Cp^*_2TiH to Cp*FvTi, and regenerating H_2.

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Registry No. Cp^*_2TiH, 131954-87-5; $Cp^*_2Ti(H)Cl$, 115912-71-5; Cp^*_2TiMe, 99476-26-3; $Cp^*_2Ti(Me\text{-}d_3)$, 135973-60-3; $Cp^*_2Ti(Me)Cl$, 107534-13-4; Cp^*_2TiEt, 99476-27-4; $Cp^*_2TiCH{=}CH_2$, 131954-86-4; Cp^*_2TiPr, 99476-28-5; $Cp^*_2TiCH_2CMe_3$, 103351-92-4; Cp^*_2TiPh, 115564-94-8; Cp*FvTi, 53436-87-6.

Supplementary Material Available: Tables of rate constants for the thermolysis of Cp^*_2TiR (R = Et, Pr) in THF, details on the synthesis of Cp^*_2TiH and $(Cp^*\text{-}d_{30})_2TiD$, and spectral data and plots of kinetic data for thermal decompositions of Cp^*_2TiR (R = Me, Pr, CH_2CMe_3, Ph) catalyzed by Cp^*_2TiH and the effect of propene on the thermolysis for R = Pr (6 pages). Ordering information is given on any current masthead page.

Synthesis and Characterization of Re(VII) Alkylidene Alkylidyne Complexes of the Type $Re(CR')(CHR')(OR)_2$ and Related Species

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Abstract: A convenient one pot synthesis of $Re(NAr)_2(py)Cl_3$ consists of addition of excess trimethylchlorosilane, pyridine, and 2,6-dimethylaniline ($ArNH_2$) to Re_2O_7 or $[NH_4][ReO_4]$ in dichloromethane. $Re(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)_2(py)Cl_3$ and $Re(N\text{-}t\text{-}Bu)_2Cl_3$ can be prepared similarly in high yield. Alkylation of these species with dineopentyl or dineophyl zinc or Grignard reagents affords complexes of the formula $Re(NR)_2(CHR')(CH_2R')$ (R = 2,6-$C_6H_3Me_2$, 2,6-C_6H_3-*i*-Pr_2 or *tert*-butyl; R' = CMe_3 or CMe_2Ph). Treatment of $Re(NR)_2(CHR')(CH_2R')$ complexes with an appropriate HCl source yields dimers of the general formula $[Re(CR')(CHR')(RNH_2)Cl_2]_2$, which exist as a mixture of two isomers. An X-ray study of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ (a = 10.05 (1) Å, b = 21.65 (3) Å, c = 10.99 (1) Å, β = 98.28 (9)°, Z = 2, fw = 1031.08, ρ(calcd) = 1.446 g/cm^3, space group = $P2_1/n$) showed it to contain two bridging halides with mutually cis alkylidene and alkylidyne ligands trans to the bridging halides. Several monomeric derivatives having the general formula $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)L_2Cl_2$ (L = *t*-$BuNH_2$, pyridine, $^1/_2$TMEDA, $^1/_2$phenylenediamine (pda)) were prepared, and related monoadducts, $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(L)Cl_2$, have been observed in solution. Treatment of $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(pda)Cl_2$ with HCl(g) in dimethoxyethane affords air- and water-stable $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ ($x > 1$). An alternative route to $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ consists of treatment of $Re(O)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ with HCl(g) in dimethoxyethane. $Re(O)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ is prepared by the acid-catalyzed hydrolysis of $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ via intermediate $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$. $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ and $Re(O)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ conproportionate in solution to give $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$. $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ is a versatile precursor to a variety of bisalkoxide complexes of the general formula $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OR)_2$ (OR = O-*t*-Bu, $OCMe_2(CF_3)$, $OCMe(CF_3)_2$, O-2,6-C_6H_3-*i*-Pr_2, $OSi(t\text{-}Bu)_3$). Syn and anti rotameric forms of the $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OR)_2$ complexes interconvert thermally or photochemically. In syn rotamers usually J_{CH} = 120–135 Hz and in anti rotamers J_{CH} = 157–184 Hz. An X-ray study of *syn*-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2(THF)$ (a = 9.891 (1) Å, b = 17.543 (2) Å, c = 16.570 (2) Å, β = 95.90 (2)°, Z = 4, fw = 759.69, ρ = 1.764 g/cm^3, space group = $P2_1/n$) showed it to have a structure approximately halfway between a face-capped tetrahedron (THF trans to the neopentylidyne ligand) and a trigonal bipyramid.

Introduction

Rhenium is one of three metals (molybdenum and tungsten being the other two) that are active for the metathesis of olefins in classical metathesis systems.[1,2] Although both homogeneous and heterogeneous molybdenum and tungsten catalysts are known, rhenium catalysts of the classical type (e.g., Re_2O_7 on alumina) are heterogeneous. One of the potential advantages of rhenium catalysts is that they may tolerate functionalities (e.g., the ester in methyl oleate) more than tungsten or molybdenum catalysts.[3] Approximately ten years ago evidence began to accumulate in favor of the highest possible oxidation state for tungsten metathesis catalysts (d^0 if the alkylidene ligand is viewed as a dianion).[4-7] Therefore we felt that it should be possible to prepare well-characterized, soluble Re(VII) alkylidene complexes. At that time organometallic chemistry of Re(VII) was extremely rare.[8-10] We chose to attempt to synthesize complexes of Re(VII) containing imido ligands in the belief that imido complexes would not be reduced as readily as oxo complexes in alkylation reactions and that unwanted bimolecular reactions might be slowed down or prevented entirely if imido ligands are present instead of oxo ligands.

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In 1983, Nugent[11] reported that $ReO_3(OSiMe_3)$ reacts with 3 equiv of (*t*-Bu)NH($SiMe_3$) in hexane over the course of 2 days to yield highly soluble, crystalline, yellow Re(N-*t*-Bu)$_3$($OSiMe_3$) in ~65% yield. We found that addition of HCl in ether to this material yielded 1 equiv of *tert*-butylammonium chloride and bright orange, highly crystalline Re(N-*t*-Bu)$_2Cl_3$ in 83% yield.[12] Re(N-*t*-Bu)$_2Cl_3$ could be alkylated to give Re(N-*t*-Bu)$_2R_3$ species, but when R = CH_2-*t*-Bu, Re(N-*t*-Bu)$_2$(CH-*t*-Bu)(CH_2-*t*-Bu), a yellow oil was formed by α hydrogen abstraction, instead of Re(N-*t*-Bu)$_2$(CH_2-*t*-Bu)$_3$. An analogous alkylidene complex, Re(N-*t*-Bu)$_2$(CHSiMe_3)(CH_2SiMe_3), was formed quantitatively upon photolysis of Re(N-*t*-Bu)$_2$(CH_2SiMe_3)$_3$. Unfortunately, neither alkylidene complex reacted with olefins, even very reactive olefins such as norbornene. Perhaps the most surprising finding was that 3 equiv of 2,4-lutidinium hydrochloride would react with Re(N-*t*-Bu)$_2$(CH-*t*-Bu)(CH_2-*t*-Bu) in dichloromethane as shown in eq 1 to give [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$ as an orange powder in 70% yield. Four-coordinate species such as Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$, Re(C-*t*-Bu)(CH-*t*-Bu)($OSiMe_3$)$_2$,

$$\text{Re(N-}t\text{-Bu)}_2\text{(CH-}t\text{-Bu)(CH}_2\text{-}t\text{-Bu)} \xrightarrow[-t\text{-BuNH}_3\text{Cl}]{+3\text{lutHCl}} \xrightarrow{-3\text{lut}} 0.5[\text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(}t\text{-BuNH}_2\text{)Cl}_2]_2 \quad (1)$$

or Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ were prepared from [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$, but these complexes also did not react with internal olefins. Addition of a Lewis acid such as $AlCl_3$ *did* yield catalytically active solutions, e.g., Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$ in the presence of aluminum trichloride in dichloromethane would metathesize 170 equiv of *cis*-2-pentene to equilibrium in 15 min at room temperature.[13] (By that time active tungsten catalysts had been prepared by treating tungsten alkyl complexes with Lewis acids.[6]) However, no catalytically active intermediates were observed, so metathesis by Re(VII) still was not proven. The tedious syntheses of *tert*-butylimido complexes prevented any systematic exploration of Re(VII) at that stage.

Two events led to a reevaluation of the possibility of metathesis by complexes of the type Re(CR′)(CHR′)(OR)$_2$. First, facile routes to aryl imido complexes were developed that consisted of reactions between $ReO_3(OSiMe_3)$ and aryl isocyanates (aryl = 2,6-$C_6H_3X_2$, X = Me, *i*-Pr, Cl) to give various oxo imido species, which when treated with pyridinium hydrochloride gave crystalline, green Re(Naryl)$_2$(py)Cl_3 complexes in 70–90% overall yield based on $ReO_3(OSiMe_3)$.[14,15] Re(NAr)$_2$(py)Cl_3 (Ar = 2,6-$C_6H_3Me_2$) reacted cleanly with 1.5 equiv of dineopentyl zinc at −40 °C to give highly soluble, orange Re(NAr)$_2$(CH-*t*-Bu)(CH_2-*t*-Bu) quantitatively, a species that is analogous to previously synthesized Re(N-*t*-Bu)$_2$(CH-*t*-Bu)(CH_2-*t*-Bu). Second, complexes of the type M(CH-*t*-Bu)(NAr′)(OR)$_2$ (M = Mo or W; Ar′ = 2,6-C_6H_3-*i*-Pr$_2$) had been found to be very active metathesis catalysts for ordinary olefins when OR is strongly electron-withdrawing (e.g., OCMe(CF_3)$_2$).[16] Therefore we became convinced that Re(CR′)(CHR′)(OR)$_2$ complexes would be active for the metathesis of olefins if OR were strongly electron-withdrawing and, moreover, that relatively facile routes to such species could be developed using arylimido ligands as "protecting groups" in reactions analogous to those that had been outlined previously in *tert*-butylimido chemistry.

In this paper we describe the synthesis and characterization of complexes of the type Re(CR′)(CHR′)(OR)$_2$ and related species. Reactions of such species with olefins to give metallacyclobutane complexes, productive metathesis, reduced rhenium (Re(V)) species, and polymers (from cyclic olefins) will be described in subsequent papers.

Results

Improved Synthesis of Imido Species. A preparation of Re(NAr)$_2$(py)Cl_3 (Ar = 2,6-$C_6H_3Me_2$) that is superior to that involving ArNCO and $ReO_3(OSiMe_3)$[15] is shown in eq 2. The reaction is over in 2 h at 25 °C, and Re(NAr)$_2$(py)Cl_3 can be isolated in 86% yield after removal of pyridinium hydrochloride and recrystallization of the crude product from benzene. The procedure is equally successful starting with [NH_4][ReO_4], a

$$0.5\ Re_2O_7 + \begin{matrix}2\ ArNH_2\\ 7\ Me_3SiCl\\ \text{excess py}\end{matrix} \xrightarrow[-3.5\ (SiMe_3)_2O\\ -4\ pyHCl]{CH_2Cl_2} \begin{matrix}Cl\\ ArN{=}Re{-}py\\ ArN{=}Re{-}Cl\\ Cl\end{matrix} \quad (2)$$

somewhat less expensive rhenium source. It is most convenient to use 3 equiv of aniline in the procedure, even though only two are necessary, in order for the reaction to proceed relatively rapidly and completely. (When only two are used, the product yield is reduced to ~50% in approximately the same time period.) The most important step in this type of reaction probably is attack by aniline at the metal followed by proton transfer (either directly or stepwise employing an external base) to an oxo ligand to yield the imido analogue and water. The water then reacts with Me_3SiCl to yield hexamethyldisiloxane and HCl, and the HCl is removed from the reaction as the pyridinium salt, thereby driving what would otherwise likely be an equilibrium (see below) to the right. (More complicated variations involving ArNH($SiMe_3$) cannot be discounted but would be expected to be slower for steric reasons than reactions involving $ArNH_2$.) Re(NAr′)$_2$(py)Cl_3[15] (Ar′ = 2,6-C_6H_3-*i*-Pr$_2$) can be prepared in a similar fashion in high yield. Related syntheses of tungsten[17] and molybdenum[18] imido complexes have been developed recently.

The potential generality and superiority of this approach is illustrated by the synthesis of Re(N-*t*-Bu)$_3$($OSiMe_3$)[11] (eq 3). Upon adding *tert*-butylamine and trimethylchlorosilane to a

$$0.5Re_2O_7 + 9t\text{-BuNH}_2 + 6Me_3SiCl \xrightarrow[-6t\text{-BuNH}_3\text{Cl}\\ -2.5(SiMe_3)_2O]{CH_2Cl_2} \text{Re(N-}t\text{-Bu)}_3\text{(OSiMe}_3\text{)} \quad (3)$$

suspension of rhenium heptoxide in dichloromethane, a bright, lemon-yellow color is generated and flocculent white *t*-BuNH_3Cl precipitates immediately. In this case *tert*-butylamine acts as the trap for HCl. If the reaction is filtered after 20 min, Re(N-*t*-Bu)$_3$($OSiMe_3$) can be recovered from the filtrate in >90% yield (compared with a ~65% yield after 2 days[11]). Re(N-*t*-Bu)$_2Cl_3$ is not a product of this reaction because the HCl that is generated is removed efficiently by *tert*-butylamine, and Re(N-*t*-Bu)$_3$($OSiMe_3$) therefore is not protonated. However, when the crude reaction mixture containing Re(N-*t*-Bu)$_3$($OSiMe_3$) and *t*-BuNH_3Cl is treated with excess HCl at 0 °C, the color of the solution darkens to orange-red and an additional equivalent of *t*-BuNH_3Cl precipitates. Re(N-*t*-Bu)$_2Cl_3$[12] then can be isolated from the filtrate as large orange cubes in 85% overall yield (from Re_2O_7). Twenty grams of Re(N-*t*-Bu)$_2Cl_3$ can be prepared in about 3 h, a vast improvement over the previously reported synthesis. Therefore [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$ is now readily accessible and the preferred route to reported molecules such as Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$ or Re(C-*t*-Bu)(CH-*t*-Bu)(CH_2-*t*-Bu)$_2$. Excess *tert*-butylamine reacts with Re(N-*t*-Bu)$_2Cl_3$ to give Re(N-*t*-Bu)$_3$Cl quantitatively, most likely by double dehydrohalogenation of intermediate Re(N-*t*-Bu)$_2Cl_3$(*t*-BuNH_2) by *tert*-butylamine.

Alkylation of Re(NAr)$_2$(py)Cl_3 with 1.5 equiv of dineopentylzinc in dichloromethane produces Re(NAr)$_2$(CH-*t*-Bu)(CH_2-*t*-Bu)[15] rapidly and in high yield (eq 4); the alkylidene ligand

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Table I. Relevant NMR Data for Rhenium Alkylidene Complexes[a]

complex	δ *CHR'*	δ CHR'	J_{CH}	δ *C*R
$ReO_2(CHCMe_2Ph)(CH_2CMe_2Ph)$	12.69[b]	283.5[b]	140	
Re(O)(NAr)(CH-*t*-Bu)(CH_2-*t*-Bu)	12.29	272.4	130	
	12.72	278.6	139	
$Re(NAr)_2(CHCMe_2Ph)(CH_2CMe_2Ph)$	12.26	269.2[b]	140	
$Re(N\text{-}t\text{-}Bu)_2(CHCMe_2Ph)(CH_2CMe_2Ph)$	12.00	259.5[b]	135	
$[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ (55%)	14.49	286.3	130	292.1
	14.47			
$[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(Ar'NH_2)Cl_2]_2$	14.38			
	14.54			
$[Re(CCMe_2Ph)(CHCMe_2Ph)(t\text{-}BuNH_2)Cl_2]_2$	13.43	294.5	127	290.1
	13.48	296.0	119	289.6
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2$[d]	15.22			
	15.11			
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(Ar'NH_2)Cl_2$[d]	15.26			
	15.15			
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(py)Cl_2$[d]	15.18			
	15.09			
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(TMEDAHCl)Cl_2$[d] (75%)	14.94	304.4	127	297.7
	15.06	303.5	122	298.4
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(t\text{-}BuNH_2)_2Cl_2$	14.53	298.6[b]	131	286.2[b]
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(py)_2Cl_2$	14.04	295.3	121	298.4
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(TMEDA)Cl_2$[b]	13.13	291.7	120	291.8
$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(pda)Cl_2$	13.52	292.0[b]	118	295.6[b]
$Re(CCMe_2Ph)(CHMe_2Ph)(pda)Cl_2$[c]	13.25	285.4	122	280.4
$[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$[c]	13.26	285.8	125	293.9
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ (25%)	10.15	231.0	120[b]	288.5
(*anti*)	11.59	229.5	157	298.2
syn-$Re(CCMe_2Ph)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$	10.36	230.4[b]	124	287.3[b]
(*anti*)	11.68	228.3[b]	157	294.8[b]
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OSi(t\text{-}Bu)_3]_2$	10.40	233.6	125	294.6
(*anti*)	12.40	239.6	155	305.9
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe_2(CF_3)]_2$	10.52	238.4	123	292.2
(*anti*)	11.95	238.9	156	300.3
syn-$Re(CCMe_2Ph)(CHCMe_2Ph)[OCMe_2(CF_3)]_2$	10.73	238.6[b]	122	294.0[b]
(*anti*)	12.06	238.1[b]	160	297.0[b]
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OAr')_2$	10.72	240.0	119	293.7
(*anti*)	12.32	242.2	161	301.6
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2$ (65%)	11.08	248.8	127	295.8
(*anti*)	12.48	251.5	158	304.2
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2(PMe_3)$[b]	12.07	266.8	110	292.3
(*anti*)	12.50	265.2	148	296.8
anti-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe_2(CF_3)]_2(PMe_3)$	12.84			
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OAr')_2(PMe_3)$	13.00	283.0	110	298.7
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OAr')_2(t\text{-}BuNH_2)$	11.06	234.4[b]	123	293.1[b]
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OAr')_2(ArNH_2)$	10.49	239.0[b]	128	293.7[b]
syn-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OAr')_2(py)$	10.92			296.2

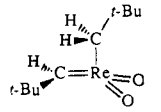
[a] Spectra recorded in C_6D_6 unless otherwise noted. [b] CD_2Cl_2. [c] THF-d_8. [d] Observed in situ.

is formed by α hydrogen abstraction in intermediate $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)_3$. An analogous alkylation employing Zn-

$$Re(NAr)(py)Cl_3 \xrightarrow[-1.5ZnCl_2\text{-}py\text{-}CMe_4]{1.5Zn(CH_2\text{-}t\text{-}Bu)_2} Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \quad (4)$$

$(CH_2CMe_2Ph)_2$ gives $Re(NAr)_2(CHCMe_2Ph)(CH_2CMe_2Ph)$, a new compound that is similar to the neopentylidene species. (See Table I for NMR data.) The neophyl system has several advantages over the neopentyl system. First, neophyl Grignard reagents can be prepared smoothly, unlike the sometimes fickle neopentyl Grignard reagent. Second, the phenyl ring and the potentially inequivalent methyl groups in the neophyl ligand are two additional NMR probes. Third, neophyl chloride is a small fraction of the cost of neopentyl chloride. If $PhMe_2CCH_2MgCl$ is used to alkylate $Re(NAr)_2Cl_3$, $Re(NAr)_2(CHCMe_2Ph)(CH_2CMe_2Ph)$ is obtained as a dark orange oil contaminated by $PhMe_2C(CH_2)_2CMe_2Ph$. Such a crude product often can be used directly for subsequent chemistry and the $PhMe_2C(CH_2)_2CMe_2Ph$ impurity removed at a later stage. At this point the neophyl system has not been as extensively explored as the neopentyl system, but what has been done so far for Re, and more extensively for Mo,[18] suggests that the chemistry of neopentyl and neophyl-based compounds is very similar, as one might expect.

$ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ has been prepared by photolysis of $ReO_2(CH_2\text{-}t\text{-}Bu)_3$ in pyridine with a medium pressure mercury lamp.[19] (In comparison $Re(NR)_2(CH_2\text{-}t\text{-}Bu)_3$ compounds apparently decompose thermally to $Re(NR)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ (R = *t*-Bu or Ar).) $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ is inactive for the metathesis of olefins. An X-ray study revealed that $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ has a pseudotetrahedral geometry in which the plane of the alkylidene ligand lies perpendicular to a plane defined by the neopentyl ligand, rhenium, and C_α of the alkylidene ligand, viz.



This structure can be explained if the ReO_2 fragment is viewed as being analogous to a metallocene fragment, with each oxo behaving as a $2\pi,1\sigma$ ligand, as has been proposed for the $M(NR)_2$ fragment in a variety of pseudotetrahedral species.[20,21] We propose that the structures of $Re(NR)_2(CHCMe_2Ph)(CH_2CMe_2Ph)$ and $Re(NR)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ (R = *t*-Bu or Ar) are analogous to that of $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ on

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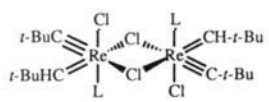
Table II. Intramolecular Bond Distances (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$

Bond Distances			
Re–C(6)	1.76 (1)	Re–Cl(1)	2.619 (3)
Re–C(1)	1.89 (1)	Re–Cl(2)	2.397 (4)
Re–N	2.21 (1)	Re*–Cl(1)	2.673 (4)
Bond Angles			
C(6)–Re–C(1)	100.6 (5)	Re–C(6)–C(7)	167 (1)
C(6)–Re–N	101.3 (5)	N–Re–Cl(1)	79.0 (3)
C(6)–Re–Cl(2)	92.9 (4)	N–Re–Cl(1)	78.9 (3)
C(6)–Re–Cl(1)	172.3 (4)	Cl(2)–Re–Cl(1)	85.2 (1)
C(1)–Re–N	96.1 (4)	Cl(2)–Re–Cl(1)	85.1 (1)
C(1)–Re–Cl(2)	95.6 (4)	Cl(1)–Re–Cl(1)	77.1 (1)
C(1)–Re–Cl(1)	163.9 (4)	Re–Cl(1)–Re	102.9 (1)
C(1)–Re–Cl(1)	87.0 (4)	Re–N–C(11)	120.7 (7)
N–Re–Cl(2)	159.6 (3)		

the basis of NMR data, i.e., the imido ligands are inequivalent and the methylene protons in the neophyl or neopentyl ligands are diastereotopic.

Synthesis and X-ray Structure of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$. Addition of excess HCl(g) to $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ in dimethoxyethane yields $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ in 85% isolated yield as pale orange crystals (eq 5). Remarkably, the synthesis of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ can be carried out on the benchtop in air with

$$2\ Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) + 6\ HCl \xrightarrow[-\ ArNH_3Cl]{dme} L = ArNH_2 \quad (5)$$



aqueous HCl! This result is particularly interesting because metal–carbon double and triple bonds are formed in the presence of both oxygen and water. We have no reason to suspect that the mechanism of forming $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ differs substantially from that proposed for the formation of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(t\text{-}BuNH_2)Cl_2]_2$.[12] A key feature is that the alkylidene ligand is the first to lose a proton (to form the alkylidyne ligand and an amido ligand), and the alkyl ligand then loses a proton to form the alkylidene ligand.

The structure of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$, as determined in an X-ray study, is shown in Figure 1. (Bond distances and angles can be found in Table II.) The coordination sphere around each metal is a distorted octahedron with relatively long, approximately equal Re–Cl bonds trans to the neopentylidene and neopentylidyne ligands. The rhenium–carbon bonds of both the alkylidene ligand (1.89 (1) Å) and the alkylidyne ligand (1.76 (1) Å) are similar to those observed in previously characterized $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(py)_2I_2$ (1.873 (9) and 1.742 (9) Å).[12] The Re≡C bond length is also identical to that found in $Re(\eta^5\text{-}C_5Me_5)(C\text{-}t\text{-}Bu)Br_3$ (1.755 (6) Å).[22] Note that the *tert*-butyl group of the neopentylidene ligand is pointing toward the neopentylidyne ligand, the syn orientation. The Re–C_α–C_β angle of the alkylidene ligand (140 (1)°) is among the smallest observed for a high oxidation state *syn*-alkylidene complex. The Re–C_α–C_β angle of the alkylidyne ligand (167 (1)°) is somewhat smaller than is normally observed in high oxidation state metal alkylidyne complexes, probably for steric reasons.[23] (It is bent away from the *syn*-neopentylidene ligand.) The C(1)–Re–C(6) angle between the alkylidene and alkylidyne α carbon atoms (100.6 (5)°) is comparable to that observed in $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(py)_2I_2$ (98.11 (42)°).[12] The tendency for mutually cis multiply bonded ligands to repel one another has been observed many times previously in similar complexes, e.g., $W(O)(CH\text{-}t\text{-}Bu)(PMe_3)_2Cl_2$,[24]

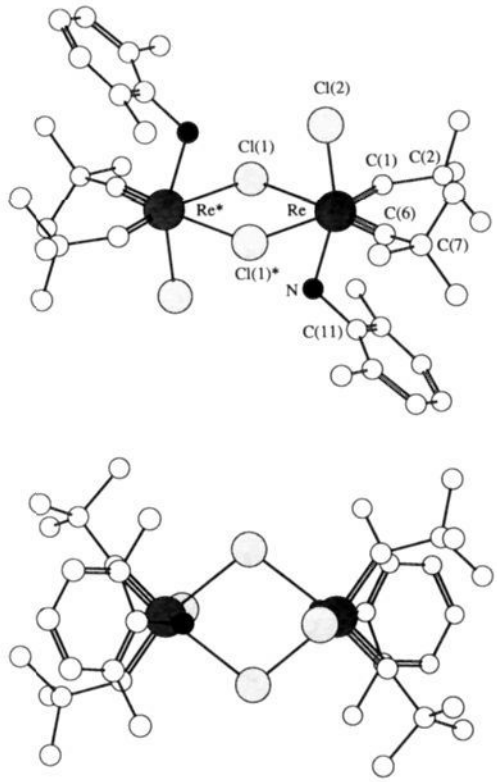


Figure 1. Two views of the structure of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$.

$W(O)(CH\text{-}t\text{-}Bu)(PEt_3)_2Cl_2$,[25] $Ta(CH\text{-}t\text{-}Bu)_2(mesityl)(PMe_3)_2$,[26] $W(C\text{-}t\text{-}Bu)(PHPh)(PMe_3)_2Cl_2$,[27] and $Mo(NAr')(CH\text{-}t\text{-}Bu)(OTf)_2(dme)$.[18]

NMR studies show that two very similar isomers of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ are present in solution in a 55:45 ratio (in C_6D_6), the major isomer having δ H_α 14.49 (in C_6D_6), δ Re≡C_α 292.1 (THF-d_8), and δ Re=C_α 286.3 (THF-d_8; J_{CH} = 130) and the minor isomer having δ H_α 14.47 (in C_6D_6). (As a result of the poor solubility of these isomers, quality ^{13}C NMR data for the minor isomer could not be obtained.) The C–H coupling constants of the alkylidene ligands in analogous isomers of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(t\text{-}BuNH_2)Cl_2]_2$[12] are identical (120, 120 Hz) and virtually identical in closely related $[Re(CCMe_2Ph)(CHCMe_2Ph)(ArNH_2)Cl_2]_2$ (119, 127 Hz; Table I). The precise nature of the isomers is uncertain. The amine ligands could be cisoid, for example, or the alkylidene ligands could be anti in an otherwise analogous centrosymmetric dimer. Dimer/monomer or dimer/tetramer equilibria are less likely since the ratio of the two isomers does not appear to vary with concentration, and, more importantly, what appear to be two isomeric, pentane soluble monomers *can* be observed in a 3:1 ratio during the early stages of the reaction.

Upon addition of HCl(g) to a solution of orange $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ in dimethoxyethane, the color darkens and $ArNH_3Cl$ precipitates. If $ArNH_3Cl$ is filtered off and the solution is reduced to dryness quickly in vacuo, the ^1H NMR spectrum of the residue in C_6D_6 shows four alkylidene resonances, two of which (at δ 14.49 and 14.47) belong to the isomers of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ mentioned above and two (δ 15.22 and 15.12) to what we propose are two isomers of $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2$. When this crude product is taken up in pentane, more $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ precipitates out and the proton NMR spectrum of the remaining material obtained by removing pentane in vacuo shows that the

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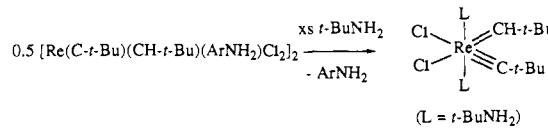
set of alkylidene resonances for the monomer have decreased relative to those for the dimer. This behavior is consistent with initial formation of two isomers of Re(C-*t*-Bu)(CH-*t*-Bu)-$(ArNH_2)Cl_2$ followed by dimerization in a hydrocarbon solvent. (Dimethoxyethane may coordinate to Re initially and therefore help stabilize monomers toward dimerization.) The isomers of the monomeric complexes do not appear to be syn and anti rotamers, as J_{CH_α} values for the two are identical. (See below for discussion of J_{CH_α} in syn and anti rotamers.)

There is abundant evidence that other monomeric complexes of the type Re(CH-*t*-Bu)(CH_2-*t*-Bu)(L)Cl_2 form, but unfortunately they cannot be isolated free of the dimeric forms, and therefore have been observed only in solution by NMR. For example, when $Re(NAr')_2$(CH-*t*-Bu)(CH_2-*t*-Bu) is treated with excess HCl (Ar' = 2,6-C_6H_3-*i*-Pr_2), two isomers of monomeric Re(C-*t*-Bu)(CH-*t*-Bu)(Ar'NH_2)Cl_2 are the only observed organometallic products initially (δ H_α = 15.26 and 15.15). These dimerize in pentane (qualitatively much more slowly than those of Re(C-*t*-Bu)(CH-*t*-Bu)($ArNH_2$)Cl_2, as one might expect for steric reasons) to give [Re(C-*t*-Bu)(CH-*t*-Bu)(Ar'NH_2)Cl_2]$_2$ (δ H_α = 14.38 and 14.54).

On the other hand some bis adducts can be isolated. For example, addition of excess *tert*-butylamine to [Re(C-*t*-Bu)(CH-*t*-Bu)($ArNH_2$)Cl_2]$_2$ affords a single isomer of Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)$_2Cl_2$ in 95% yield as bright yellow fibers (eq 6). It is proposed to be the species shown on the basis of the fact that



(6)

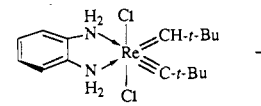
the *tert*-butylamine ligands are equivalent down to −80 °C by NMR (^1H and ^{13}C), and the NH_2 protons are diastereotopic. The reaction takes several hours to go to completion at 25 °C because the rapidly formed initial product, [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$, reacts only slowly with additional *tert*-butylamine, we presume via monomeric Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2. Once isolated, Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)$_2Cl_2$ is stable to moist air for weeks. It does not react with excess gaseous HCl(g) in a solvent such as ether to give [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$.

Addition of excess pyridine to a dichloromethane solution of [Re(C-*t*-Bu)(CH-*t*-Bu)($ArNH_2$)Cl_2]$_2$ yields pale orange Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2Cl_2$ quantitatively in less than 20 min. In contrast, [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$ does not react readily with pyridine. (In the presence of $SiMe_3I$ and pyridine, Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2I_2$ is obtained.[12]) These results are consistent with the presence of a small amount of monomeric Re(C-*t*-Bu)(CH-*t*-Bu)($ArNH_2$)Cl_2 in equilibrium with [Re(C-*t*-Bu)(CH-*t*-Bu)($ArNH_2$)Cl_2]$_2$, whereas [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2]$_2$ does not form monomeric Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH_2)Cl_2 nearly as readily. Only a single isomer of Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2Cl_2$ is observed. Addition of excess HCl(g) to Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2Cl_2$ yields 1 equiv of pyridinium chloride and two isomers of what we propose is Re(C-*t*-Bu)(CH-*t*-Bu)(py)Cl_2 in solution, on the basis of NMR characteristics that are similar to those of Re(C-*t*-Bu)(CH-*t*-Bu)-($ArNH_2$)Cl_2 (Table I). An insoluble pale pink powder precipitates from C_6D_6 or CD_2Cl_2 solutions of Re(C-*t*-Bu)(CH-*t*-Bu)(py)Cl_2 that we formulate as [Re(C-*t*-Bu)(CH-*t*-Bu)(py)Cl_2]$_2$ on the basis of its ^1H NMR spectrum in pyridine-d_5. Once [Re(C-*t*-Bu)-(CH-*t*-Bu)(py)Cl_2]$_2$ is formed, it does not react with excess pyridine readily to give Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2Cl_2$ back again.

Synthesis of Oxo Derivatives and [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$. It would be most desirable to synthesize a versatile precursor to any complex of the type Re(CR')(CHR')$(OR)_2$ that either contains no base, or a base that is relatively innocuous and labile, e.g., 1,2-dimethoxyethane. (Universal precursors of the type M(CH-*t*-Bu)(NAr')$(OTf)_2$(dme) (M = Mo or W; dme = 1,2-dimethoxyethane; OTf = triflate) react even with an electron-withdrawing alkoxide such as $OCMe(CF_3)_2$ and lose dme in the process.)[17,18] An amine is an unsatisfactory ligand for general use since alkoxides will remove amine protons in some circumstances to regenerate amido and imido species (see later). Since the bases in five-coordinate adducts of the type Re(C-*t*-Bu)-(CH-*t*-Bu)(L)Cl_2 are not protonated to give [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$, we speculated that a bidentate amine adduct of the Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2 core might stand a better chance of producing [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ upon addition of HCl, i.e., protonation of one end of the amine ligand might force the other end to dissociate and be trapped by a second equivalent of acid.

Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA)Cl_2 was synthesized in a manner analogous to that described for Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2Cl_2$. Only a single isomer was observed. Unfortunately, however, although TMEDA was protonated upon adding excess HCl(g) to Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA)Cl_2, the proton NMR characteristics of the resulting complex are virtually identical to those described for the Re(C-*t*-Bu)(CH-*t*-Bu)(L)Cl_2 species above, consistent with the formulation Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA·HCl)Cl_2, i.e., only one end of the TMEDA ligand is protonated. Two isomers are observed that have similar values for J_{CH} (122, 127 Hz) in the alkylidene ligands.

Formation of a stable monoprotonated adduct could be avoided if a diamine is used that has a rigid backbone, since when one end of the diamine is protonated it should not be able to swing away from the metal and therefore should more likely dissociate. [Re(C-*t*-Bu)(CH-*t*-Bu)($ArNH_2$)Cl_2]$_2$ reacts cleanly with 1,2-phenylenediamine (pda) in dimethoxyethane to afford the corresponding monomeric complex, Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl_2 (eq 7). When Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl_2 is treated with 2 equiv of HCl(g) in dme the diprotonated diamine precipitates out



+ 2 HCl, -pda·2HCl → [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ (7)

of solution and can be filtered off. What remains in solution is almost certainly Re(C-*t*-Bu)(CH-*t*-Bu)(dme)Cl_2, but when the dme is removed in vacuo [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ ($x > 1$) is isolated in >85% yield as a pale orange solid. [Re(C-*t*-Bu)-(CH-*t*-Bu)Cl_2]$_x$ is insoluble in noncoordinating solvents but dissolves readily in dimethoxyethane or THF. [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ is stable to air and water for several days in the solid state. Amazingly, a proton NMR spectrum of [Re(C-*t*-Bu)-(CH-*t*-Bu)Cl_2]$_x$ can be obtained in D_2O, and the complex can be recovered unchanged! When solutions of [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ in water, THF, or dme are reduced to dryness in vacuo, crystals are obtained first, but they turn to a powder when left under vacuum for more than a few minutes at room temperature. We speculate that these crystals are initially at least bis solvates, i.e., Re(C-*t*-Bu)(CH-*t*-Bu)S_2Cl_2 (S = THF, H_2O, $^1/_2$ dme). [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ also is stable to oxygen in THF as long as some water (≥1 equiv) is present, but in the absence of water, it reacts with oxygen slowly (5 h, 1 atm, THF-d_8) to yield pivaldehyde (50% versus an internal standard) and several unidentified products. The major product (38%) in the ^1H NMR spectrum appears to form at the same time as pivaldehyde. Attempts to isolate this presumably organometallic product were unsuccessful, as it apparently is unstable once the solvent is removed. Although Re(C-*t*-Bu)(O)Cl_2(THF)$_x$ is an attractive proposal for this transient species, we have no independent evidence for this formulation. Similar reactions with oxygen do not occur to any significant extent in dimethoxyethane, presumably because dme binds more strongly than THF to give a pseudooctahedral species.

Since [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ is stable to water at neutral pH and loses any coordinated water in vacuo in the solid state, we thought that addition of excess HCl to ReO_2(CH-*t*-Bu)-(CH_2-*t*-Bu) could yield [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ after removing coordinated water in vacuo from "Re(C-*t*-Bu)(CH-*t*-Bu)$(H_2O)_2Cl_2$" or "[Re(C-*t*-Bu)(CH-*t*-Bu)(H_2O)Cl_2]$_x$" (x = 1 or 2). Unfortunately, although ReO_2(CH-*t*-Bu)(CH_2-*t*-Bu) can be prepared in high yield from ReO_2(CH_2-*t*-Bu)$_3$ by photolysis,[19] ReO_2(CH_2-*t*-Bu)$_3$ itself was originally produced in only 6% yield,

making this an unlikely entry into rhenium alkylidyne chemistry on a multigram scale. Therefore we explored the possibility of hydrolyzing $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ to give $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$. If successful, one step in the synthesis of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ (formation of the pda complex) could be eliminated.

$Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ reacts with water slowly in C_6D_6 over a period of ~3 h at room temperature to give 1 equiv of 2,6-dimethylaniline and a new organometallic product quantitatively (according to ^1H NMR). The ^1H NMR spectrum of this product (δ H_α = 12.29) is similar to that of the starting material; we formulate it as $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ (eq 8). A second isomer (δ H_α = 12.72) is typically observed in trace amounts (~5%) and is discussed in more detail below. It should be noted that $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ contains simultaneously a metal–carbon double bond, a metal–oxygen double bond, and a metal–nitrogen double bond; it may be the only example. Reaction of the crude product (with the aniline present) with HCl(g) forms $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ quantitatively.

$$Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) + H_2O \xrightarrow[-ArNH_2]{\text{pentane}} Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \quad (8)$$

Further hydrolysis of $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ to give $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ requires several days to go to completion. When pyridine or aqueous NaOD is added to a C_6D_6 solution containing $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ and water, no reaction, even to give $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$, is observed after several days. However, when aqueous acids such as acetic acid, HPF_6, or HBF_4 are added to a C_6D_6 solution of $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$, $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ forms within minutes. Unfortunately, $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ reacts further with acids to give uncharacterized mixtures, so this method does not appear to be amenable to large scale preparations. However, neutral alumina will catalyze the transformation of $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ to $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ in high yield (eq 9), although this reaction occasionally does not proceed smoothly. Several grams of $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ usually can be prepared by this method.

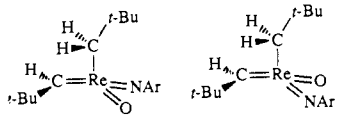
$$Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) + 2H_2O \xrightarrow[-2ArNH_2]{\text{cat.}} ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \quad (9)$$

Hydrolyses of $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ and $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ produce nonvolatile 2,6-dimethylaniline. It can be removed from the reaction mixture by adding zinc dichloride. For example, addition of $ZnCl_2$(dioxane) to a pentane solution containing 2,6-dimethylaniline and $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ yields a precipitate of $ZnCl_2(ArNH_2)_2$. Filtration affords relatively pure $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$, which then is more easily crystallized or used directly in subsequent reactions. It is important that the zinc dichloride treatment be performed in hydrocarbon solvent; in ether, for example, zinc dichloride forms an adduct with $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$, from which it cannot be removed readily.

The identity of $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ is further established by the fact that it is formed by conproportionation of $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ and $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ over a period of 2 days (eq 10). On the basis of these data alone we cannot tell whether only the oxo and imido ligands are

$$Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) + ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \rightleftarrows 2Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \quad (10)$$
(two isomers)

migrating from one metal to another. (Analogous oxo/imido exchange reactions have been observed recently between Mo centers; $Mo(NAr')_2(O\text{-}t\text{-}Bu)_2$ and $MoO_2(O\text{-}t\text{-}Bu)_2$ conproportionate to give a mixture containing $Mo(NAr')(O)(O\text{-}t\text{-}Bu)_2$.[28]) Interestingly, in the conproportionation reaction the isomer of $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ that gives rise to the H_α resonance at 12.72 ppm predominates, typically comprising ~70% of the mixture of $ReNAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ isomers. ^1H and ^{13}C NMR spectra of the two isomers are very similar (Table I). Since the structure of $Re(NAr)(O)(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ is almost certainly analogous to that of $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$, we propose that in the two isomers the *tert*-butyl group of the neopentylidene ligand may either point toward the oxo ligand or toward the imido ligand, viz.



and that interconversion of the two isomers, e.g., by intramolecular rotation about the Re=C bond, is slow on the chemical time scale.

Addition of 2 equiv of HCl(g) to $ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ in dimethoxyethane affords $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ in high yield after removing the dimethoxyethane and water in vacuo (eq 11). Presumably water and/or dme adducts are present initially, even in the solid state (see above), but both water and dme are lost in vacuo. This synthetic method bypasses the need to make $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(ArNH_2)Cl_2]_2$ and $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(pda)Cl_2$. Therefore $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ can be prepared from Re_2O_7 or $[NH_4]ReO_4$ in four high yield steps (eq 12). It is the precursor that is required for preparing compounds containing relatively electrophilic alkoxides (see below).

$$Re(O)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) + 2HCl \xrightarrow[-2H_2O]{\text{DME}} [Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x \quad (11)$$

$$Re_2O_7 \rightarrow Re(NAr)_2(py)Cl_3 \rightarrow Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \rightarrow ReO_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu) \rightarrow [Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x \quad (12)$$

Synthesis of Alkoxide Complexes, $Re(CR')(CHR')(OR)_2$ (R' = *t*-Bu or CMe_2Ph). $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ reacts with 2 equiv of lithium *tert*-butoxide in tetrahydrofuran to yield previously reported $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$[12] quantitatively, while addition of 2 equiv of $LiOCMe_2(CF_3)$ or $KOCMe(CF_3)_2$ yields $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe_2(CF_3)]_2$ or $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe(CF_3)_2]_2$, respectively (eq 13). If only 1 equiv

$$[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x + 2MOR \xrightarrow[-2MCl]{\text{THF}} Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OR)_2 \quad (13)$$
M = K or Li

of lithium alkoxide is added to $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ a 50% yield of $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(OR)_2$ is obtained. $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe_2(CF_3)]_2$, like $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$, is a low-melting yellow solid that is extremely soluble in pentane. It can be obtained as yellow crystals from pentane at −40 °C, but these melt to an orange oil at room temperature. All three derivatives sublime readily (30–40 °C, 10^{-5} Torr) but show some tendency to decompose when left in the solid state at room temperature for more than several hours. They are stable indefinitely in solution (0.1 M in C_6D_6) or as solids when stored at −40 °C.

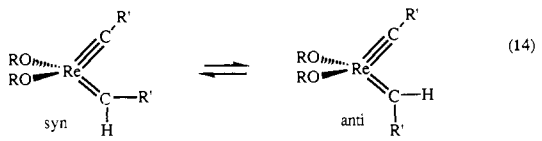
When bisalkoxide complexes are first obtained from $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$, exclusively one alkylidene complex is observed. When these complexes are heated, a mixture of two alkylidene complexes is obtained, the ratio varying with the steric bulk and electronic nature of the ligands. The new alkylidene H_α resonance is always found downfield of the H_α resonance in the initial species. Consistently J_{CH} is relatively low (~120–125) in the initial isomer and relatively high (~155–160) in the second isomer (Table I). All data are fully consistent with the isomers being syn and anti rotamers, respectively, the syn rotamer being that in which the substituent on the alkylidene ligand points toward the alkylidyne ligand (eq 14). (Syn and anti isomers are well-known in $M(CHR')(NAr')(OR)_2$ complexes.[29]) Syn and anti

(28) Mitchell, J.; Gibson, V. C., personal communication.
(29) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

Table III. Intramolecular Bond Distances (Å) and Bond Angles (deg) for the Non-Hydrogen Atoms of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[$OCMe(CF_3)_2$]$_2$(THF)

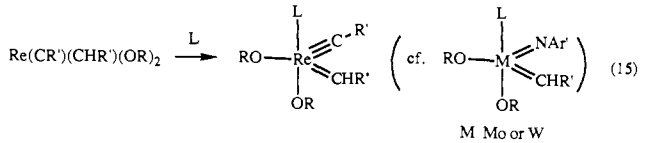
Bond Distances			
Re–O(1)	1.954 (7)	Re–C(1)	1.75 (1)
Re–O(2)	1.954 (7)	Re–C(2)	1.85 (1)
Re–O(3)	2.398 (8)	C(1)–C(11)	1.46 (2)
		C(2)–C(15)	1.47 (2)
Bond Angles			
O(1)–Re–O(2)	128.6 (3)	O(3)–Re–C(1)	168.7 (4)
O(1)–Re–O(3)	73.1 (3)	O(3)–Re–C(2)	88.7 (4)
O(1)–Re–C(1)	104.6 (5)	C(1)–Re–C(2)	102.5 (6)
O(1)–Re–C(2)	107.0 (4)	Re–O(1)–C(3)	142.7 (8)
O(2)–Re–O(3)	73.8 (3)	Re–O(2)–C(7)	142.9 (8)
O(2)–Re–C(1)	100.3 (4)	Re–C(1)–C(11)	175 (1)
O(2)–Re–C(2)	110.4 (4)	Re–C(2)–C(15)	151 (1)

rotamers can be interconverted, either thermally or photochemically, as discussed in the next section. The final equilibrium values are listed in Table IV.



(14)

Nitrogen or phosphorous base adducts of Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$ species can be prepared readily by adding excess base to a solution of the alkylidene complex at room temperature. For example, PMe_3 yields five-coordinate monoadducts in which the phosphine ligand is firmly bound to the metal on the NMR time scale. The syn rotamer gives rise to a syn adduct and given syn/anti mixture to the same mixture of syn/anti adducts. In both syn and anti rotamers the alkoxide ligands are inequivalent by NMR. One plausible structure is a trigonal bipyramid in which the alkylidyne and alkylidene ligands lie in the equatorial plane (eq 15). This structure is attractive on the basis of the recent



(15)

crystallographic characterization of syn and anti adducts of M(CH-*t*-Bu)(NAr')$(OR)_2$ complexes.[29] However, the X-ray structure of an analogous THF adduct (see next section) shows it to be approximately a trigonal bipyramid in which the axial THF is bound trans to the neopentylidyne ligand. Therefore other possible structures for the phosphine adducts cannot be ruled out, and there is no reason why syn and anti structures need be analogous. (In one type of Mo complex it has been shown that syn and anti rotamers have the same basic structure.[29])

Phenoxide complexes can be prepared by adding 2 equiv of the appropriate lithium phenoxide to [Re(C-*t*-Bu)(CH-*t*-Bu)$Cl_2]_x$ in dichloromethane (e.g., eq 16). Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2$ is obtained as a dark orange oil. The initial rotamer is again virtually pure syn, but the anti rotamer forms upon heating (slowly) or

$$[\text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)Cl}_2]_x + 2\text{LiOAr'(ether)} \xrightarrow[-2\text{LiCl}]{\text{CH}_2\text{Cl}_2} \text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(OAr')}_2 \quad (16)$$

photolysis (more rapidly). If tetrahydrofuran is the solvent, then five-coordinate tetrahydrofuran adducts are isolated as bright yellow crystals. These adducts become sticky in vacuo as THF is lost (according to proton NMR studies), but loss of THF soon slows considerably so that the final sticky materials that are obtained contain approximately 0.75 equiv of THF, i.e., Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2(THF)_x$ ($1 > x > 0.75$). All of the Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$ complexes discussed so far react with excess HCl(g) to afford [Re(C-*t*-Bu)(CH-*t*-Bu)$Cl_2]_x$ quantitatively, although isolation and purification is difficult when the alcohol that is formed is relatively nonvolatile.

In the first report of Re(C-*t*-Bu)(CH-*t*-Bu)$(O\text{-}t\text{-Bu})_2$,[12] rotamers were not mentioned. However, when Re(C-*t*-Bu)(CH-*t*-Bu)$(O\text{-}t\text{-Bu})_2$ is prepared from [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-$BuNH_2)Cl_2]_2$ we find that a mixture of syn and anti rotamers, in fact, is formed. Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe_2(CF_3)]_2$ also can be prepared from [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-$BuNH_2)Cl_2]_2$, the product in this case being predominantly the anti rotamer. When [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-$BuNH_2)Cl_2]_2$ is treated with LiOAr', pure *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2$ is formed. However, when [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-$BuNH_2)Cl_2]_2$ is treated with KOC-$Me(CF_3)_2$, an unidentifiable mixture of products is formed. In contrast, [Re(C-*t*-Bu)(CH-*t*-Bu)$(ArNH_2)Cl_2]_2$ does not react cleanly with MO-*t*-Bu, $MOCMe_2(CF_3)$, or $MOCMe(CF_3)_2$ (M = Li or K) to afford Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$ derivatives. (We suspect that bound aniline in [Re(C-*t*-Bu)(CH-*t*-Bu)-$(ArNH_2)Cl_2]_2$ is more prone to lose a proton to give an amido ligand than bound *tert*-butylamine, as one might expect on the basis of the relative acidities of the two amines.)

When 2 equiv of LiOAr' are added to [Re(C-*t*-Bu)(CH-*t*-Bu)$(ArNH_2)Cl_2]_2$ in dichloromethane or tetrahydrofuran, Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2(ArNH_2)$ is obtained in 80% isolated yield as bright yellow crystals (eq 17). [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-$BuNH_2)Cl_2]_2$ affords Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2$(*t*-$BuNH_2)$ in a similar yield, while Re(C-*t*-Bu)(CH-*t*-Bu)-$(OAr')_2$(py) is obtained from Re(C-*t*-Bu)(CH-*t*-Bu)$(py)_2Cl_2$. The *tert*-butylamine ligand in Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2$(*t*-$BuNH_2)$ must be lost readily since treating a pentane solution of Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2$(*t*-$BuNH_2)$ with methyl trifluoromethanesulfonate yields a precipitate of white *t*-$BuNH_2Me^+OTf^-$ and a solution containing Re(C-*t*-Bu)(CH-*t*-Bu)$(OAr')_2$.

$$[\text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(ArNH}_2\text{)Cl}_2]_2 + 2\text{LiOAr'(ether)} \xrightarrow[-2\text{LiCl}]{\text{CH}_2\text{Cl}_2} \text{Re(C-}t\text{-Bu)(CH-}t\text{-Bu)(OAr')}_2\text{(ArNH}_2\text{)} \quad (17)$$

X-ray Study of Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$(THF). When reaction mixtures containing *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$ are reduced to dryness in vacuo at room temperature, yellow-orange crystals of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$(THF) are obtained initially. Over a period of 45 min in vacuo this solid melts to an orange oil that does not contain THF and has an NMR spectrum that is consistent with it being Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$. In C_6D_6 solution, the THF ligand in *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2$-(THF) exchanges rapidly on the NMR time scale.

Views of the structure of Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe-$(CF_3)_2]_2$(THF) are shown in Figures 2 and 3. Since the alkoxide and alkylidene ligands are bent away from the alkylidyne ligand (100–105°, Table III) toward the weakly bound THF ligand (73–89°, Re–O(3) = 2.398 (8) Å), the geometry is best described as a face-capped tetrahedron. The structure also could be described as a severely distorted trigonal bipyramid in which the central rhenium atom lies 0.18 Å above the plane defined by the three "equatorial" atoms (O(1), O(2), and C(2)). The alkylidene and alkylidyne ligands are mutually cis, with the C(1)–Re–C(2)

Table IV. Activation Parameters and Equilibria Data for Alkylidene Isomerization in Complexes of the General Formula Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$[a]

OR	$\Delta G^{\ddagger}_{298}$[b]	$\Delta H^{\ddagger}_{298}$[b]	$\Delta S^{\ddagger}_{298}$[c]	rel rate[d]	% anti (Δ)	% anti (*hν*)
$OCMe_3$	25.3 (2)	19.5 (9)	−20 (2)	494	72 (1)	30 (1)
$OCMe_2(CF_3)$	28.0 (2)	23.4 (9)	−15 (2)	25	81 (1)	32 (1)
$OCMe(CF_3)_2$	30.3 (2)	25.5 (9)	−16 (2)	1	81 (1)	34 (1)

[a] Toluene-d_8 solvent. 1,4-Dichlorobenzene was used as an internal standard. [b] kcal mol^{-1}. [c] Eu. [d] 110 °C.

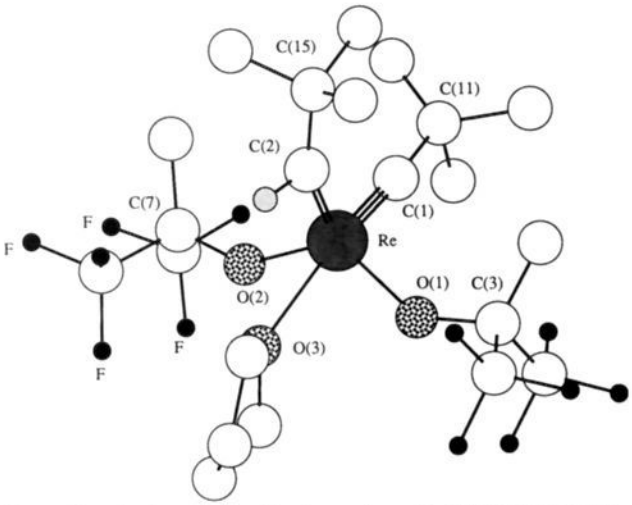


Figure 2. A view of the structure of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)-$[OCMe(CF_3)_2]_2(THF)$.

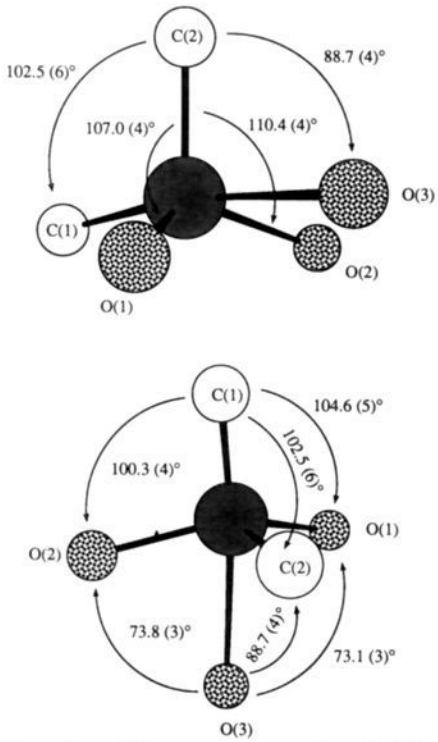


Figure 3. Two views of the core geometry of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe(CF_3)_2]_2(THF)$.

angle (102.5 (6)°) being typical of mutually cis ligands that are multiply bonded to the metal, as discussed previously for [Re(C-*t*-Bu)(CH-*t*-Bu)$(ArNH_2)Cl_2]_2$. The neopentylidene Re=C distance of 1.85 (1) Å is slightly shorter than Re=C distances in [Re(C-*t*-Bu)(CH-*t*-Bu)$(ArNH_2)Cl_2]_2$ (1.89 (1) Å) and Re(C-*t*-Bu)(CH-*t*-Bu)$(py)_2I_2$ (1.873 (9) Å), while the Re–C(2)–C(15) angle of 151 (1)° is more comparable to that in Re(C-*t*-Bu)(CH-*t*-Bu)$(py)_2I_2$ (150.3 (7)°) than in [Re(C-*t*-Bu)(CH-*t*-Bu)$(ArNH_2)Cl_2]_2$ (140 (1)°). The neopentylidyne is slightly bent (175 (1)°), and the Re–C(1) distance of 1.75 (1) Å is typical of high oxidation state rhenium alkylidyne complexes. The THF ligand is apparently only weakly bound as evidenced by the Re–O(3) distance (2.398 (8) Å), which is statistically longer than that in *syn*-Re(CH-*t*-Bu)(NAr')$(OC_6F_5)_3$(THF) (2.339 (5) Å),[30] and by the facile loss of THF from the complex in vacuo. The Re–O–C angles of the alkoxide ligands (142.7 (8)° and 142.9 (8)°

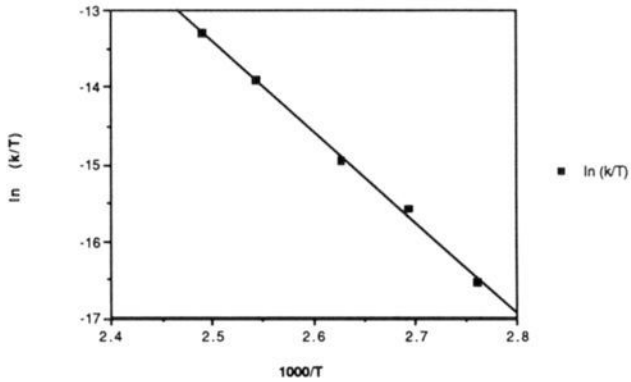


Figure 4. Eyring plot of rate constants for the syn/anti rotamer interconversion in Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe_2(CF_3)]_2$.

suggest that each may be donating some π electron density to the metal, although the magnitude of that angle alone is not a good measure of the extent of π bonding in an alkoxide ligand.[31]

An interesting feature of this structure is the bonding of the THF ligand in a position cis to the alkylidene ligand, but not one that is adjacent to one π-face of the neopentylidene Re=C bond. Therefore, if the THF were replaced by an olefin, the neopentylidene ligand would not be oriented correctly for a metallacyclobutane ring to form without rearrangement of the ligand sphere or a ninety degree rotation of the alkylidene ligand. Given that alkylidene rotation in this species is extremely slow (ca. 10^{-10} s^{-1}) at room temperature (see next section) and is even slower in five-coordinate species, it seems highly improbable that alkylidene rotation could precede formation of a metallacycle in this system.

Interconversion of Syn and Anti Rotamers. As mentioned above, syn and anti rotamers interconvert slowly thermally and more rapidly photochemically (in benzene or toluene upon irradiation with a medium pressure Hg lamp). Several experiments were carried out in order to determine whether alkylidene rotation is in fact an intramolecular process, and how the rate of rotation varies with the nature of the alkoxide.

A mixture of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)$(O\text{-}t\text{-}Bu)_2$ and *syn*-Re$(CCMe_2Ph)(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$ was photolyzed in C_6D_6 though Pyrex with a medium pressure mercury lamp for 1 h. Each syn complex turned into a mixture of syn and anti rotamers (30% and 32% anti, respectively), but there was no evidence for any "crossover" products (e.g., Re(C-*t*-Bu)$(CHCMe_2Ph)(O\text{-}t\text{-}Bu)_2$). Photolysis for an additional 9 h produced no further change. Heating equilibrated mixtures to 60 °C for several hours also yielded no crossover products. These data suggest that alkylidene or alkylidyne ligands do not transfer from one metal to another under the conditions employed for interconversion of rotamers.

On the other hand, an NMR spectrum of a mixture of Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe_2(CF_3)]_2$ and Re(C-*t*-Bu)(CH-*t*-Bu)$(O\text{-}t\text{-}Bu)_2$ showed that Re(C-*t*-Bu)(CH-*t*-Bu)$[OCMe_2(CF_3)](O\text{-}t\text{-}Bu)$ was present within minutes at 25 °C as approximately 90% of the mixture. Therefore, O-*t*-Bu and $OCMe_2(CF_3)$ ligands exchange rapidly on the chemical time scale at room temperature in complexes of this type. Alkoxide exchange recently also has been found to be rapid in systems of the type M(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-$Pr_2)(OR)_2$.[28]

The rates of thermal interconversion of rotamers in three Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$ compounds (OR = O-*t*-Bu, $OCMe_2(CF_3)$, and $OCMe(CF_3)_2$) were determined by approach to equilibrium kinetics employing conventional NMR techniques. The rate of rotamer equilibration was found to follow first order kinetics over a range of temperatures (~80 to 140 °C) and to be independent of concentration in the range 2–15 mM. Activation parameters and equilibrium ratios are shown in Table IV and an Eyring plot for the five rate constants determined in the $OCMe_2(CF_3)$ case is shown in Figure 4. Full details can be found in the Experimental Section. The rotamers of Re(C-*t*-Bu)(CH-

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t-Bu)(O-2,6-C_6H_3-*i*-Pr_2)$_2$ interconvert at a rate that qualitatively is intermediate between those of Re(C-*t*-Bu)(CH-*t*-Bu)-[$OCMe_2(CF_3)$]$_2$ and Re(C-*t*-Bu)(CH-*t*-Bu)[$OCMe(CF_3)_2$]$_2$. However, Re(C-*t*-Bu)(CH-*t*-Bu)(O-2,6-C_6H_3-*i*-Pr_2)$_2$ decomposes to a significant extent above 100 °C, and so could not be studied thoroughly. Alkylidene ligand rotation is a relatively slow process. For example, Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$ requires approximately 45 min at 100 °C to reach equilibrium, while Re(C-*t*-Bu)(CH-*t*-Bu)[$OCMe(CF_3)_2$]$_2$ requires 7 h at 144 °C to reach equilibrium. At 110 °C the calculated relative rates of alkylidene rotation in these two species are approximately 500:1, respectively. Addition of THF (up to 10 equiv; free exchange is observed at room temperature) did not change the rate of interconversion of rotamers of Re(C-*t*-Bu)(CH-*t*-Bu)[$OCMe_2(CF_3)$]$_2$ at 113 °C, while addition of 1 equiv of PMe_3 (which forms an adduct in which PMe_3 does *not* exchange on the NMR time scale at room temperature) to Re(C-*t*-Bu)(CH-*t*-Bu)[$OCMe(CF_3)_2$]$_2$ stopped alkylidene ligand rotation entirely in the temperature range where rotation was observed for the pseudotetrahedral species. Therefore, as was found in complexes of the type M(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$,[29] alkylidene ligands appear to rotate more readily in pseudotetrahedral species than in higher coordinate species. The difference in the barrier to rotation in complexes of the type M(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$ and those reported here is dramatic; for M(CH-*t*-Bu)(N-2,6-C_6H_3-*i*-Pr_2)$(OR)_2$ species, values for $\Delta G^{\ddagger}_{298}$ were usually in the range of 16–18 kcal mol^{-1}.

Discussion

A potentially important and interesting feature of the chemistry of rhenium(VII) complexes that contain alkyl ligands that can lose α protons readily to give alkylidene and alkylidyne ligands is that α protons are transferred to oxo or imido ligands. Proton "transfer" is perhaps most likely to consist of a stepwise protonation/deprotonation reaction, since in d^0 complexes no CH_α bond actually can oxidatively add to the metal to give (e.g.) an alkylidyne/hydride intermediate. From a kinetic perspective it is sensible to propose that the rate of protonation of oxo, imido, and carbon-based ligands (M≡CR or M=CHR) would follow the order O > N > C, since two electron pairs are accessible on oxygen and none on carbon. Therefore formation of metal–carbon multiple bonds at the expense of metal–oxygen or metal–nitrogen multiple bonds could be ascribed largely to favorable kinetics, although there does appear to be some thermodynamic preferences for metal–nitrogen or metal–carbon bonds relative to metal–oxygen bonds for metals to the right in the transition series. As we have shown here, metal–carbon multiple bonds can be formed even in the presence of water, and alkylidyne/alkylidene complexes can be stable to water at neutral pH. Presumably other ligands that contain potentially acidic protons will be tolerated by rhenium catalysts of this type and perhaps also relatively reactive functionalities (e.g., the carbonyl group in an aldehyde or ketone). The implications for the development of olefin metathesis catalysts that will tolerate protons and certain functionalities would seem to be significant. Realistically it is unlikely that such functionality-tolerant catalysts will be as active as the more functionality-sensitive electrophilic catalysts. For example, water[32,33] and alcohol-tolerant[1] ruthenium-based catalysts, whose mode of reactivity admittedly has not been elucidated, react readily only with highly strained olefins such as norbornenes.

A unifying theme in metathesis by well-defined d^0 alkylidene or alkylidyne complexes is four-coordination, i.e., Mo and W complexes of the type M(CHR′)(NAr′)$(OR)_2$[17,18] are active olefin metathesis catalysts and M(CR′)$(OR)_3$ (M = Mo or W)[23] and Re(CR′)(NAr′)$(OR)_2$[34] complexes are active acetylene metathesis catalysts (the latter only in special circumstances). In each case a substrate can attack the metal relatively easily to give a five-coordinate intermediate metallacyclobutane complex (or metallacyclobutadiene complex in the case of acetylene metathesis), presumably on a pseudotetrahedral face that would allow a metallacycle to form. There is only one such face in complexes of the type M(CR′)$(OR)_3$, but if two multiply-bound ligands are present, then there are two such faces. In acetylene metathesis by complexes of the type Re(CR′)(NAr)$(OR)_2$[34] attack at one of the two possible faces (C, N, O) was proposed to lead to a relatively stable, inactive type of metallacyclobutadiene intermediate, while attack at the other possible face (C, O, O) was proposed to lead to metathesis. Complexes of the type M-(CHR′)(NAr′)$(OR)_2$ are attacked by bases[29] and, it is proposed, olefins,[35,36] most readily on the C, N, O face. d^0 Re complexes of the type reported here are also members of this class of pseudo-tetrahedral complexes in which either the C, C, O or C, O, O face in theory could be attacked and give rise to a metallacyclobutane intermediate. However, the most stable structure of a five-coordinate adduct depends (inter alia) on the nature of the base; the structure of the rhenium PMe_3 adduct when OR = $OCMe(CF_3)_2$, according to NMR studies, is different from that found for the rhenium THF adduct. (A M(CHR′)(NAr′)-$(OR)_2$(quinuclidine) complex also was observed that had a different structure than that of a phosphine adduct, but that structure could not be identified unambiguously.[29]) It seems more likely that an incoming base or olefin can attack the metal on several faces and that the structurally characterized example reported here is simply the most stable or the most crystalline of the possible THF adducts. Therefore, knowing the structure of a given base adduct in order to extrapolate to the structure of the weak olefin adduct that forms first in olefin metathesis reactions is perhaps of much less value than we believed initially. Of course, there is also no guarantee that the most stable "olefin adduct" leads to productive metathesis most quickly. In spite of all the structural knowledge that has been accumulated to date, we are now considerably less certain that we can determine what the fastest metathetical pathway in a high oxidation state alkylidene complex is in a given set of circumstances and whether any observable metallacyclobutane complex actually lies on the fastest reaction pathway.

A second common theme in the case of Mo and W complexes of the type M(CHR′)(NAr)$(OR)_2$ and complexes of the type Re(CR′)(CHR′)$(OR)_2$ reported here is the presence of syn and anti rotamers. The reason why syn and anti rotamers form is clear; the imido and alkylidyne ligands each use two d orbitals to form two π bonds to the metal, leaving only the orbital that is δ with respect to the neopentylidyne carbon atom or imido nitrogen atom to form a π bond to the alkylidene carbon atom. Therefore the alkylidene ligand must be bound so that its substituent either points toward or away from the alkylidyne or the imido ligand. The alkylidene ligand can rotate readily about the M=C bond only

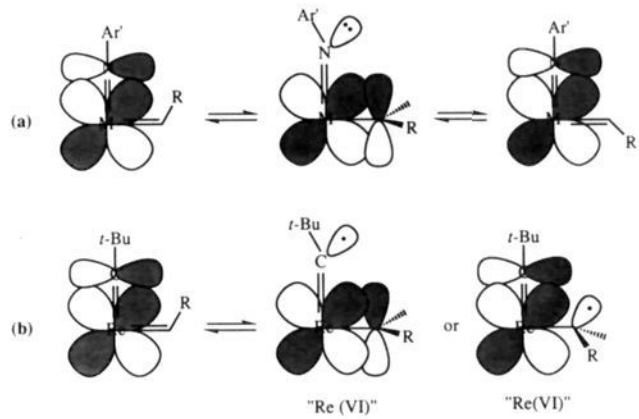

Figure 5. A schematic representation of the orbitals involved in stabilizing intermediates in alkylidene ligand rotation (a) M(NAr′)(CH-*t*-Bu)$(OR)_2$ (M = Mo, W) and (b) Re(C-*t*-Bu)(CH-*t*-Bu)$(OR)_2$.

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if the appropriate orbital is available to stabilize the intermediate (Figure 5). In an imido complex (Figure 5a) the d orbital in the N–M–C plane can become available to form a M≡C π bond if the imido nitrogen atom does not donate its electron pair to the metal. However, in an alkylidyne complex the analogous d orbital is used to form the covalent Re≡C triple bond. A plausible valence bond description of an intermediate or transition state in which the CHR ligand can rotate is shown in Figure 5b. One electron is placed in a metal orbital (not shown) to give formally Re(VI), while the remaining electron is located either on the alkylidyne carbon atom or the alkylidene carbon atom. Neither situation is especially attractive energetically and would account for the relatively high barrier to alkylidene ligand rotation. Such a "diradical" transition state is also attractive in view of the fact that the rate of alkylidene ligand rotation increases dramatically in the presence of light.

The reason why CH coupling constants are typically small for syn rotamers and relatively large for anti rotamers can be traced to some small degree of interaction of the electrons in the C–H bond with the metal centers in the syn isomer (now called agostic interactions[37]). Low values for alkylidene CH coupling constants (75–100 Hz) were observed routinely in coordinatively unsaturated niobium and tantalum complexes;[38] in some cases (especially reduced alkylidene complexes) the "distortion" of the alkylidene ligand was severe, with M–C_α–C_β angles approaching 180° and M–C_α–H_α angles <90°. A severely distorted d^0 tungsten methylene ligand also has been observed spectroscopically in W(η^5-C_5Me_5)$Me_3(CH_2)$.[39] Apparently, however, in d^0 complexes of Mo, W, or Re in which another π bonded ligand is present an alkylidene ligand is much less likely to distort in this manner, possibly because the orbitals that would be involved in agostic interactions are involved in π bonding to the second ligand. Even in these circumstances a nonbonding orbital that lies in the plane that contains the multiply bound ligands and is oriented away from the multiple bonds can receive electron density from the C–H bond in the syn rotamer.[29] In the next paper in this series we discuss an example of a *six*-coordinate complex that has syn and anti rotameric forms in which the C–H coupling constants are virtually identical, presumably because there is no longer an orbital available trans to the other multiply bound ligand that can interact with the C–H electron pair.

Conclusion

We have designed neopentylidene and neophylidene complexes of the type Re(CR′)(CHR′)$(OR)_2$ that potentialy are active for the metathesis of olefins and have developed relatively facile routes to a universal catalyst precursor that takes advantage of imido ligands as protecting groups. Re(CR′)(CHR′)$(OR)_2$ complexes have many of the features found in related tungsten and molybdenum imido alkylidene complexes, e.g., four-coordination, the presence of alkylidene rotamers, the tendency to readily coordinate a fifth ligand, and control of metal electrophilicity via variations in the nature of the OR ligand. We shall show in future publications that such species are in fact active metathesis catalysts and (inter alia) that metallacyclobutane complexes can be observed.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric/nitric acid (95/5 v/v), sodium bicarbonate, and then water, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether, tetrahydrofuran, toluene, benzene, and 1,2-diethoxyethane were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane was distilled from calcium hydride under nitrogen. Tetrahydrofuran-d_8 was vacuum distilled from sodium benzophenone ketyl. Methanol-d_4 (Cambridge Isotopes) was used as received. All other NMR solvents were deaerated by sparging with nitrogen and stored over activated molecular sieves (Linde, 3 Å) in the drybox.

Rhenium heptoxide (99.99%) was purchased from Aesar. Ammonium perrhenate, 2,6-dimethylaniline, 2,6-diisopropylaniline, trimethylchlorosilane, and 1,2-phenylenediamine were purchased from Aldrich.

NMR spectra were recorded on either 250 or 300 MHz machines (^1H) in C_6D_6, unless otherwise noted. ^1H and ^{13}C data are listed in parts per million downfield from tetramethylsilane and were referenced using the residual protonated solvent resonance. ^{19}F NMR spectra are listed in parts per million downfield from CF_3Cl and were referenced externally. Coupling constants are listed in hertz. Obvious multiplicities and routine coupling constants usually are not listed. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer.

Preparation of Compounds. Re$(NAr)_2$(py)Cl_3. 2,6-Dimethylaniline (23 mL, 0.19 mol) and pyridine (40 mL, 0.50 mol) were added to a suspension of Re_2O_7 (15 g, 0.031 mol) in 250 mL of CH_2Cl_2 under nitrogen. The solution became red, although most of the Re_2O_7 remained suspended. The mixture was cooled to −40 °C and trimethylchlorosilane (63 mL, 0.50 mmol) was added quickly dropwise. Once addition was complete, the reaction was stirred at room temperature for 1 h, during which time the color changed from dark red to dark green. The volatile components were removed in vacuo, and the dark green residue was extracted with boiling benzene. Dark green crystals formed as the volume of the filtered extract was decreased in vacuo. A small amount of pentane was added to complete crystallization. The dark green crystals were collected and washed liberally with pentane: yield 31.5 g (83%). Reactions using $[NH_4][ReO_4]$ as the rhenium source proceed analogously. This compound has been reported previously.[15]

Re$(NAr')_2$(py)Cl_3. This compound was prepared as described for Re$(NAr)_2$(py)Cl_3 from Re_2O_7 (0.50 g, 1.03 mmol), 2,6-diisopropylaniline (1.2 mL, 6.2 mmol), pyridine (1.34 mL, 16.5 mmol), and trimethylchlorosilane (2.1 mL, 16.5 mmol) in 40 mL of dichloromethane. The residue was extracted with toluene: yield 1.10 g (76%). This compound has been reported previously.[15]

Re(N-*t*-Bu)$_2Cl_3$. Trimethylchlorosilane (14.8 mL, 115 mmol) was added to a suspension of Re_2O_7 (4.00 g, 8.26 mmol) in 150 mL of dichloromethane under dinitrogen. The solution was cooled in an ice bath and *tert*-butylamine (17.4 mL, 165 mmol) was added quickly dropwise. The solution rapidly turned bright yellow and (*t*-Bu)NH_3Cl precipitated. The solution was stirred at room temperature for 20 min and then cooled again in an ice bath. Excess HCl(g) was bubbled through the solution until the yellow color had changed to dark red. The mixture was then degassed, taken into the glovebox, and filtered. The filtrate was reduced to dryness in vacuo, and the orange residue was extracted with ether. The mixture was filtered, the volume of the filtrate was reduced to 20 mL, and 20 mL of pentane was added to complete crystallization. Large orange cubes were collected by filtration and washed with pentane: yield 5.7 g (79%). This compound has been reported previously.[12]

Re(N-*t*-Bu)$_3$(OSiMe$_3$). Trimethylchlorosilane (0.37 mL, 2.9 mmol) was added to a suspension of Re_2O_7 (0.10 g, 0.21 mmol) in 2 mL of CH_2Cl_2. Excess *tert*-butylamine (0.44 mL, 4.1 mmol) was then added, and the solution turned yellow. After 5 min, all starting material had dissolved, and a flocculent precipitate of (*t*-Bu)NH_3Cl appeared. After 30 min the solution was filtered and reduced to dryness in vacuo to afford yellow crystals: yield 0.18 g (89%). This compound has been reported previously.[11]

Re(N-2,6-$C_6H_3Me_2$)$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph). To a −40 °C solution of Re$(NAr)_2$(py)Cl_3 (4.00 g, 6.6 mmol) in 45 mL of CH_2Cl_2 was added dropwise neophyl magnesium chloride (19.7 mmol, 15.6 mL of a 1.26 M solution in ether). The dark green color immediately changed to dark red. After stirring at room temperature for 45 min, the solution was reduced to dryness in vacuo, extracted with pentane, and filtered through a Celite pad to afford a thick orange oil in near quantitative yield. The product was contaminated with approximately 10% $PhMe_2C(CH_2)_2CMe_2Ph$, from which it could not be separated: ^1H NMR (C_6D_6) δ 12.26 (s, 1, C*H*CMe$_2$Ph), 7.37 (d, 2, H_{aryl}), 7.31 (d, 2, H_{aryl}), 7.13 (t, 2, H_{aryl}), 7.01 (m, 3, H_{aryl}), 6.86 (m, 7, H_{aryl}), 3.52 (AB quartet, 2, CH_2CMe$_2$Ph), 2.18 and 2.14 (s, 6 each, $C_6H_3Me_2$), 1.66, 1.51, 1.46 and 1.45 (s, 3 each, CMe_2Ph); ^{13}C NMR (CD_2Cl_2) δ 269.2 (*C*HCMe$_2$Ph, J_{CH} = 140), 155.7, 155.5, 152.5 and 150.3 (C_i), 134.2 and 131.9 (s, C_m), 128.4, 128.3, 128.0, 127.9, 126.2, 126.0, 125.7, 125.6, and 124.7 (C_{aryl}), 52.5 and 40.6 (*C*Me$_2$Ph), 41.9 (*C*H$_2$CMe$_2$Ph), 32.9, 32.8, 32.4, and 30.6 (CMe_2Ph), 19.4 (N-2,6-$C_6H_3Me_2$).

Re(N-*t*-Bu)$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph). To a −40 °C solution of Re(N-*t*-Bu)$_2Cl_3$ (2.0 g, 4.6 mmol) in 45 mL of CH_2Cl_2 was added dropwise neophyl magnesium chloride (13.8 mmol, 11 mL of a 1.26 M

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solution in ether). During the addition the orange solution darkened, became lighter orange, and then finally darkened again. After stirring at room temperature for 40 min, the solution was reduced to dryness in vacuo, extracted with pentane, and filtered through a Celite pad to afford a dark orange oil in near quantitative yield. The product was contaminated with approximately 10% $PhMe_2C(CH_2)_2CMe_2Ph$, from which it could not be separated: ^1H NMR (C_6D_6) δ 12.00 (s, 1, C*H*CMe$_2$Ph), 7.90 (br s, 1, H$_{aryl}$), 7.47 and 7.42 (d, 2 each, H$_{aryl}$), 7.15 and 7.08 (t, 2 each, H$_{aryl}$), 6.77 (br s, 1, H$_{aryl}$), 3.27 and 2.99 (d, 1 each, C*H*$_2$CMe$_2$Ph, J_{HH} = 14 Hz), 1.69, 1.54, 1.51, and 1.48 (s, 3 each, CMe$_2$Ph), 1.27 and 1.24 (s, 9, NC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 295.5 (*C*HCMe$_2$Ph, J_{CH} = 135), 154.1 and 151.9 (C_i), 128.3, 128.3, 126.3, and 126.2 (C_{ortho}, C_{meta}), 125.8 and 125.7 (C_p), 70.2 (N*C*Me$_3$), 50.6 and 38.8 (*C*Me$_2$Ph), 39.3 (*C*H$_2$CMe$_2$Ph), 33.8, 33.5, 32.1, and 31.1 (C*Me*$_2$Ph), 32.7 and 32.3 (C*Me*$_3$).

Re(NAr)(O)(CH-*t*-Bu)(CH$_2$-*t*-Bu), Isomer I. Water (0.25 mL) was added to a solution of Re(NAr)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) (1.00 g, 1.77 mmol) in 30 mL of benzene in air. The solution was stirred for 4 h and then reduced to dryness in vacuo to afford an orange oil containing the product, 1 equiv of 2,6-dimethylaniline, and small amounts of Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu). The aniline was removed by dissolving the crude oil in 30 mL of pentane in the glovebox and adding ZnCl$_2$(dioxane) (0.40 g, 1.77 mmol, 2-fold excess). The precipitated ZnCl$_2$(ArNH$_2$)$_2$ was removed by filtration. Attempts to purify the material further by chromatography were unsuccessful and sublimation resulted in disproportionation to Re(NAr)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) and rhenium–oxo species: ^1H NMR δ 12.29 (s, 1, C*H*CMe$_3$), 6.87 (s, 3, H$_{aryl}$), 3.08 and 2.87 (d, 1 each, C*H*$_2$CMe$_3$, J_{HH} = 14), 2.31 (s, 6, C$_6$H$_3$*Me*$_2$), 1.09 and 1.00 (s, 9 each, C*Me*$_3$); ^{13}C NMR δ 272.4 (*C*HCMe$_3$, J_{CH} = 130), 153.9 (C_i), 132.8 (C_o), 128.3 and 127.0 ($C_{m,p}$), 46.1 and 32.1 (*C*Me$_3$), 38.2 (*C*H$_2$CMe$_3$, J_{CH} = 131), 33.0 and 30.7 (C*Me*$_3$), 19.7 (C$_6$H$_3$*Me*$_2$).

Re(NAr)(O)(CH-*t*-Bu)(CH$_2$-*t*-Bu), Isomer II. Equal quantities (0.14 mmol) of Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) and Re(ArN)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) were dissolved in 800 μL of C_6D_6. After 2 days the proton NMR spectrum revealed a mixture of starting materials and primarily one isomer of Re(NAr)(O)(CH-*t*-Bu)(CH$_2$-*t*-Bu): ^1H NMR δ 12.72 (s, 1, C*H*CMe$_3$), 6.87 (m, 3, H$_{aryl}$), 3.31 and 2.88 (d, 1 each, C*H*$_2$CMe$_3$, J_{HH} = 14), 2.40 (s, 6, C$_6$H$_3$*Me*$_2$), 1.03 and 1.01 (s, 9 each, C*Me*$_3$); ^{13}C NMR δ 278.6 (*C*HCMe$_3$, J_{CH} = 139), 154.2 (C_i), 136.1, 133.6, 128.6, 127.9, and 127.5 (C_{aryl}), 44.5 (*C*Me$_3$), 31.0 and 30.1 (C*Me*$_3$), 19.6 and 19.5 (2,6-C$_6$H$_3$*Me*$_2$). The resonance for C*H*$_2$CMe$_3$ could not be assigned.

Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu). To a solution of Re(NAr)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) (15 g, 0.27 mol) in 150 mL of pentane was added on the benchtop a previously prepared mixture of water (1.2 g, 0.066 mol) on activated neutral alumina (10.8 g, 10% loading by weight). The flask was then wrapped in foil to exclude light, and the mixture was stirred for 2 days. The solution was then returned to the drybox, and zinc dichloride dioxanate (11.8 g, 0.53 mol) was added. The solution was stirred overnight. The precipitated ZnCl$_2$(ArNH$_2$)$_2$ was removed by filtration and the volume of the filtrate was reduced in vacuo to give an extremely thick orange oil that was pure enough by ^1H NMR to be used without further purification: yield 7.86 g (82%). The product may be crystallized from cold pentane, although it is exceedingly soluble, particularly when small amounts of impurities are present. Spectral data were consistent with those published.[19] Anal. Calcd for $C_{10}H_{21}O_2Re$: C, 33.41; H, 5.89. Found: C, 33.81; H, 5.95.

Re(O)$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph). This compound was prepared in high yield in a manner analogous to that used to prepare Re(O)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) starting with Re(NAr)$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph): ^1H NMR (CD_2Cl_2) δ 12.69 (s, 1, C*H*CMe$_2$Ph), 7.40–7.20 (m, 10, H$_{aryl}$), 3.46 and 3.14 (d, 1 each, C*H*$_2$CMe$_2$Ph, J_{HH} = 14), 1.71, 1.64, 1.43, 1.42 (s, 3 each, C*Me*$_2$Ph); ^{13}C NMR (CD_2Cl_2) δ 283.5 (*C*HCMe$_2$Ph, J_{CH} = 140), 149.8 and 146.8 (C_i), 129.0, 128.6, 127.3, 126.5, and 126.2 (C_{aryl}), 52.1 and 38.6 (*C*Me$_2$Ph), 41.2 (*C*H$_2$CMe$_2$Ph, t, J_{CH} = 127), 31.3, 31.1, 30.7, and 28.5 (C*Me*$_2$Ph). Anal. Calcd for $C_{20}H_{25}O_2Re$: C, 49.67; H, 5.21. Found: C, 49.99; H, 5.57.

[Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$]$_2$. A solution of Re(NAr)(CH-*t*-Bu)(CH$_2$-*t*-Bu) (4.64 g, 8.2 mmol) in dimethoxyethane (100 mL) was cooled to 0 °C and treated with HCl(g) (590 mL, 26 mmol). The orange solution immediately darkened, and a white precipitate formed. After stirring the mixture at 25 °C for 2.5 h, the solvent was removed in vacuo, leaving a beige powder. The product was extracted away from insoluble ArNH$_3$Cl with benzene, and the mixture was filtered through a pad of Celite. The filtrate was then reduced to dryness in vacuo, and the residue was washed with pentane, leaving a faintly orange powder: yield 3.4 g (80%); ^1H NMR (major isomer) δ 14.49 (s, 2, C*H*CMe$_3$), 6.7–6.5 (m, 6, H$_{aryl}$), 6.91 and 6.33 (d, 2 each, N*H*$_2$, J_{HH} = 13), 2.37 and 2.17 (s, 6 each, C$_6$H$_3$*Me*$_2$), 1.39 and 1.08 (s, 18 each, C*Me*$_3$); (minor isomer) δ 14.47 (s, 2, C*H*CMe$_3$), 2.32 and 2.29 (s, 6 each, 2,6-C$_6$H$_3$*Me*$_2$), 1.40 and 1.01 (s, 18 each, C*Me*$_3$), amine resonances were coincidental; ^{13}C NMR (THF-d_8) (major isomer) δ 292.1 (*C*CMe$_3$), 286.3 (*C*HCMe$_3$, J_{CH} = 130), 144.2 (C_i), 128.7 (C_m), 123.7 (C_o), 119.5 (C_p), 53.4 and 46.8 (*C*Me$_3$), 31.5 and 28.5 (C*Me*$_3$). Anal. Calcd for $C_{36}H_{60}Cl_4N_2Re_2$: C, 41.77; H, 5.84; N, 2.71. Found: C, 42.11; H, 6.00; N, 2.50.

Observation of Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$. ^1H NMR (major isomer) δ 15.22 (s, 1, C*H*CMe$_3$), 8.50 (v br s, 2, *H*$_2$NAr), 6.60 (t, 1, H$_p$), 6.40 (d, 2, H$_m$), 2.13 (s, 6, 2,6-C$_6$H$_3$*Me*$_2$), 1.49 and 1.35 (s, 9 each, C*Me*$_3$); (minor isomer) δ 15.11 (s, 1, C*H*CMe$_3$), 1.47 and 1.40 (s, 9 each, C*Me*$_3$), amine resonances were coincidental with those for the major isomer.

[Re(C-*t*-Bu)(CH-*t*-Bu)(Ar'NH$_2$)Cl$_2$]$_2$. ^1H NMR (major isomer) δ 14.38 (s, 2, C*H*CMe$_3$), 7.10–6.80 (m, 6, H$_{aryl}$), 7.35 and 6.36 (d, 2 each, N*H*$_2$, J_{HH} = 13), 4.14 and 3.63 (s, 2 each, C*H*Me$_2$), 1.51 and 1.03 (s, 18, C*Me*$_3$); (minor isomer) δ 14.54 (s, 2, C*H*CMe$_3$), 7.10–6.80 (m, 6, H$_{aryl}$), 3.78 and 3.80 (s, 2 each, C*H*Me$_2$), 1.42 and 1.07 (s, 18 each, C*Me*$_3$); CH*Me*$_2$ doublets at 1.55, 1.47, 1.40, 1.31, 1.29, 1.22, 1.21, and 1.14 were not assigned to individual isomers. This compound was not sufficiently soluble to obtain an adequate ^{13}C NMR spectrum. Anal. Calcd for $C_{44}H_{76}Cl_4N_2Re_2$: C, 46.06; H, 6.68; N, 2.44. Found: C, 45.76; H, 6.64; N, 2.03.

Observation of Re(C-*t*-Bu)(CH-*t*-Bu)(Ar'NH$_2$)Cl$_2$. This compound was prepared in a manner analogous to that used to prepare the ArNH$_2$ derivative: ^1H NMR (major isomer) δ 15.26 (s, 1, C*H*CMe$_3$), 8.80 (v br s, 2, *H*$_2$NAr), 7.05–6.75 (m, 3, H$_{aryl}$), 3.40 (br s, 2, C*H*Me$_2$), 1.49 and 1.34 (s, 9 each, C*Me*$_3$), 1.20 (br s, 12, CH*Me*$_2$); (minor isomer) δ 15.15 (s, 1, C*H*CMe$_3$), 1.47 and 1.38 (s, 9 each, C*Me*$_3$), amine resonances were coincidental.

[Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(*t*-BuNH$_2$)Cl$_2$]$_2$. A −40 °C solution of neophyl magnesium chloride (12.6 mL of 1.10 M in diethyl ether, 13.8 mmol) was added to a −40 °C solution of Re(N-*t*-Bu)$_2$Cl$_3$ (2.00 g, 4.6 mmol) in 50 mL of CH_2Cl_2. The reaction was stirred at room temperature for 20 min and reduced to dryness in vacuo. The residue was extracted with pentane, and the mixture was filtered. The filtrate was reduced to dryness in vacuo to afford crude Re(N-*t*-Bu)$_2$(CHCMe$_2$Ph)(CH$_2$CMe$_2$Ph) as an orange oil. This oil was dissolved in 30 mL of CH_2Cl_2, and solid 2,4-lutidinium chloride (1.98 g, 13.8 mmol) was added. The solution was stirred at room temperature for 4 h. The solution was then reduced to dryness in vacuo. The residue was extracted with benzene, and the extract mixture was filtered through Celite. This filtrate was reduced in volume and pentane was added to precipitate the product as a yellow-orange powder: yield 1.94 g (71%); ^1H NMR (CD_2Cl_2, major isomer) δ 13.43 (s, 2, C*H*-*t*-Bu), 5.64 and 3.88 (br d, 2 each, N*H*$_2$, J_{HH} = 14), 1.90, 1.82, 1.64, 1.44 (s, 6 each, C*Me*$_2$Ph), 0.96 (NH$_2$C*Me*$_3$); (minor isomer) δ 13.48 (s, 2, C*H*-*t*-Bu), 5.34 and 4.08 (br d, 2 each, N*H*$_2$, J_{HH} = 13), 1.92, 1.86, 1.62, 1.43 (s, 6 each, C*Me*$_2$Ph), 0.95 (NH$_2$C*Me*$_3$); the aryl resonances (δ 7.75–7.70 (m) and 7.50–7.10 (m)) for each isomer could not be differentiated; ^{13}C NMR (CD_2Cl_2, major isomer) δ 294.5 (*C*HCMe$_2$Ph, J_{CH} = 127), 290.1 (*C*CMe$_2$Ph), 147.0 and 144.4 (C_i), 60.6 (NH$_2$*C*Me$_3$), 54.9 and 54.0 (*C*Me$_2$Ph), 29.3 (NH$_2$C*Me*$_3$), 29.9, 29.0, 28.1, and 27.2 (C*Me*$_2$Ph); (minor isomer) δ 296.0 (*C*HCMe$_2$Ph, J_{CH} = 119), 289.6 (*C*CMe$_2$Ph), 147.5 and 144.5 (C_i), 60.6 (NH$_2$*C*Me$_3$), 54.9 and 54.0 (*C*Me$_2$Ph), 29.4 (NH$_2$C*Me*$_3$), 29.6, 28.0, and 27.4 (C*Me*$_2$Ph, one resonance was obscured); ten aryl resonances were observed in this mixture (δ 127.1, 128.6, 126.9, 128.0, 127.1, 126.0, 126.8, 128.5, 127.2, and 128.5 in decreasing intensity). An analytical sample was prepared by Dr. Amjad Farooq. Anal. Calcd for $C_{48}H_{68}N_2Re_2$: C, 48.56; H, 5.77; N, 2.36. Found: C, 48.56; H, 5.77; N, 2.06.

Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH$_2$)$_2$Cl$_2$. Excess *tert*-butylamine (0.3 mL) was added to a suspension of [Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$]$_2$ (108 mg, 0.096 mmol) in 3 mL of THF. After 15 min all the starting material dissolved to yield an orange solution. After 16 h the volume was reduced to approximately 0.5 mL in vacuo, and pentane (10 mL) was added to afford silky yellow fibers that were collected by filtration and washed liberally with pentane: yield 108 mg (95%); ^1H NMR δ 14.53 (s, 1, C*H*CMe$_3$), 4.36 and 4.23 (br d, 2 each, N*H*$_2$, J_{HH} = 14), 1.40 and 1.36 (s, 9 each, C*Me*$_3$), 1.18 (s, 18, H$_2$NC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 298.6 (*C*HCMe$_3$, J_{CH} = 131), 286.2 (*C*CMe$_3$), 53.3 and 49.1 (*C*Me$_3$), 52.8 (H$_2$N*C*Me$_3$), 31.0 and 28.8 (C*Me*$_3$), 29.5 (NH$_2$C*Me*$_3$).

Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2$Cl$_2$. Excess pyridine (0.70 mL, 8.5 mmol) was added to a solution of [Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$]$_2$ (1.00 g, 0.96 mmol) in 50 mL of CH_2Cl_2. The color changed from red to orange. After stirring 30 min at room temperature, the solution was reduced to dryness in vacuo, and the resulting orange solid was washed liberally with pentane. Residual dimethylaniline was removed by reprecipitating the product from dichloromethane with pentane: yield 0.95 g (90%); ^1H NMR δ 14.04 (s, 1, C*H*CMe$_3$), 9.28 (d, 4, H$_o$), 6.77 (t, 2, H$_p$), 6.48 (t, 4, H$_m$), 1.61 and 1.34 (s, 9 each, C*Me*$_3$); ^{13}C NMR δ 298.4 (*C*CMe$_3$), 295.3 (*C*HCMe$_3$, J_{CH} = 121), 151.1 (C_p), 137.3 and 123.8 (C_o and C_m), 53.6 and 47.9 (*C*Me$_3$), 31.7 and 28.3 (C*Me*$_3$).

Observation of Re(C-*t*-Bu)(CH-*t*-Bu)(py)Cl_2. ^{1}H NMR (major isomer) δ 15.18 (s, 1, C*H*CMe$_3$), 8.85 (br s, 2, H_o), 6.65 (br s, 2, H_m), 6.35 (br s, 1, H_p), 1.55 and 1.41 (s, 9 each, C*C*Me$_3$); (minor isomer) δ 15.09 (s, 1, C*H*CMe$_3$), 1.52 and 1.46 (s, 9 each, C*C*Me$_3$); amine resonances were coincidental with those for the major isomer.

Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA)Cl_2. This compound was prepared analogously to Re(C-*t*-Bu)(CH-*t*-Bu)(py)$_2Cl_2$ using excess tetramethylethylenediamine: ^{1}H NMR (CD_2Cl_2) δ 13.13 (s, 1, C*H*CMe$_3$), 2.87 (s, 4, CH_2), 2.68 (s, 12, N*Me*$_2$), 1.37 and 1.30 (s, 9 each, C*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 291.8 (*C*CMe$_3$), 291.7 (d, *C*HCMe$_3$, J_{CH} = 120), 59.6 and 59.0 (CH_2, J_{CH} = 137, 136), 53.6 and 47.4 (*C*Me$_3$), 51.5 and 48.0 (N*Me*$_2$), 31.2 and 28.7 (C*Me*$_3$). An analytical sample was recrystallized from dichloromethane by adding pentane. Anal. Calcd for $C_{16}H_{35}Cl_2N_2Re$: C, 37.49; H, 6.88; N, 5.47. Found: C, 37.58; H, 6.96; N, 5.47.

Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA·HCl)Cl_2. This compound was prepared quantitatively by adding 1 or more equiv of HCl(g) to Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA)Cl_2 in dimethoxyethane or benzene: ^{1}H NMR (major isomer) δ 15.06 (s, 1, C*H*CMe$_3$), 8.00 (br s, 1, N*H*), 3.80 (br s, 4, CH_2), 2.50 (s, 12, N-*Me*$_2$), 1.48 and 1.37 (s, 9 each, C*Me*$_3$); (minor isomer) δ 14.94 (s, 1, C*H*CMe$_3$), 1.46 and 1.41 (s, 9 each, C*Me*$_3$); amine resonances were coincidental with those for the major isomer. Partial ^{13}C NMR (major isomer) δ 304.4 (*C*HCMe$_3$, J_{CH} = 127), 297.7 (*C*CMe$_3$); (minor isomer) δ 303.5 (*C*HCMe$_3$, J_{CH} = 122), 298.4 (*C*CMe$_3$).

Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl_2. 1,2-Phenylenediamine (0.31 g, 2.9 mmol) was added to [Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl_2]$_2$ (1.5 g, 1.45 mmol) in 40 mL of THF. The orange solution darkened rapidly, and after 25 min the solvent was removed in vacuo. The resulting pale orange solid was washed with pentane and then twice reprecipitated from THF by adding pentane to give 1.39 g of product (95% yield): ^{1}H NMR δ 13.52 (s, 1, C*H*CMe$_3$), 7.31 (m, 4, H_{aryl}), 4.74 (br s, 4, NH_2), 1.38 and 1.32 (s, 9, C*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 295.6 (*C*CMe$_3$), 292.0 (*C*HCMe$_3$, J_{CH} = 118), 138.1 ($C_{1,2}$), 130.1, 129.0, 128.4, and 127.5 (C_{3-6}), 52.9 and 47.0 (*C*Me$_3$), 31.2 and 28.1 (C*Me*$_3$).

Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(pda)Cl_2. This compound was prepared from [Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(ArNH$_2$)Cl_2]$_2$ in a manner analogous to Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl_2: ^{1}H NMR (THF-d_8) δ 13.25 (s, 1, C*H*CMe$_2$Ph), 7.78 (d, 2, H_{aryl}), 7.30 (m, 6, H_{aryl}), 7.16 (m, 5, H_{aryl}), 7.02 (t, 1, H_p), 5.64 (s, 4, NH_2), 1.75 and 1.41 (s, 6 each, C*Me*$_2$Ph); ^{13}C NMR (THF-d_8) δ 290.4 (*C*CMe$_2$Ph), 285.4 (*C*HCMe$_2$Ph, J_{CH} = 122), 152.2 and 148.1 (C_i), 141.1 and 140.4 ($C_{1,2}$(pda)), 129.6, 129.6, 128.5, 128.0, 127.2, 127.1, 126.6 and 125.5 (C_{aryl}), 59.8 and 54.5 (*C*Me$_2$Ph), 30.2 and 28.4 (C*Me*$_2$Ph). Anal. Calcd for $C_{26}H_{31}Cl_2N_2Re$: C, 49.68; H, 4.97; N, 4.46. Found: C, 49.53; H, 4.76; N, 4.34.

[Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ from Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl_2. Addition of HCl(g) (98 mL, 4.4 mmol) via syringe to a dimethoxyethane solution of Re(C-*t*-Bu)(CH-*t*-Bu)(pda)Cl_2 (1.0 g, 1.98 mmol) immediately yielded a white precipitate of pda·2HCl. After 20 min, the precipitate was removed by filtration, and the orange filtrate was taken to dryness in vacuo. The resulting orange solid was washed with pentane: yield 0.67 g (85%); ^{1}H NMR (THF-d_8) δ 13.26 (s, 1, C*H*CMe$_3$), 1.35 and 1.26 (s, 9, C*Me*$_3$); ^{13}C NMR (THF-d_8) δ 293.9 (*C*CMe$_3$), 285.8 (*C*HCMe$_3$, J_{CH} = 125), 53.59 and 46.66 (*C*Me$_3$), 31.4 and 28.4 (C*Me*$_3$). Anal. Calcd for $C_{10}H_{19}Cl_2Re$: C, 30.30; H, 4.83. Found: C, 30.21; H, 4.84.

[Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ from ReO_2(CH-*t*-Bu)(CH_2-*t*-Bu). Water (94 μL, 5.2 mmol) and aqueous HCl (0.46 mL, 5.2 mmol) were added to 0.94 g of Re(O)$_2$(CH-*t*-Bu)(CH_2-*t*-Bu) (2.6 mmol) in 20 mL of dimethoxyethane (in air). The orange-red solution immediately turned dark purple-red and then lightened to orange-red over a period of 30 min. The reaction mixture was reduced to dryness in vacuo and taken into the glovebox. The slightly purple, light orange powder was triturated with 10 mL of THF and then washed thoroughly on a pad of Celite with pentane and dichloromethane. The orange material that remained was removed from the Celite pad by dissolving it in THF. The filtrate was reduced in volume to yield light orange crystals of Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2(THF)$_2$, which quickly lost THF in vacuo to afford 0.88 g of pale orange THF-free product (85% yield). This compound may also be prepared using anhydrous HCl(g) in the absence of water.

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OSi(*t*-Bu)$_3$]$_2$.** Solid potassium silox (0.26 g, 1.01 mmol) was added to a stirred solution of [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ (0.20 g, 0.51 mmol) in 2 mL of THF. After 2 h the solution was reduced to dryness in vacuo, and the residue was extracted with pentane. The mixture was filtered through Celite, and the filtrate was reduced to dryness to afford crystalline orange-yellow product quantitatively. An analytical sample was recrystallized from pentane: ^{1}H NMR δ 10.40 (s, 1, C*H*CMe$_3$), 1.40 and 1.39 (s, 9, C*Me*$_3$), 1.20 (s, 54, OSi(*t*-Bu)$_3$); ^{13}C NMR δ 294.6 (*C*CMe$_3$), 233.6 (*C*HCMe$_3$, J_{CH} = 125), 54.5 and 44.8 (*C*Me$_3$), 33.3 and 30.9 (C*Me*$_3$), 30.3 (OSi(*t*-Bu$_3$), 24.0 (OSi(*C*Me$_3$)$_3$). Anal. Calcd for $C_{34}H_{73}O_2Si_2Re$: C, 53.99; H, 9.73. Found: C, 53.86; H, 9.71.

***syn/anti*-Re(C-*t*-Bu)(CH-*t*-Bu)[OSi(*t*-Bu)$_3$]$_2$.** A mixture of syn and anti rotamers was prepared by photolyzing of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(silox)$_2$ with a medium pressure mercury lamp for 5 h in C_6D_6: ^{1}H NMR (anti rotamer) δ 12.40 (s, 1, C*H*CMe$_3$), 1.43 and 1.41 (s, 9, C*Me*$_3$), 1.22 (s, 54, OSi(*t*-Bu)$_3$); ^{13}C NMR (anti rotamer) δ 305.9 (*C*CMe$_3$), 239.6 (*C*HCMe$_3$, J_{CH} = 155), 55.4 and 41.8 (*C*Me$_3$), 31.8 and 30.0 (C*Me*$_3$), 30.4 (OSi(C*Me*$_3$), 23.9 (OSi(*C*Me$_3$).

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$.** Solid lithium *tert*-butoxide (0.61 g, 7.57 mmol) was added to a solution of [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ (1.50 g, 3.78 mmol) in 10 mL of THF. The flask was wrapped in foil, and the solution was stirred at room temperature for 1 h. The solvents were removed in vacuo, and the residue was extracted with pentane. The mixture was filtered through Celite, and the filtrate was reduced to dryness in vacuo to afford a quantitative yield of the syn isomer as an oily yellow-orange solid: ^{1}H NMR δ 10.15 (s, 1, C*H*CMe$_3$), 1.37 and 1.36 (s, 9 each, C*Me*$_3$), 1.20 (s, 18, OC*Me*$_3$); ^{13}C NMR (C-D_2Cl_2) δ 288.5 (*C*CMe$_3$), 231.0 (*C*HCMe$_3$, J_{CH} = 120), 77.9 (O*C*Me$_3$), 53.9 and 43.9 (*C*Me$_3$), 33.5, 32.2 and 31.1 (C*Me*$_3$). This compound has been reported previously.[12]

***syn/anti*-Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$.** A rotameric mixture can be prepared either by photolysis of the pure syn rotamer in pentane or benzene with a medium pressure mercury or fluorescent desk lamp or by reacting [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH$_2$)Cl_2]$_2$ with 4 equiv of lithium *tert*-butoxide in a manner analogous to that described above. The syn/anti ratio in the latter case depends on reaction conditions and extent of exposure to ambient light: ^{1}H NMR (anti isomer) δ 11.59 (s, 1, C*H*CMe$_3$), 1.42 and 1.36 (s, 9 each, C*Me*$_3$), 1.24 (s, 18, OC*Me*$_3$); ^{13}C NMR (CD_2Cl_2) δ 298.2 (*C*CMe$_3$), 229.5 (*C*HCMe$_3$, J_{CH} = 157), 77.5 (O*C*Me$_3$), 53.3 and 39.8 (*C*Me$_3$), 32.8, 31.7 and 30.1 (C*Me*$_3$).

***syn/anti*-Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$.** These complexes are prepared from [Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(*t*-BuNH$_2$)Cl_2]$_2$ in a manner analogous to that described for *syn*- and *anti*-Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$: ^{1}H NMR (syn rotamer) δ 10.36 (s, 1, C*H*CMe$_3$), 1.71 and 1.69 (s, 6 each, C*Me*$_2$Ph), 1.16 (s, 18, OC*Me*$_3$); (anti rotamer) δ 11.68 (s, 1, C*H*CMe$_3$), 1.88 and 1.70 (s, 6 each, C*Me*$_2$Ph), 1.17 (s, 18, OC*Me*$_3$); aryl resonances (δ 7.69 (d), 7.58 (d), 7.42 (d), 7.29–7.00 (m)) could not be uniquely assigned to each rotamer; ^{13}C NMR (CD_2Cl_2, syn rotamer) δ 287.3 (*C*CMe$_3$), 230.4 (*C*HCMe$_3$, J_{CH} = 124), 152.1 and 147.9 (C_i), 128.5, 127.2, 126.9, 126.73, 125.8 (C_{aryl}), 78.7 (O*C*Me$_3$), 59.9 and 50.9 (*C*Me$_3$), 32.7, 32.1, and 30.4 (C*Me*$_3$); ^{13}C NMR (CD_2Cl_2, anti rotamer) δ 294.8 (*C*CMe$_3$), 228.3 (*C*HCMe$_3$, J_{CH} = 157), 153.3 and 146.4 (C_i), 128.7, 128.2, 128.2, 127.0, 126.4 (C_{aryl}), 78.5 (O*C*Me$_3$), 60.8 and 46.3 (*C*Me$_3$), 33.0, 31.0, and 29.8 (C*Me*$_3$).

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe$_2$(CF$_3$)]$_2$.** Solid lithium trifluoro-*tert*-butoxide (0.34 g, 2.52 mmol) was added to a solution of [Re(C-*t*-Bu)(CH-*t*-Bu)Cl_2]$_x$ (0.50 g, 1.26 mmol) in 5 mL of THF. The solution was stirred in a foil-wrapped vial for 45 min and reduced to dryness in vacuo. The residue was extracted with pentane, and the mixture was filtered through Celite. Reduction of the filtrate to dryness in vacuo afforded the product quantitatively: ^{1}H NMR δ 10.52 (s, 1, C*H*CMe$_3$), 1.24 and 1.22 (s, 9 each, C*Me*$_3$), 1.13 and 1.10 (s, 6 each, OC*Me*$_2$(CF$_3$)); ^{13}C NMR δ 292.22 (*C*CMe$_3$), 238.40 (*C*HCMe$_3$, J_{CH} = 123), 126.72 (*C*F$_3$, J_{CF} = 288), 79.02 (O*C*Me$_2$(CF$_3$), J_{CF} = 36), 53.37 and 43.88 (*C*Me$_3$), 32.12 and 29.91 (C*Me*$_3$), 24.74 and 24.33 (OC*Me*$_2$(CF$_3$)). An analytical sample was prepared by sublimation (40 °C, 10^{-5} torr). Anal. Calcd for $C_{18}H_{31}F_6O_2Re$: C, 37.30; H, 5.39. Found: C, 36.98; H, 5.63.

***syn/anti*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe$_2$(CF$_3$)]$_2$.** A rotameric mixture of products can be prepared by photolysis of the pure syn rotamer in pentane or benzene with a medium pressure mercury or fluorescent desk lamp or by reacting [Re(C-*t*-Bu)(CH-*t*-Bu)(*t*-BuNH$_2$)Cl_2]$_2$ with 4 equiv of lithium trifluoro-*tert*-butoxide in a manner analogous to that described in earlier syntheses. The rotameric ratio depends on reaction conditions and extent of exposure to ambient light: ^{1}H NMR (anti isomer) δ 11.95 (s, 1, C*H*CMe$_3$), 1.23 and 1.21 (s, 9 each, C*Me*$_3$), 1.24 and 1.13 (s, 6 each, OC*Me*$_2$(CF$_3$)); ^{13}C NMR δ 300.31 (*C*CMe$_3$), 238.89 (*C*HCMe$_3$, J_{CH} = 156), 127.27 (*C*F$_3$, J_{CF} = 284), 79.06 (O*C*Me$_2$(CF$_3$), J_{CF} = 23), 54.30 and 40.69 (*C*Me$_3$), 30.64 and 29.29 (C*Me*$_3$), 25.81 and 25.67 (OC*Me*$_2$(CF$_3$)).

***syn/anti*-Re(CCMe$_2$Ph)(CHCMe$_2$Ph)[OCMe$_2$(CF$_3$)]$_2$.** A mixture of rotamers was prepared from [Re(CCMe$_2$Ph)(CHCMe$_2$Ph)(*t*-BuNH$_2$)Cl_2]$_2$ in a manner analogous to the synthesis of *syn*- and *anti*-Re(C-*t*-Bu)[OCMe$_2$(CF$_3$)]$_2$: ^{1}H NMR (syn rotamer) δ 10.73 (s, 1, C*H*CMe$_2$Ph), 7.50–7.43 (m, 4, H_{aryl}), 7.25–7.00 (m, 6, H_{aryl}), 1.77 and 1.56 (s, 6 each, C*Me*$_2$Ph), 1.13 and 1.02 (s, 6, OC*Me*$_2$(CF$_3$)); (anti rotamer) δ 12.06 (s, 1, C*H*CMe$_2$Ph), 7.50–7.43 (m, 4, H_{aryl}), 7.25–7.00 (m, 6, H_{aryl}), 1.77 and 1.57 (s, 6 each, C*Me*$_2$Ph), 1.08 and 1.00 (s, 6, OC*Me*$_2$(CF$_3$)); ^{13}C NMR (CD_2Cl_2, syn rotamer) δ 294.0 (*C*CMe$_2$Ph), 238.6 (*C*HCMe$_2$Ph, J_{CH} = 122), 151.5 and 147.7 (C_i), 78.2

($OCMe_2CF_3$), 60.8 (CMe_2Ph), 32.3, 32.4, 25.5, and 25.0 (CMe_2Ph); aryl resonances at 128.8, 128.2, 127.3, 126.7, and 126.1 were not uniquely assignable to individual rotamers; CF_3 resonances were obscured; (anti rotamer) δ 297.0 ($CCMe_2Ph$), 238.1 ($CHCMe_2Ph$, J_{CH} = 160), 151.5 and 145.0 (C_i), 79.7 ($OCMe_2CF_3$), 61.7 and 47.2 (CMe_2Ph), 29.3, 29.2, 25.9, and 25.8 (CMe_2Ph). Anal. Calcd for $C_{28}H_{35}F_6O_2Re$: C, 47.79; H, 5.01. Found: C, 47.50; H, 5.04.

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$.** Solid potassium hexafluoro-*tert*-butoxide (1.66 g, 7.56 mmol) was added to a solution of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ (1.50 g, 3.78 mmol) in 15 mL of THF. The solution was stirred for 1 h in a foil-wrapped flask and reduced to dryness in vacuo. The residue was extracted with pentane, the extract was filtered through Celite, and the filtrate was reduced to dryness in vacuo. When first obtained the material is a crystalline THF adduct. Drying in vacuo for 30 min causes these crystals to melt to an orange oil that is pure syn rotamer by NMR: ^{1}H NMR δ 11.08 (s, 1, $CHCMe_3$), 1.17 and 1.14 (s, 9 each, CMe_3), 1.13 (s, 6, $OCMe(CF_3)_2$); ^{13}C NMR δ 295.80 ($CCMe_3$), 248.82 ($CHCMe_3$, J_{CH} = 127), 124.02 (CF_3, J_{CF} = 289), 81.29 ($OCMe(CF_3)_2$), 54.77 and 45.24 (CMe_3), 31.96 and 29.95 (CMe_3), 20.40 ($OCMe(CF_3)_2$). An analytical sample prepared by sublimation (40 °C, 10^{-5} Torr) was a yellow, crystalline solid that melted at room temperature. Anal. Calcd for $C_{18}H_{25}F_{12}O_2Re$: C, 31.44; H, 3.66. Found: C, 31.41; H, 3.77.

***syn*/*anti*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$.** This mixture is prepared by photolysis of the syn rotamer in pentane or benzene with either a medium pressure mercury lamp or a fluorescent desk lamp: ^{1}H NMR (anti rotamer) δ 12.48 (s, 1, $CHCMe_3$), 1.23 and 1.17 (s, 9 each, CMe_3), 1.21 (s, 6, $OCMe(CF_3)_2$); ^{13}C NMR δ 304.18 ($CCMe_3$), 251.52 ($CHCMe_3$, J_{CH} = 158), 123.60 (CF_3, J_{CF} = 286), 81.45 ($OCMe(CF_3)_2$), 54.82 and 41.37 (CMe_3), 29.99 and 29.32 (CMe_3), 15.31 ($OCMe(CF_3)_2$).

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OAr′)$_2$.** Solid LiOAr′(ether) (0.46 mmol) was added to a suspension of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2]_x$ (90 mg, 0.23 mmol) in 2 mL of dichloromethane. After stirring for 1 h the solution was reduced to dryness in vacuo, and the residue was extracted with pentane. The extract was filtered through Celite, and the filtrate was reduced in vacuo to give an orange oil that was pure syn rotamer by NMR: ^{1}H NMR δ 10.69 (s, 1, $CHCMe_3$), 7.09 (d, 4, H_m), 6.98 (t, 2, H_p), 3.54 (sept, 4, $CHMe_2$), 1.30 (d, 24, $CHMe_2$, J_{HH} = 7), 1.20 and 0.97 (s, 9 each, CMe_3); ^{13}C NMR δ 293.7 ($CCMe_3$), 240.0 ($CHCMe_3$, J_{CH} = 119), 164.0 (C_i), 136.7 (C_o), 123.2 (C_m), 122.1 (C_p), 54.9 and 45.1 (CMe_3), 23.6 and 23.0 ($CHMe_2$), 32.4 and 30.1 ($CHMe_2$), 27.9 and 23.6 (CMe_3).

***syn*/*anti*-Re(C-*t*-Bu)(CH-*t*-Bu)(OAr′)$_2$.** This mixture is prepared by photolysis of the syn rotamer in pentane or benzene with either a medium pressure mercury lamp or a fluorescent desk lamp: ^{1}H NMR (anti rotamer) δ 12.31 (s, 1, $CHMe_3$), 7.08 (d, 4, H_m), 6.98 (t, 2, H_p), 3.54 (sept, 4, $CHMe_2$), 1.34 (d, 24, $CHMe_2$, J_{HH} = 7), 1.23 and 0.92 (s, 9 each, CMe_3); ^{13}C NMR δ 301.6 ($CCMe_3$), 242.2 ($CHCMe_3$, J_{CH} = 161), 161.8 (C_i), 136.1 (C_o), 123.2 (C_m), 122.0 (C_p), 55.5 and 42.6 (CMe_3), 23.5 and 23.2 ($CHMe_2$), 30.5 and 28.0 ($CHMe_2$), 27.3 and 24.2 (CMe_3).

***syn*/*anti*-Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$(PMe$_3$).** These adducts are obtained by adding 1 or more equiv of PMe_3 to $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ in pentane followed by removing all solvents in vacuo. The yield is quantitative, the rotameric ratio being that of the starting alkoxide complex: ^{1}H NMR (syn rotamer, CD_2Cl_2) δ 12.07 (d, 1, $CHCMe_3$, J_{PH} = 6), 1.53 (d, 9, PMe_3, J_{PH} = 10), 1.36, 1.29, 1.16, and 1.13 (s, 9 each, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 292.3 ($CCMe_3$, J_{CP} = 23), 266.8 ($CHCMe_3$, J_{CH} = 110, J_{CP} = 18), 74.0 and 72.7 ($OCMe_3$), 52.4 and 46.7 (CMe_3), 34.3, 32.7, 31.2, and 31.0 (CMe_3), 20.0 (PMe_3, J_{CP} = 33); ^{1}H NMR (anti rotamer, CD_2Cl_2) δ 12.50 (d, 1, $CHCMe_3$, J_{PH} = 9), 1.53 (d, 9, PMe_3, J_{PH} = 10), 1.33, 1.31, 1.23 and 1.17 (s, 9 each, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 296.8 ($CCMe_3$, J_{CP} = 22), 265.2 ($CHCMe_3$, J_{CH} = 148, J_{CP} = 21), 73.9 and 73.3 ($OCMe_3$), 53.4 and 44.5 (CMe_3), 34.5, 33.8, 30.9 and 30.1 (CMe_3), 19.2 (PMe_3, J_{CP} = 27).

***anti*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe$_2$(CF$_3$)]$_2$(PMe$_3$).** PMe_3 (50 μL, 0.48 mmol) was added to a pentane solution of *syn*- and *anti*-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe_2(CF_3)]_2$ (0.25 g, 0.43 mmol). After 1 h the solvent was removed in vacuo to afford a quantitative yield of microcrystalline orange solid containing a mixture of syn and anti PMe_3 adducts. Fractional crystallization from cold dichloromethane afforded crystals that were pure *anti*-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)[OCMe_2(CF_3)]_2(PMe_3)$ by ^{1}H NMR: ^{1}H NMR δ 12.84 (d, 1, $CHCMe_3$, J_{PH} = 9), 1.94, 1.74, 1.47, 1.46 (s, 3 each, $OCMe_2(CF_3)$), 1.14 (d, PMe_3, J_{PH} = 10), 1.12 and 1.07 (s, 9 each, CMe_3). Anal. Calcd for $C_{21}H_{40}F_6O_2PRe$: C, 38.46; H, 6.14. Found: C, 38.24; H, 6.04.

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OAr′)$_2$(PMe$_3$).** A 2-fold excess of trimethylphosphine (55 μL, 0.54 mmol) was added to a solution of *syn*-$Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(dipp)_2$ (204 mg, 0.27 mmol) in 4 mL of pentane. The solution was left for 20 min and then chilled. Light yellow needles were filtered off and washed with pentane: yield 180 mg (90%); ^{1}H NMR δ 13.00 (d, 1, $CHCMe_3$, J_{PH} = 5), 7.35 and 7.10 (d, 2 each, H_m), 7.05 and 6.85 (t, 1 each, H_p), 3.80 and 3.62 (sept, 2 each, $CHMe_2$), 1.55, 1.52, 1.32, and 1.29 (d, 3 each, $CHMe_2$, J_{HH} = 7), 1.23 and 1.16 (d, 6 each, $CHMe_2$, J_{HH} = 7), 1.21 (d, 9, PMe_3, J_{PH} = 7), 1.12 and 0.86 (s, 9 each, CMe_3); ^{13}C NMR δ 298.7 ($CCMe_3$), 283.0 ($CHCMe_3$, J_{CH} = 110), 168.4 and 159.6 (C_i), 137.6 and 137.3 (C_m), 150.5, 122.6, 122.4, 119.2, and 118.1 (other C_{aryl} resonances, some overlap), 53.22 and 47.32 (CMe_3), 30.25 and 29.15 (CMe_3), 27.24, 26.79, 26.49, 25.63, 23.90, 23.72, 21.79, and 21.49 (*i*-Pr carbons), 18.03 (PMe_3, J_{CP} = 29). Anal. Calcd for $C_{37}H_{62}O_2PRe$: C, 58.78; H, 8.34. Found: C, 58.94; H, 8.27.

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OAr′)$_2$(*t*-BuNH$_2$).** Solid LiOAr′(ether) (1.91 g, 7.4 mmol) was added to a −40 °C solution of $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(t\text{-}BuNH_2)_2Cl_2$ (2.0 g, 3.7 mmol) in 15 mL of dichloromethane. After 2 h the solvent was removed in vacuo, and the residue was recrystallized from pentane to afford large yellow crystals which were washed with cold pentane and stored at −40 °C: yield 2.02 g (73%); ^{1}H NMR δ 11.06 (s, 1, $CHCMe_3$), 7.13 (d, 4, H_m), 6.94 (t, 2, H_p), 3.56 (sept, 4, $CHMe_2$), 2.63 (s, 2, NH_2), 1.40, 1.24, and 0.64 (s, 9 each, CMe_3), 1.33 and 1.31 (d, 12 each, $CHMe_2$, J_{HH} = 7); ^{13}C NMR (−80 °C, CD_2Cl_2) δ 293.1 ($CCMe_3$), 234.4 ($CHCMe_3$, J_{CH} = 123), 165.8 (C_i), 135.5 (both C_o), 122.3, 121.1, and 118.6 ($C_{m,p}$), 51.6, 50.8, and 44.0 (CMe_3), 31.4, 30.8, 28.4, 27.8, 25.6, 24.1, 23.6, 20.8, and 19.7 (CH_3).

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OAr′)$_2$(ArNH$_2$).** Solid LiOAr′(ether) (0.75 g, 2.9 mmol) was added to a solution of $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(H_2NAr)Cl_2]_2$ (0.75 g, 0.73 mmol) in 20 mL of dichloromethane at −40 °C. After 45 min the solvent was removed in vacuo, and the residue was recrystallized from pentane to afford large, yellow cubes that were washed with 3 × 5 mL of cold pentane: yield 0.92 g (79%); ^{1}H NMR δ 10.49 (s, 1, $CHCMe_3$), 7.1–6.9 (m, 6, H_{aryl}), 3.60 (sept, 4, $CHMe_2$), 3.81 (s, 2, NH_2), 2.13 (s, 6, $C_6H_3Me_2$), 1.38 and 1.34 (d, 12 each, $CHMe_2$, J_{HH} = 7), 1.30 and 0.77 (s, 9 each, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 293.7 ($CCMe_3$), 239.0 ($CHCMe_3$, J_{CH} = 128), aryl oxide [165.2 (C_i), 137.1 (C_o), 123.0, (C_m), 121.0 (C_p)], arylimido [141.5 (C_i), 125.8 (C_o), 128.9 (C_m), 121.6 (C_p)], 53.8 and 45.0 (CMe_3), 32.3 and 29.9 (CMe_3), 27.7 ($CHMe_2$), 23.9 and 23.7 ($CHMe_2$), 18.8 ($C_6H_3Me_2$). Anal. Calcd for $C_{42}H_{64}NO_2Re$: C, 62.97; H, 8.05; N, 1.75. Found: C, 62.94; H, 8.33; N, 1.88.

***syn*-Re(C-*t*-Bu)(CH-*t*-Bu)(OAr′)$_2$(py).** Solid LiOAr′(ether) (0.70 g, 2.7 mmol) was added to a −40 °C solution of $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl_2(py)_2$ (0.75 g, 1.35 mmol) in 10 mL of dichloromethane. After 40 min the solvents were removed in vacuo, and the residue was recrystallized from pentane to afford analytically pure, bright yellow crystals which were washed with 3 × 5 mL cold pentane (0.82 g (80%)): ^{1}H NMR (C_6D_6) δ 10.92 (s, 1, $CHCMe_3$), py [9.46 (d, 2, H_o), 6.90 (t, 1, H_p), 6.71 (t, 2, H_m)], aryl oxide [7.19 (d, 4, H_m), 6.98 (t, 2, H_p)], 3.67 (sept, 4, $CHMe_2$), 1.33 and 1.28 (d, 12 each, $CHMe_2$, J_{HH} = 7), 1.34 and 0.72 (s, 9 each, CMe_3); ^{13}C NMR (CD_2Cl_2, −66°) δ 295.8 ($CCMe_3$), 234.9 (*CH*-*t*-Bu), aryl oxide [166.5 (C_i), 136.5, 135.8 (C_o), 122.5, 121.5 (C_m), 119.0 (C_p)], py [149.0 (C_o), 138.4 (C_p), 124.3 (C_m)], 53.1 and 43.8 (CMe_3), 31.6 and 30.4 (CMe_3); other resonances at 29.2, 28.1, 26.5, 25.4, 24.0, 22.4, 21.0, and 19.8. Anal. Calcd for $C_{39}H_{58}NO_2Re$: C, 61.71; H, 7.70; N, 1.85. Found: C, 61.94; H, 8.00; N, 1.72.

Crystal Structure of [Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$]$_2$. An orange parallelpiped of $C_{36}H_{56}N_2Cl_4Re_2$ having approximate dimensions of 0.30 × 0.23 × 0.20 mm was mounted on a glass fiber. All measurements were made on an Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71079 Å) and a 12 KW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $25.10 < 2\theta < 34.97°$ corresponded to a monoclinic cell with dimensions a = 10.05 (1) Å, b = 21.65 (3) Å, c = 10.99 (1) Å, and β = 98.28 (9)°. For Z = 2 and fw = 1031.08, the calculated density is 1.446 g/cm^3. On the basis of the systematic absences of $h0l$ ($h + l \neq 2n$) and $0k0$ ($k \neq 2n$) the space group was determined to be $P2_1/n$. The data were collected at −65 ± 1 °C using the ω–2θ scan technique to a maximum 2θ value of 55.0°. ω scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.33° with a take-off angle of 6.0°. Scans of (1.42 ± 0.35 tan θ)° were made at a speed of 16.0°/min (in ω). The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of eight rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The counter aperture dimensions were 6.0 mm × 6.0 mm. The diameter of the incident beam collimator was 0.5 mm, and the crystal detector distance was 31 cm.

Of the 5843 reflections which were collected, 5543 were unique (R_{int} = 0.099); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 150 reflections remained constant throughout data collection time indicating crystal and

electronic stability (no decay correction was applied).

The linear absorption coefficient for Mo Kα is 54.3 cm^{-1}. An empirical absorption correction, using the program DIFABS,[40] was applied which resulted in transmission factors ranging from 0.68 to 1.48. The data were corrected for Lorentz and polarization effects.

The structure was solved by a combination of the Patterson method and direct methods. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealized positions (d_{C-H} = 0.95 Å), and were assigned isotropic thermal parameters which were 20% greater than the $B_{equivalent}$ value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 3476 observed reflections ($I > 3.00\sigma(I)$) and 235 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of R = 0.043 and R_w = 0.071.

The standard deviation of an observation of unit weight was 1.80. The weighting scheme was based on counting statistics and include a factor (p = 0.05) to downweight the intense reflections. Plots of $\sum w(|F_o| - |F_c|)^2$ versus $|F_o|$, reflection order in data collection, (sin θ/λ, and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier correspond to 1.09 and -1.16 e$^-$/Å^3, respectively.

Neutral atom scattering factors were taken from Cromer and Waber.[41] Anomalous dispersion effects were included in F_{calc};[42] the values of $\Delta f'$ and $\Delta f''$ were those of Cromer.[41] All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation.

Crystal Structure of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$(THF). Yellow crystals of *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$(THF) were prepared by cooling a saturated pentane solution. Data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo Kα radiation. Of the 7149 reflections which were collected, 6766 were unique (R_{int} = 0.062); equivalent reflections were merged. The intensities of three representative reflections which were measured after every 60 min of X-ray exposure time remained constant throughout data collection time indicating crystal and electronic stability (no decay correction was applied). The data were corrected for Lorentz and polarization effects. The structure was solved by a combination of the Patterson method and direct methods. The final cycle of full-matrix least-squares refinement (TEXRAY Structure Analysis Package, Molecular Structures Corporation (1985)) was based on 3697 observed reflections ($I > 3.00\sigma(I)$) and 343 variable parameters and converged (largest parameter shift was 0.03 times its esd) with unweighted and weighted agreement factors of R = 0.052 and R_w = 0.049. The maximum and minimum peaks on the final difference Fourier correspond to 0.78 and -1.94 e$^-$/Å^3, respectively. The nonhydrogen atoms were refined anisotropically. Crystal data are a = 9.891 (1) Å, b = 17.543 (2) Å, c = 16.570 (2) Å, β = 95.90 (2)°, Z = 4, fw = 759.69, ρ = 1.764 g/cm^3, space group = $P2_1/n$.

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Supplementary Material Available: ORTEP drawing and a fully labeled drawing for [Re(C-*t*-Bu)(CH-*t*-Bu)(ArNH$_2$)Cl$_2$]$_2$ and *syn*-Re(C-*t*-Bu)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$(THF) and a listing of final positional and thermal parameters (14 pages); table of final observed and calculated structure factors (68 pages). Ordering information is given on any current masthead page.

Structural Characterization of Zinc(II) Complexes of Octaethyloxophlorin Dianion and Octaethyloxophlorin Radical Anion

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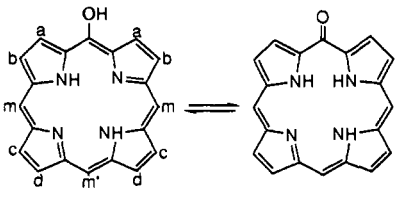
Abstract: The zinc(II) complex of octaethyloxophlorin dianion, Zn^{II}(OEPOH), readily dissolves in pyridine (py) to form red, air-sensitive solutions from which crystalline {(py)Zn^{II}(OEPOH··py)} has been isolated. The X-ray crystal structure reveals the presence of a five-coordinate zinc with an axial pyridine ligand and a planar oxophlorin macrocycle. The meso-hydroxyl substituent is hydrogen bonded to a second pyridine. Oxidation of red pyridine solutions of Zn^{II}(OEPOH) gives green solutions from which crystals of the stable free radical complex {(py)Zn^{II}(OEPO$^{\cdot}$)}(py) have been isolated. The X-ray crystal structure shows that the zinc(II) ion is five-coordinate with a single axial pyridine ligand. A second, uncoordinated pyridine is trapped on the opposite side of the oxophlorin radical. The structure suffers from inversion disorder as is typical for five-coordinate porphyrin complexes and from disorder of the meso-oxo substituent. The crystal packings of these two closely related substances, which differ only by an electron and a proton, are compared.

Introduction

Relatively little is known about the coordination of metal ions by oxophlorins, **1**, which are porphyrin derivatives that have an



1a **1b**

oxo or hydroxy group at one of the meso positions.[1] Iron oxophlorin complexes are important intermediates in the destruction of porphyrins in vivo in the process catalyzed by heme oxygenase[2] and in vitro in the process of porphyrin oxidation known as coupled oxidation.[3] They are formed by meso-hydroxylation of heme by dioxygen and undergo further attack by dioxygen to eventually form biliverdin as shown in eq 1. An understanding of the chemistry surrounding porphyrin degradation requires further information about the nature of the oxophlorin intermediates.

(1) Clezy, P. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. II, p 103.
(2) O'Carra, P. In *Porphyrins and Metalloporphyrins*; Smith, K. M., Ed.; Elsevier: Amsterdam, 1976; p 123.
(3) Bonnet, R.; Dimsdale, M. J. *J. Chem. Soc., Perkin Trans 1* **1972**, 2540.

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