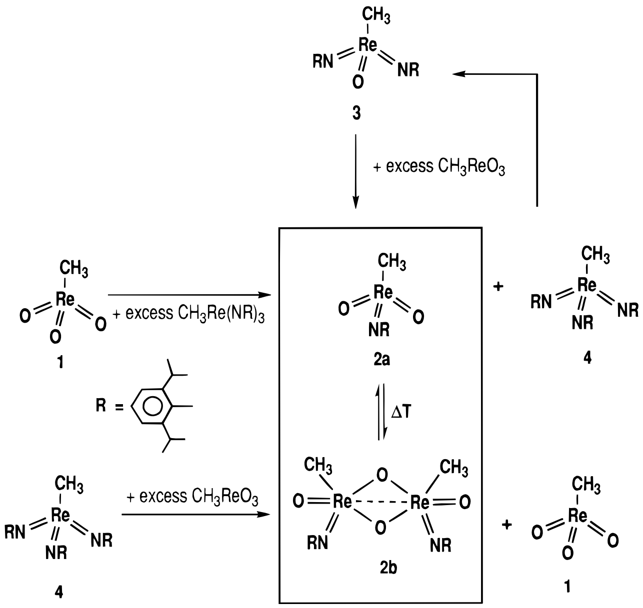
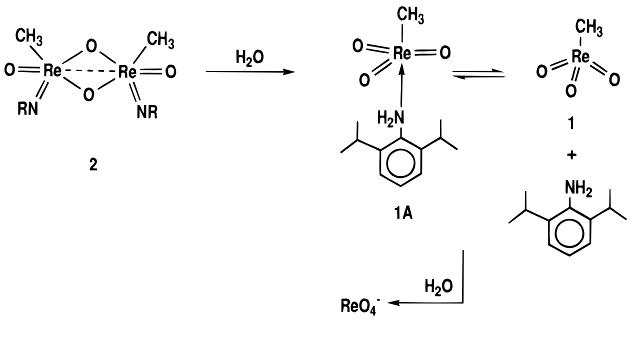
Scheme 1



Scheme 2



Scheme 3



sized by mixing either the bis(imido)rhenium complex **3** or the tris(imido)rhenium complex **4** with **1** in the correct stoichiometry (Scheme 2). This result indicates that intermolecular oxo *and* imido ligand exchange is quite common in this chemistry (see NMR results below) and can be utilized in the preparation of mixed oxo/imido complexes. The reaction between **1** and **3** to generate **2** is much faster than that between **1** and the tris(imido) derivative **4**. It is particularly interesting to monitor the progress of the reaction of **1** with 1 equiv of **4** by ^1H NMR. The reaction initially (in 10 min) generated only **2** with excess **4**, while **3** was not observed until a much later stage of the reaction (after several hours). This perhaps indicates once **3** is generated as the byproduct, it reacts with **1** at a much faster rate than **1** reacts with **4**. Consequently, **1** is totally consumed, the reaction is temporarily stopped, and eventually **3** is regenerated by the ligand exchange between **2** and **4**. The fact that **3** reacts more readily with **1** compared to the reaction of **4** with **1** is very likely due to the steric bulk of the imido ligands in **4** (see for comparison the X-ray section).

Compounds **2**−**4** are moisture sensitive but thermally stable. We found that the influence of the polarity of the solvent, which was previously believed to dictate the dimerization behavior of these compounds,[4] is *not* significant. Namely, only monomers, without any bridging groups, were observed at room temperature by ^1H NMR after long standing in either polar or nonpolar solvents. The previously claimed dimeric derivatives turned out to be a mixture of the monomeric compounds and decomposition products caused by the reaction of monomer with trace amounts of water (Scheme 3). However, both **2** and **3** show, also in contrast to earlier reports, a temperature-dependent dynamic behavior. The ^{17}O NMR spectra at 100 °C in toluene-d_8 **2** show a single peak at $\delta(^{17}O) = 770$ ppm. Cooling to room temperature leads to a significant broadening of the signal and a high-field shift to $\delta(^{17}O) = 747$ ppm. Further cooling causes again a broadening and a shift to higher field. At −90 °C, no signal is detectable. Using diethyl ether as solvent, similar observations can be made at low temperatures. At −110 °C, two broad signals appear, one at $\delta(^{17}O) = 670$ ppm and one at $\delta(^{17}O) = 267$ ppm. The ^1H NMR shows three high-field signals at room temperature and above: a septet at $\delta(^1H) = 3.64$ ppm (belonging to the isopropyl proton), a doublet at $\delta(^1H) = 1.08$ ppm (CH_3 groups of the imido ligand), and a singlet at $\delta(^1H) = 1.85$ (belonging to the Re−CH_3 group). At −90 °C, the signal of the Re−CH_3 group has shifted to 0.95 ppm, the doublet to 1.14 ppm, and the multiplet to 3.81 ppm.

In the case of compound **3**, the situation is similar. The ^{17}O NMR signal at room temperature observed at $\delta(^{17}O) = 738$ ppm in toluene-d_8 broadens during cooling and disappears at ca. −10 °C. At −30 °C, two broad signals can be observed, one at $\delta(^{17}O) = 748$ ppm and one at $\delta(^{17}O) = 297$ ppm. Both signals become sharper when the solution is further cooled, leading to signals at $\delta(^{17}O) = 766$ and 276 ppm at −90 °C. The situation in CD_2Cl_2 as a solvent is similar. The low-field signal is less pronounced at lower temperatures, and the high-field signal increases with falling temperature. The ^1H NMR of **3** shows also three high-field signals: a septet at $\delta(^1H) = 3.56$ ppm, belonging to the isopropyl H, two doublets at 1.06 and 1.08 ppm, representing the isopropyl CH_3 groups, and a singlet at 1.51 ppm for the Re−CH_3 group. At −90 °C, the Re−CH_3 signal has shifted to $\delta(^1H) = 1.43$ ppm, the signal of the isopropyl proton has split into two septets, one at 3.80 and the other at 3.64 ppm, and the doublet at 1.07 ppm has also split into three doublets at 1.12, 1.08, and 1.09 ppm.

In our opinion, the interpretation of these observations is as follows: in solution, equilibria exist between the monomeric and dimeric forms of complexes **2** and **3**. Cooling the solutions shifts the equilibria to the dimeric forms. Above a certain temperature (above −100 °C for **2**; around −30 °C for **3**), the monomers become the predominant species (see also the IR section). The bridging oxygen atoms give rise to the ^{17}O NMR signals below $\delta(^{17}O) = 300$ ppm, and the terminal oxygens the signal above ca. 700 ppm. These data are in good accord with published data for related complexes with bridging and terminal oxo ligands.[2,5] It is also interesting to note that the dimer in the case of **3** is observable at higher temperatures than the dimer in the case of **2**. It seems that the presence of a higher number of bulky imido ligands is helpful for the dimerization of the complexes by oxo bridges. This assumption is supported by our X-ray structure determinations and results of Wilkinson et al., who examined mixed imido/oxo rhenium complexes with aryl ligands in the solid state.[6] The ^{17}O NMR results prove that the imido ligands are stronger donors than the oxo ligands. The ^{17}O NMR signal at room temperature is found for **1** at $\delta(^{17}O) = 830$ ppm, for **2** at $\delta(^{17}O) = 747$ ppm, and for **3** at $\delta(^{17}O) = 738$ ppm in toluene.

Dimerization of compound **1** or its higher congeners of the formula R−ReO_3 (R = alkyl, aryl) has never been observed in solution.[2] However, there is evidence that oxygen ligand exchange takes place in solution between ^{17}O-labeled and unlabeled organorhenium(VII) oxides and OsO_4, respectively.[5c] It was not clear before this study whether traces of water or intramolecular oxo bridges are responsible for this phenomenum.[5c] In view of the above-mentioned results for mixed imido/oxo complexes, exchange between labeled and unlabeled oxygen ligands via oxygen bridges seems to be most likely. It is also possible that dimerization processes such as those described here play an important part in the polymerization of **1** in water.[2] In the case of the tris(imido) derivative **4**, however, we found no indications for the presence of bridging groups by NMR spectroscopy. Only three high-field sets of ^1H NMR signals can be observed, regardless of the temperature (+100 °C, $\delta(^1H) = 3.55$ (septet, isopropyl H), 2.54 (singlet, Re−CH_3), 1.06 ppm (doublet, isopropyl CH_3); −90 °C, $\delta(^1H) = 3.69$, 2.79, 1.06 ppm). The previously reported "dimer"[4] turned out to be a mixture of compounds **3** and **4**. Although it cannot be totally ruled out that a quick exchange between the terminal and bridging imido groups of **4** as a dimer takes place over the examined temperature range, our (see below) and Wilkinson's[6] X-ray examinations of **4** and related complexes give no indication of dimeric species of organotris(imido)rhenium(VII) compounds. The steric bulk of the imido ligands probably prevents the dimerization of **4**.

The results presented also shed light on earlier examinations of intermetallic exchange of oxo and imido ligands.[7,8] The observed structures (see below) may be regarded as model complexes for the exchange intermediates of oxo/imido ligands as proposed by Gibson et al.[7a] The ^{17}O NMR results and the preparation of complex **2** (which requires intermolecular oxygen *and* imido ligand exchange by means of bridging) strongly support the assumptions concerning the four-center ligand exchange mechanism and also verify Gibson's predictions concerning the synthetic applications of such exchanges.[7a]

Another noteworthy fact is the temperature-dependent shift of the Re−CH_3 signal in the ^1H NMR in toluene in the cases of **1**−**3**. The Re−CH_3 protons of **1** are observed at 1.55 ppm at +100 °C and at 0.80 ppm at −90 °C. In the case of **2**, the signals shift from 1.90 to 0.95 ppm; in the case of **3**, they shift from 1.51 to 1.43 ppm in the same temperature range. For compound **4**, which contains no oxygen atoms, a comparable high-field shift is not observed. In contrast, the signal is shifted from 2.54 to 2.79 ppm. In no other solvents (except benzene) has a comparatively strong shift change of the Re−CH_3 protons been observed.[5,7] One possible explanation is the formation of a charge transfer complex between the aromatic solvent and the electron-deficient Re center. The higher the electron deficiency of the Re center, the stronger is the effect. UV/vis spectroscopic results also show significant differences in the absorption maxima of these complexes between aromatic and nonaromatic solvents.[2b]

Reactions. Although bulky aromatic imido complexes of rhenium(VII) oxides can be handled in air briefly without noticeable decomposition, compounds **2**−**4** are susceptible to hydrolysis in solution. In all cases, these compounds react with H_2O slowly to decrease the imido-to-oxo ratio by liberating amines and eventually converting to **1** (Scheme 3; see also IR results).

Mixed oxo/imido complexes, such as **3**, can also exchange oxo and imido ligands with other organorhenium oxides, such as (methylcyclopentadienyl)rhenium trioxide (**5**). There is an immediate reaction of **3** and **5** in a 1/1 stoichiometric ratio (eq 1). In about 2 h, the exchange of oxo and imido ligands is complete and compound **6** is generated. Even with a bulky (2,6-

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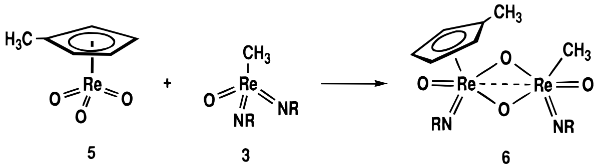

5 3 6 (1)

diisopropylphenyl)imido group, **6** retains the η^5 coordination with the substituted cyclopentadienyl ring. In solution, **6** exchanges its oxo and imido ligands intramolecularly. The ^{1}H NMR spectrum of **6** at room temperature shows only one doublet ($\delta = 1.17$ ppm, $^3J_{H-H} = 6.96$ Hz) for the methyl substituent on the (diisopropylphenyl)imido groups. The exchange slows at lower temperatures, and the doublet splits into two sets of doublets below −30 °C.

IR Spectroscopy. In agreement with the solid-state structures of **2** and **3**, their IR spectra show the presence of terminal and bridging oxo groups. The IR spectrum of **2** (KBr) shows a very strong band at 953 cm^{-1}. This band can be assigned to the terminal oxo stretching vibration.[9] A strong absorption at 703 cm^{-1} indicates that **2** contains bridging oxo groups in the solid state.[9] Exposure of compound **2** to air or moisture leads to two new Re=O vibrations (958 and 934 cm^{-1}) due to the formation of **1A**. After 12 h in air, the band at 934 cm^{-1} is the most pronounced Re=O vibration while the vibrations at 953 and 703 cm^{-1} decrease significantly in intensity. Compound **3** has a very strong band at 680 cm^{-1} representing the bridging oxo groups, ν(Re−O−Re), while no terminal oxo−rhenium stretching modes are observed. Complex **3** also decomposes slowly during exposure to air or moisture under formation of **1A**, as detectable from the changes in the IR spectrum. In the case of derivative **6**, the ν(Re=O) IR frequencies are shifted to even lower wavenumbers (921 ($CH_3Re{=}O$) and 907 cm^{-1} (CpRe=O)) due to the presence of the methylcyclopentadienyl group. Two bridging Re−O−Re vibrations are observed, as expected from the lower symmetry of the complex (772, 747 cm^{-1}). All compounds have a number of bands in the frequency range in which rhenium−imido stretching modes ν(Re=N) are expected. The assignment of these bands is tentative (see Experimental Section) due to the uncertainty in the assignment of metal−nitrogen stretching modes, caused by its coupling to the nitrogen−carbon stretching and even to C−C and C−H modes.[6,10] IR spectra recorded in diethyl ether solution at room temperature do not show bridging Re−O−Re vibrations. Instead, in the case of compound **3**, a strong band can be observed at 924 cm^{-1}, due to the terminal Re=O stretching vibration. In the case of **2**, two Re=O bands can be observed in solution, one at 928 cm^{-1} and one at 985 cm^{-1}. In this case, the Re−O−Re band is also conspicuously absent. These results strongly support the conclusions drawn from the NMR measurements (see above).

X-ray Crystallography. To be able to compare the NMR measurements in solution with the solid-state structures, we determined the structures of compounds **2**−**4** by X-ray structure analysis. PLATON[18] representations of molecules **2**−**4** are shown in Figures 1−3, and selected bond distances and bond angles are given in Tables 1−3.

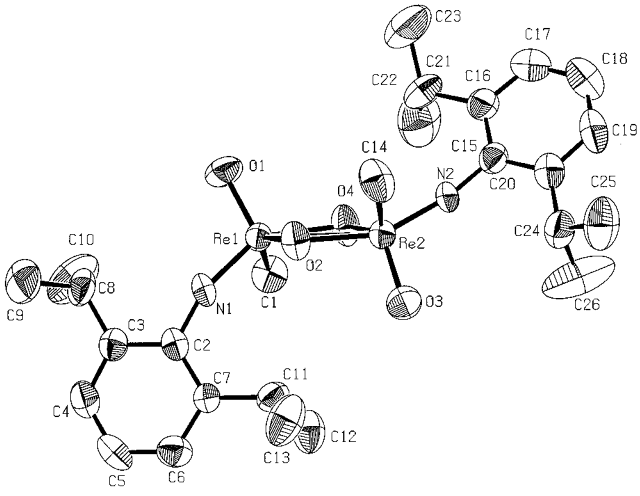

Figure 1. PLATON representation of **2**. Thermal ellipsoids are shown at the 50% probability level; hydrogen atoms are omitted for clarity.

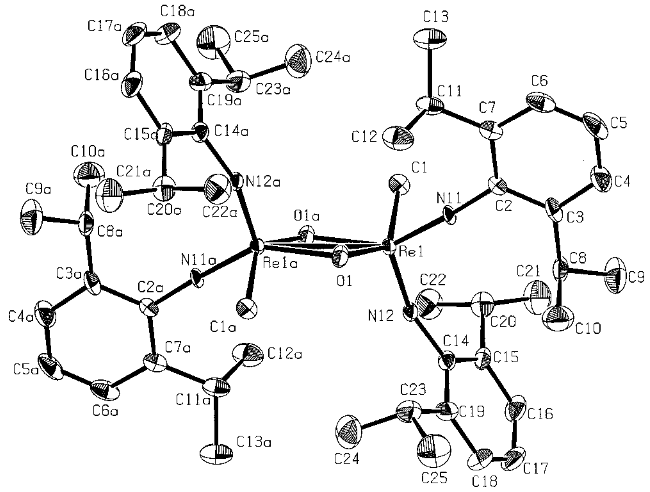

Figure 2. PLATON representation of **3**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity. A symmetry operation ($-x$, $-y$, $-z$) is applied to atoms labeled by "a".

Compounds **2** and **3** display dimeric structures. In both cases, pentagonally coordinated Re centers are linked by two bridging oxygen atoms. The Re−Re distance is rather long and indicates only a very weak bonding interaction (3.0902(10)−3.1186(3) Å). Compound **4** is monomeric with a distorted tetrahedral coordination sphere for the Re center. These results are in accord with some earlier structural examinations of related compounds.[6,10] **3** is the first bis(imido)monooxoorganorhenium(VII) complex characterized by X-ray crystallography. Up to now, only two monoimidodioxoorganorhenium(VII) structures have been published, namely [Re(N^{t}Bu)(O)(μ-O)(xylyl)]$_2$ and [Re(N^{t}Bu)(O)(μ-O)(mesityl)]$_2$.[6] Both complexes have unsymmetrical Re−O bridges (2.081(8)/1.867(8) Å in the xylyl case and 1.791(7)/2.364(7) Å in the mesityl case). In the methyl derivative **2**, the bridges are less unsymmetrical (1.891(8)/1.997(8) Å) but still significantly different. Wilkin-

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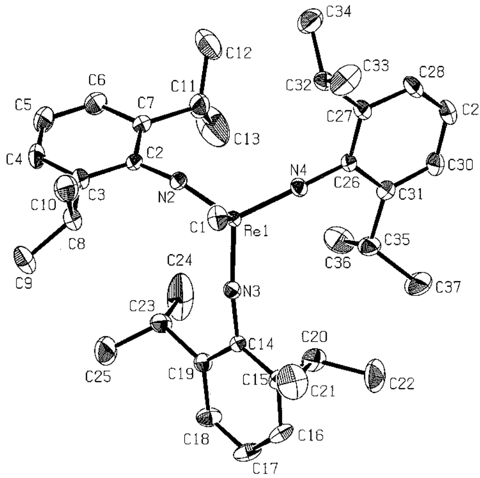

Figure 3. PLATON representation of **4**. Thermal ellipsoids are shown at the 30% probability level; hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for the Dimeric Compound 2

Re(1)−O(1)	1.702(9)	Re(1)−O(2)−Re(2)	105.2(4)
Re(1)−N(1)	1.730(8)	Re(2)−O(4)−Re(2)	105.2(4)
Re(1)−O(2)	1.891(8)	O(1)−Re(1)−N(2)	106.9(4)
Re(1)−O(4)	1.997(8)	O(1)−Re(1)−O(2)	113.9(4)
Re(1)−C(1)	2.135(12)	N(1)−Re(1)−O(2)	98.5(4)
Re(1)−Re(2)	3.0902(10)	N(1)−Re(1)−O(4)	144.3(4)
Re(2)−O(3)	1.686(10)	O(2)−Re(1)−O(4)	74.7(3)
Re(2)−N(2)	1.738(9)	O(1)−Re(1)−C(1)	102.7(4)
Re(2)−O(4)	1.895(8)	N(1)−Re(1)−C(1)	87.3(4)
Re(2)−O(2)	1.999(8)	O(2)−Re(1)−C(1)	139.1(4)
Re(2)−C(14)	2.106(14)	O(4)−Re(1)−C(1)	77.3(4)

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for the Dimeric Compound 3[a]

Re(1)−O(1)	1.885(4)	Re(1)−O(1)−Re(1)	105.9(2)
Re(1)−O(1)a	2.022(3)	O(1)−Re(1)−N(11)	98.8(2)
Re(1)−N(11)	1.740(4)	O(1)−Re(1)−N(12)	114.5(2)
Re(1)−N(12)	1.730(4)	O(1)−Re(1)−C(1)	137.4(2)
Re(1)−C(1)	2.141(6)	Re(1)a−Re(1)−O(1)	38.6(1)
Re(1)−Re(1)	3.1190(3)	Re(1)a−Re(1)−N(12)	113.1(1)
N(11)−C(2)	1.368(7)	Re(1)a−Re(1)−C(1)	107.6(2)
N(12)−C(14)	1.412(7)	Re(1)−N(11)−C(2)	172.1(4)
O(1)a−Re(1)−N(11)	147.4(2)	Re(1)−N(12)−C(14)	157.7(4)
O(1)a−Re(1)−C(1)	77.2(2)	O(1)a−Re(1)−N(12)	102.6(2)

[a] A symmetry operation ($-x$, $-y$, $-z$) is applied to atoms labeled by "a".

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for the Monomeric Compound 4

Re(1)−N(3)	1.748(3)	N(3)−Re(1)−N(4)	115.6(2)
Re(1)−N(4)	1.758(4)	N(3)−Re(1)−N(2)	114.8(2)
Re(1)−N(2)	1.766(3)	N(4)−Re(1)−N(2)	116.2(2)
Re(1)−C(1)	2.109(5)	N(3)−Re(1)−C(1)	101.8(2)
N(2)−C(2)	1.373(5)	N(4)−Re(1)−C(1)	103.0(2)
N(3)−C(14)	1.391(5)	N(2)−Re(1)−C(1)	102.4(2)
N(4)−C(26)	1.390(5)	C(2)−N(2)−Re(1)	166.3(3)
		C(14)−N(3)−Re(1)	168.8(3)
		C(26)−N(4)−Re(1)	169.5(3)

son et al. argued that the longer Re−O bond distance in the axial case might be due to either a trans influence of the imido group or packing effects. In complex **3**, the Re_2O_2 units of the two crystallographically independent molecules are also rather asymmetric (1.885(4)/2.022(3) and 1.916(3)/1.994(3) Å).

The terminal $Re{=}O$ bond lengths (1.69(1) and 1.70(1) Å) in the case of **2** are in the usual range of $Re{=}O$ double bonds observed in organorhenium(VII) oxides (ca. 1.68−1.72 Å).[2] Concerning the bridging Re−O bonds, two significantly different bond lengths can be observed (see above). However, both of them are still in the usual range of Re−O single bonds. Re−O bond distances for $O{\rightarrow}Re(VII)$ donor interactions are known to range between 2.30 and 2.45 Å.[2,5c,11] The asymmetry of the Re_2O_2 units could therefore be formally interpreted in terms of a dimer, consisting of two strongly interacting "monomeric units". Thus, the observed cleavage of the dimers in solution is in agreement with the structural findings in the solid state: thermal movements at higher temperatures are obviously able to cleave the two weaker of the four Re−O single bonds of the crystalline compounds, leading to the monomeric compounds in solution.

Packing effects due to bulky ligands and donor effects of the imido and organyl substituents might also influence the Re−O bond lengths as observed in the two crystallographically independent molecules in the unit cell of compound **3** (see above). We have also observed the formation of unsymmetric $Re^{VII}{}_2O_2$ units in related complexes, namely $[ReO_2(\mu\text{-}O)C_2H_4C(CH_3)HO(CH_3)]_2$ and $[ReO_3(\mu\text{-}OCH_3)(CH_3OH)]_2$ in the solid state.[5e,12]

There are two possible explanations for the monomeric structures of **4** and the related published and structurally very similar derivatives ($[C_6H_5Re(NC_6H_3\text{-}(i\text{-}C_3H_7)_3]$ and $[C_6H_2(CH_3)_3Re(NC(CH_3)_3)_3]$).[9,13] First, the imido ligands used to date are too bulky to favor dimerization. The other reason might be that imido groups are stronger donors than oxygen atoms. Thus, three imido groups in one molecule may be sufficient to provide steric and electronic saturation of the metal center.

It should be noted, in this context, that several analogous Tc complexes, most notably $(\eta^1\text{-}C_5H_5)Tc(NAr)_3$ and $CH_3Tc(NAr)_3$, are known.[14] All bond distances and bond angles of the latter compound are identical to those of **4** within estimated error. The entire class $RM(NR')_3$ (M = Tc, Re) display very similar structural features. This kind of structural similarity has already been noted for the RMO_3 (M = Tc, Re) complexes. The chemical and spectroscopic similarities of the latter class of compounds are extremely widespread,[2] and the same seems to be true for the $RM(NR')_3$ compounds.

Conclusions

Imido/oxo rhenium(VII) organyl complexes can be easily synthesized by mixing organorhenium(VII) trioxides with organorhenium(VII) tris(imides). Oxo and imido ligand exchange takes place via bridging ligand groups. In solution, there is an equilibrium between *monomers* (main product at high temperatures) and *dimers* (low temperatures). In the solid state, dimeric

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compounds with bridging oxygen atoms can be isolated. These dimers can formally be regarded as consisting of two very strongly interacting monomeric units, leading to one shorter and one longer Re–O bond in the bridges. Mixing compounds with different organyl ligands leads to defined products with mixed ligands. By means of this method, a broad variety of yet unknown derivatives with interesting characteristics and applications should be accessible.

Experimental Section

All reactions were performed with standard Schlenk techniques under oxygen-free and water-free nitrogen or argon atmospheres. Solvents were dried with standard methods and distilled under N_2 or argon. Infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer (resolution 4 cm^{-1}); the ^1H and ^{17}O NMR spectra were acquired at 399.78 and 54.21 MHz, respectively, on FT-JEOL GX 400 and Bruker DPX 400 instruments. All NMR solvents were "freeze–pump–thaw" degassed and stored over molecular sieves before use. Elemental analyses were performed in the microanalytical laboratory of our institute. Mass spectra were obtained with Finnigan MAT 311A- and MAT 90 spectrometers. ^{17}O labeled **1** was prepared according to refs 5b and 15.[15] For ^{17}O NMR experiments, **2** and **3** were also prepared ^{17}O labeled from ^{17}O-labeled **1** according to the procedures described below. Compound **5** was prepared according to ref 8. For in situ NMR studies, each component was weighted separately and transferred to an NMR tube under Ar atmosphere. The NMR sample tube was stored under Ar in a Schlenk tube when the sample needed to be kept for longer periods of time.

Bis[(μ-oxo)(2,6-diisopropylphenylimido)methyloxorhenium (VII)] (2). A 100 mg (0.08 mmol) sample of **3** and 48 mg (0.18 mmol) of **1** were dissolved in 5 mL of CH_2Cl_2, and the solution was stirred for 1 h, resulting in a yellow solution. The solvent was then removed by vacuum, and the residue was recrystallized in pentane and methylene chloride (9/1 vol/vol) at −60 °C. A 120 mg (90%) quantity of analytically pure **2** as yellow-brown microcrystals was collected. ^1H NMR (400 MHz, 23 °C, $CDCl_3$): δ 1.29 (d, $^3J_{H-H} = 6.96$ Hz, 24 H), 2.45 (s, 6 H), 3.66 (sept, $^3J_{H-H} = 6.96$ Hz, 4 H), 7.2–7.4 (m, 6 H). ^{13}C NMR (100 MHz, 23 °C, $CDCl_3$): δ 23.3 (s, 8 C), 28.7 (s, 6 C), 122.8 (s, 4 C), 132.0 (s, 4 C), 146.6 (s, 2 C), 151.7 (s, 2 C). ^{17}O NMR (54 MHz, 23 °C, $CDCl_3$): δ 747 (s). IR (KBr), cm^{-1}: ν(Re=O) 953 s, ν(Re–O–Re) 703 vs, ν(Re=N) 1384 s, 1341 m, ν(C–H) 2962 s, 2925 m, 2870 m, 1384 s, 744 s. CI MS, *m/z*: 818, M^+. Anal. Found: C, 38.16; H, 4.96; N, 3.35. Calcd for $C_{26}H_{40}N_2O_4Re_2$ (M_r 817.03): C, 38.22; H, 4.93; N, 3.43.

Bis[(μ-oxo)bis(2,6-diisopropylphenylimido)methylrhenium (VII)] (3). A solution of 200 mg (0.80 mmol) of **1** and 343 μL (1.6 mmol, 327 mg) of 2,6-diisopropylphenyl isocyanate in 30 mL of 1,2-dimethoxyethane was refluxed for 16 h. The solvent in the resulting deep red solution was then removed under vacuum at 50 °C. The residue was redissolved in 16 mL of diethyl ether and hexanes (1/1 vol/vol), and the solution was cooled to −30 °C to produce the analytically pure product as orange microcrystals, which were then collected by filtration and dried. Yield: 390 mg (86%). ^1H NMR (400 MHz, 23 °C, $CDCl_3$): δ 1.13 (d, $^3J_{H-H} = 6.96$ Hz, 24 H), 1.16 (d, $^3J_{H-H} = 6.96$ Hz, 24 H), 2.43 (s, 6 H), 3.42 (sept, $^3J_{H-H} = 6.96$ Hz, 8 H), 7.14 (br s, 12 H). ^{13}C NMR (100 MHz, 23 °C, $CDCl_3$): δ 22.8 (s, 8 C), 23.4 (s, 8 C), 28.5 (s, 10 C), 122.3 (s, 8 C), 127.8 (s, 8 C), 142.6 (s, 4 C), 151.9 (s, 4 C). ^{17}O NMR (54 MHz, 25 °C, Tol-d_8): δ 738 (br s). IR (KBr), cm^{-1}: ν(Re–O–Re) 680 vs, ν(Re=N) 1332 s, 1290 s, ν(C–H) 2962 s, 2923 m, 2870 m, 1384 s, 749 s. CI MS, *m/z*: 569, $[M/2]^+$; peaks at higher mass indicate a dimeric compound. Anal. Found: C, 52.76; H, 6.59; N, 4.72. Calcd for $C_{50}H_{74}N_4O_2Re_2$ (M_r = 1135.58): C, 52.89; H, 6.57; N, 4.93.

Tris((2,6-diisopropylphenyl)imido)methylrhenium(VII) (4). A solution of 100 mg (0.40 mmol) of **1** and 284 μL (1.33 mmol, 269 mg) of 2,6-diisopropylphenyl isocyanate in 30 mL of 1,2-dimethoxyethane was refluxed for 12 h. The solvent in the resulting deep red solution was then removed. The viscous red residue was dried under vacuum at 65 °C for 10 h to remove unreacted isocynate. Yield: 280 mg (96%) of **4** as a dark red solid. Further recrystallization in hexanes at −30 °C afforded dark red crystals in about 85% yield. ^1H NMR (400 MHz, 23 °C, $CDCl_3$): δ 1.08 (d, $^3J_{H-H} = 6.96$ Hz, 36 H), 2.46 (s, 3 H), 3.45 (sept, $^3J_{H-H} = 6.96$ Hz, 6 H), 7.02–7.10 (m, 9 H). ^{13}C NMR (100 MHz, 23 °C, $CDCl_3$): δ 23.1 (s, 12 C), 28.5 (s, 7 C), 122.0 (s, 6 C), 125.3 (s, 6 C), 140.5 (s, 3 C), 153.0 (s, 3 C). IR (KBr), cm^{-1}: ν(Re=N) 1334 vs, 1292 vs, ν(C–H) 2961 vs, 2924 m, 2870 m, 1384 s, 752 s. CI MS, *m/z*: 728, M^+. Anal. Found: C, 59.44; H, 7.52; N, 5.44. Calcd for $C_{37}H_{54}N_3Re$ (M_r = 727.06): C, 61.12; H, 7.49; N, 5.78.

[((2,6-Diisopropylphenyl)imido)methyloxorhenium(VII)]bis(μ-oxo)[((2,6-diisopropylphenyl)imido)(methylcyclopentadienyl)oxorhenium(VII)] (6). A 40 mg (0.128 mmol) sample of (methylcyclopentadienyl)trioxorhenium(VII) and 73 mg (0.128 mmol) of **3** were dissolved in 8 mL of CH_2Cl_2. The red-brown solution gradually became be dark brown. The solvent was removed at room temperature under vacuum after 6 h. The resulting brown solid was recrystallized in CH_2Cl_2 and hexanes (1/10 v/v) to give 80 mg (70%) of **6** as brown microcrystals. ^1H NMR (400 MHz, 23 °C, $CDCl_3$): δ 1.17 (d, $^3J_{H-H} = 6.96$ Hz, 24 H), 2.44 (s, 3 H), 2.73 (s, 3 H), 3.14 (sept, $^3J_{H-H} = 6.96$ Hz, 4 H), 6.61 (t, $^3J_{H-H} = 2.56$ Hz, 2 H), 6.87 (t, $^3J_{H-H} = 2.56$ Hz, 2 H), 7.2–7.3 (m 6 H). ^{13}C NMR (100 MHz, 23 °C, $CDCl_3$): δ 14.0 (s, 1 C), 23.8 (s, 4 C), 23.9 (s, 4 C), 28.6 (s, 5 C), 107.4 (s, 2 C), 109.8 (s, 2 C), 123.3 (s, 4 C), 130.7 (s, 1 C), 131.7 (s, 4 C), 144.1 (s, 2 C), 150.8 (s, 2 C). IR (KBr), cm^{-1}: ν(Re=O) 921 m, 907 vs, 852 m, ν(Re–O–Re) 772 m, 747 m, ν(Re=N) 1384 s, 1325 m, ν(C–H) 2965 s, 2925 m, 2869 m, 1384 s, 746 s. CI MS, *m/z*: 706, $[M - NR]^+$; 569, $[M - MeCpReO_3]^+$. Anal. Found: C, 42.11; H, 4.98; N, 3.09. Calcd for $C_{31}H_{44}N_2O_4Re_2$ (M_r = 881.12): C, 42.26; H, 5.03; N, 3.18.

X-ray Crystallography. Suitable single crystals for X-ray diffraction studies were obtained by slowly cooling saturated solutions of complexes **2**–**4** to −30 °C. All structures were solved and refined by a combination of direct methods, difference Fourier syntheses, and least-squares methods. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the ref 16.[16] All calculations were performed on a DEC 3000 AXP workstation with the STRUX-V system,[17] including the programs PLATON-92,[18] PLUTON-92,[18] SIR-92,[19]and SHELXL-93.[20]

Data Collection and Structure Solution and Refinement for Complexes 2–4. A summary of the collection and refinement data is reported in Table 4. Preliminary examination and data collection for compounds **3** and **4** were carried

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Table 4. Crystallographic Data for Compounds 2−4

	2	**3**	**4**
Crystal Data			
empirical formula	$C_{26}H_{40}N_2O_4Re_2$	$C_{50}H_{74}N_4O_2Re_2$	$C_{37}H_{54}N_3Re$
fw	817.01	1135.56	727.05
color	brown	orange	orange
cryst size (mm)	0.38 × 0.13 × 0.05	0.28 × 0.04 × 0.04	0.40 × 0.32 × 0.14
cryst system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$Fdd2$
a (Å)	19.922(3)	19.0347(12)	36.8535(8)
b (Å)	13.138(3)	15.2465(8)	39.9810(17)
c (Å)	11.357(3)	18.0530(12)	10.5930(3)
β (deg)	93.324(8)	105.828(6)	
V (Å^3)	2967.5(11)	5040.8(6)	15608.2(9)
Z	4	4	16
T (K)	293	200	173
ρ_{calcd} (g cm^{-3})	1.829	1.496	1.238
μ (cm^{-1})	81.8	48.4	31.4
F_{000}	1568	2272	5952
Data Collection			
λ (Å)	0.710 73	0.710 73	0.710 73
scan method	ω scan	imaging plate	imaging plate
θ range (deg)	1.0−25.0	1.5−25.1	2.43−27.77
data collcd (h,k,l)	+23,+15,±13	±22,±17,±21	±46,±52,±13
Refinement[a]			
no. of rflns collcd	5622	58 174	51 671
no. of indep rflns	5202	8132	9031
no. of obsd rflns	5202 (all data)	8132 (all data)	9031 (all data)
R_{int}	0.0169	0.0652	0.0324
R1	0.0354	0.0252	0.0222
wR2	0.1047	0.0482	0.0712
GOF	1.072	0.830	1.121
Flack param, χ			0.000(8)[b]
$\Delta\rho_{max/min}$ (e Å^{-3})	+2.35/−2.13	+0.88/−0.93	+1.14/−0.50

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(NO - NV)]^{1/2}$; $w \equiv$ SHELXL-93 weights. [b] Refinements of the enantiomorphic model resulted in larger R values (wR2 = 0.1175).

out on an imaging plate diffraction system (IPDS; Stoe&Cie) equipped with a rotating anode (Enraf-Nonius FR591) and graphite monochromated Mo $K\alpha$ radiation. The data collection was performed at 200 K (173 K) within the θ range $1.55° < \theta < 25.1°$ ($2.43° < \theta < 27.77°$) with an exposure time of 5.0 (3.0) min per image (either oscillation or rotation scan modes from $\varphi = 25.0$ to 360° (0 to 264°) with $\Delta\varphi = 1°$ (0.5°). A total number of 58 174 (51 671) reflections were collected; 1157 (744) systematically absent reflections were rejected from the original data set. After merging, 8132 (9031) independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. Corrections for intensity decay and/or absorption effects with the program Decay[21] were applied for **3**. The unit cell parameters were obtained by least-squares refinements of 4448 (4590) reflections with the program Cell.[21] Final cell constants for **2** were obtained by least-squares refinement of 25 automatically centered reflections ($7.1° < \theta < 22.54°$) on an Enraf-Nonius CAD4 diffractometer ($\lambda = 0.710\,73$ Å; graphite monochromator): range of measurement $1.0° < \theta < 25.0°$; ω-scan, scan width $(1.0 + 0.25 \tan\theta)°$ (±25%) before and after each reflection to determine the background; $t_{max} = 60$ s; orientation control reflections were monitored every 200 reflections, and the intensities of three reflections were checked every 3600 s (5622 measured reflections, 5202 independent reflections). A semiempirical absorption correction based on six ψ-scan reflections was made (T_{max}/T_{min}: 99.9/49.2%).

All "heavy atoms" of the asymmetric unit were anisotropically refined. All hydrogen atoms were calculated in ideal positions (riding model) for **2**−**4**. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with SHELXL weighting schemes and stopped at shift/error < 0.001 in the case of compound **4**. A potential solvent area volume of 242.1 Å^3 was found. The solvent molecule was not resolved due to low residual electron densities (<1 e/Å^3).

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Supporting Information Available: Complete tables of crystal data and refinement details, atomic positional and thermal parameters, bond lengths and angles, and temperature-dependent ^{17}O NMR data (58 pages). Ordering information is given on any current masthead page.

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