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Rhenium(VII) Monoimido Alkylidene Complexes: Synthesis, Structure, and Lewis-Acid-Cocatalyzed Olefin Metathesis

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Five-coordinate alkylidene complexes of the general type Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ (NAr = N-2,6-C_6H_3-*i*-Pr_2; OAr′ = OC_6F_5 (**1a**), O-2,6-$C_6H_3Cl_2$ (**1b**), OC_6Cl_5 (**1c**)) can be prepared in high yield by treating [Re(C-*t*-Bu)(NHAr)Cl$_3$]$_2$ with 6 equiv of potassium phenoxide. Re(CH-*t*-Bu)(NAr)(O-2,6-$C_6H_3Cl_2$)$_3$ ($P2_1/c$, *a* = 11.461 (3) Å, *b* = 32.86 (1) Å, *c* = 11.680 (2) Å, β = 103.31 (2)°) is essentially a square pyramid in which the alkylidene ligand occupies the apical position. Re(CH-*t*-Bu)(NAr)(OC_6F_5)$_3$(THF) (**2**) is prepared in high yield from Re(C-*t*-Bu)(NHAr)Cl$_3$(THF) and 3 equiv of KOC_6F_5. Re(CH-*t*-Bu)(NAr)(OC_6F_5)$_3$(THF) ($P\bar{1}$, *a* = 11.037 (7) Å, *b* = 17.66 (1) Å, *c* = 10.981 (6) Å, α = 90.28 (6)°, β = 93.94 (6)°, γ = 94.15 (5)°) is pseudooctahedral with THF bound at the coordination site trans to the alkylidene ligand. Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ complexes do not react with terminal, internal, or strained cyclic olefins, possibly because an olefin can bind only to the site trans to the alkylidene ligand. Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ complexes react with pyridine to form alkylidyne complexes of the type Re(C-*t*-Bu)(NAr)(OAr′)$_2$(py) (OAr′ = O-2,6-$C_6H_3Cl_2$ (**3a**), OC_6Cl_5 (**3b**)). Alkylidene complexes of the type Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ (OAr′ = O-2,6-$C_6H_3Cl_2$ (**4a**), O-2,6-$C_6H_3Me_2$ (**4b**), OAr (O-2,6-C_6H_3-*i*-Pr_2), (**4c**), O-2,6-$C_6H_3(OMe)_2$ (**4d**)) can be prepared in high yield by treating Re(C-*t*-Bu)(NAr)Cl$_2$(DME) with 1 equiv of Ar′OH. NMR data suggest that Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ complexes are isostructural with Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ complexes. Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ complexes also do not readily react with terminal, internal, or strained cyclic olefins. However, addition of $GaBr_3$ to Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ (OAr′ = O-2,6-$C_6H_3Cl_2$, O-2,6-$C_6H_3Me_2$, OAr) yields highly active catalysts that metathesize *trans*-3-heptene at a rate of ~1000 turnover min^{-1}. In some cases propagating alkylidene species can be observed by NMR spectroscopy. Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ complexes react with pyridine to produce complexes of the type Re(C-*t*-Bu)(NAr)Cl$_2$(py)$_2$.

Introduction

Olefin metathesis[1] by transition-metal alkylidene complexes[2] is now relatively well-understood. Recent efforts in our laboratories have focused on the development of well-defined catalysts of the general type M(CH-*t*-Bu)(NAr)(OR)$_2$ (M = W, Mo; Ar = 2,6-C_6H_3-*i*-Pr_2).[3] We turned to rhenium in the hope of finding general routes to other well-characterized metathesis catalysts that may have some advantage over the Mo and W catalysts. One possibility is that catalysts based on rhenium will show a greater tolerance of functional groups.[1a,4] For example, the classical system derived from Re_2O_7, Al_2O_3, and $SnMe_4$ will tolerate olefins containing ester, carboxylate, ether, and cyano functionalities significantly better than classical Mo- and W-based catalysts.[4]

A variety of high-oxidation-state rhenium alkylidene complexes have been synthesized. Among four-coordinate alkylidene complexes are Re(CH-*t*-Bu)(N-*t*-Bu)$_2$Cl,[5] Re(CH-*t*-Bu)(NAr)$_2$Cl,[6] and ReO$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu),[7] none of which, however, is active for olefin metathesis. In contrast, complexes of the general type Re(CHR)(CR)(OR)$_2$,[8] in which the M=NAr unit in Mo and W catalysts of the type M(CH-*t*-Bu)(NAr)(OR)$_2$ effectively has been replaced by the Re≡C-*t*-Bu unit, are active metathesis catalysts if OR is relatively electron-withdrawing. We also have found that replacing the M=CH-*t*-Bu unit in M(CH-*t*-Bu)(NAr)(OR)$_2$ catalysts by the Re≡C-*t*-Bu unit yields acetylene metathesis catalysts, Re(C-*t*-Bu)(NAr)(OR)$_2$.[9] Other attractive four-coordinate candidates for olefin metathesis, complexes of the type [Re(CH-*t*-Bu)(NAr)(OR)$_2$]$^+$, cationic versions of the M(CH-*t*-Bu)(NAr)(OR)$_2$ catalysts, have not yet been synthesized.

In this paper we report the synthesis, structural characterization, and reactivity of two classes of *five*-coordinate rhenium(VII) monoimido alkylidene complexes. They turn out not to be olefin metathesis catalysts themselves, but catalytic activity can be initiated in complexes that contain a halide by adding a suitable Lewis-acid cocatalyst. Cationic four-coordinate complexes are the most likely active complexes under such circumstances.

Results

Preparation of Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ Complexes. Alkylidene complexes of the type Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ can be prepared by adding 6 equiv of the appropriate potassium phenoxide to [Re(C-*t*-Bu)(NHAr)Cl$_3$]$_2$ (eq 1).[9b] Compound **1a** (OAr′ = OC_6F_5) could not be isolated in crystalline form, but **1b** (OAr′ = O-2,6-$C_6H_3Cl_2$) and **1c** (OAr′ = OC_6Cl_5) both could be obtained as red/orange crystals from dichloromethane or toluene/pentane mixtures. Re(C-*t*-Bu)(NHAr)Cl$_3$(THF) is an alternative starting material, but when KOC_6F_5 is employed, the product is Re(CH-*t*-Bu)(NAr)(OC_6F_5)$_3$(THF) (**2**). It should be noted that relatively basic alkoxides such

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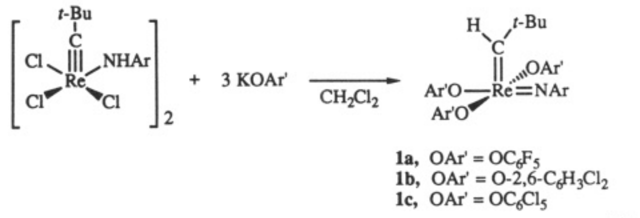

(1)

as 2,6-diisopropylphenoxide and *tert*-butoxide react with $[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3]_2$ to give $Re(C\text{-}t\text{-}Bu)(NAr)(OR)_2$ complexes.[9]

The structure of $Re(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}2,6\text{-}C_6H_3Cl_2)_3$ (**1b**) is shown in Figure 1. Relevant bond angles and distances are listed in Table I. It is essentially a square pyramid with three phenoxides and the phenylimido ligand in the basal sites; i.e., the vacant site is located trans to the alkylidene ligand. The metal sits above the basal plane (toward the alkylidene ligand) by approximately 0.24 Å. The alkylidene ligand is bent (Re–C(1)–C(2) = 139 (1)°) with the *tert*-butyl group pointing toward the imido ligand (dihedral angle N(1)–Re–C(1)–C(2) = 7 (2)°), the syn orientation. The Re=C bond length (1.87 (2) Å) is normal.[2a] The imido ligand is nearly linear (Re–N(1)–C(51) = 168 (1)°), and the short Re=N bond length (1.74 (1) Å) is consistent with donation of the nitrogen lone pair to the metal to form a pseudo triple bond.[10] Each phenoxide is bent by approximately the same amount ($Re\text{–}O\text{–}C_{ipso}$ = 129–135°), and the three Re–O distances are the same (1.98–2.00 Å). The dihedral angles that each phenyl ring makes with the O(2)/O(3)/O(4)/N(1) plane are 63° (O(2)), 106° (O(3)), 89° (O(4)), and 18° (N(1)). A potentially important feature of the structure is that one chloride (Cl(6) attached to C(46)) is separated from the metal center by only 2.832 (5) Å. Although this distance is long for a bridging rhenium–chloride bond,[11] one could regard the ortho chloride as a weakly bound sixth ligand in an octahedral complex. If the same is true in **1c**, then it would in part explain why **1b** and **1c** do not bind THF; the intramolecular interaction with chloride is more favorable. If the lone pair on the imido nitrogen and the chloride are counted, then complex **1b** (and probably **1c**) is an 18-electron species.

The structure of **2** (Figure 2, Table II) is similar to that of **1b** except THF is located trans to the alkylidene ligand in place of the weakly bound chloride. Again the metal is located above the basal plane by approximately 0.26 Å. The alkylidene is bent (Re–C(1)–C(2) = 140.3 (6)°) toward the phenylimido ligand (syn orientation) and the alkylidene–imido dihedral angle is small (N(1)–Re–C(1)–C(2) = 6.5 (8)°). The imido ligand is nearly linear (Re–N(1)–C(51) = 173.0 (5)°), suggesting that the nitrogen donates its lone pair to the metal to form a pseudo triple bond (6e total). Each phenoxide is bent to a *different* degree in this case ($Re\text{–}O\text{–}C_{ipso}$ = 128.1 (4)° (O(1)), 141.6 (4)° (O(2)), 154.4 (5)° (O(3))), as one might expect for the more electron-withdrawing, poorer π-bonding C_6F_5O ligands (C_6F_5OH, $pK_a = 5.35$; $o\text{-}C_6H_3Cl_2OH$, $pK_a = 6.80$). The phenyl rings are distorted from coplanarity with the least-squares plane defined by O(1), O(2), O(3), and N(1). The dihedral angles that each phenyl ring makes with the O(1)/O(2)/O(3)/N(1) plane are 47° (O(1)), 63° (O(2)), 58° (O(3)), and 23° (N(1)). The electron count in **2** is 18 if the electron pair on the imido ligand is included.

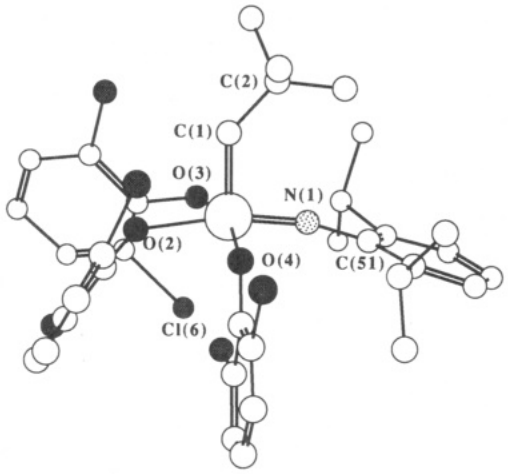

Figure 1. View of the structure of $Re(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(O\text{-}2,6\text{-}C_6H_3Cl_2)_3$.

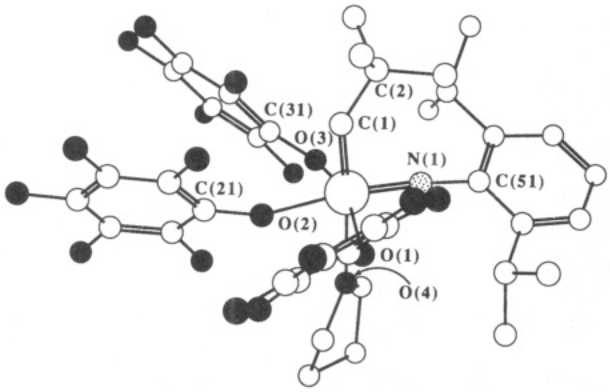

Figure 2. View of the structure of $Re(CH\text{-}t\text{-}Bu)(N\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)(OC_6F_5)_3(THF)$.

Table I. Selected Bond Distances (Å) and Angles (deg) for $Re(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}2,6\text{-}C_6H_3Cl_2)_3$[a]

Bond Distances			
Re–N(1)	1.74 (1)	N(1)–C(11)	1.38 (2)
Re–C(1)	1.87 (2)	C(1)–C(2)	1.51 (3)
Re–O(2)	2.00 (1)	O(2)–C(21)	1.34 (2)
Re–O(3)	2.00 (1)	O(3)–C(31)	1.36 (2)
Re–O(4)	1.98 (1)	O(4)–C(41)	1.35 (2)
Re–Cl(6)	2.832 (5)		
Bond Angles			
Re–C(1)–C(2)	139 (1)	C(1)–Re–O(2)	93.0 (7)
Re–O(2)–C(21)	135 (1)	C(1)–Re–O(3)	99.2 (7)
Re–O(3)–C(31)	132 (1)	C(1)–Re–O(4)	95.8 (7)
Re–O(4)–C(41)	129 (1)	N(1)–Re–C(1)	99.8 (7)
Re–N(1)–C(51)	168 (1)	O(1)–Re–O(2)	82.0 (2)
N(1)–Re–O(2)	167.2 (6)	O(1)–Re–O(3)	156.9 (2)
N(1)–Re–O(3)	92.9 (6)	O(1)–Re–O(4)	77.3 (2)
N(1)–Re–O(4)	96.5 (6)	O(2)–Re–O(3)	85.7 (2)

[a] Atoms are numbered as shown in Figure 1.

NMR data for the rhenium(VII) monoimido neopentylidene complexes are listed in Table III. In general, the alkylidene carbon and proton resonances are found at relatively low field and CH_α coupling constants are relatively large. A low value of J_{CH} in alkylidene complexes of earlier d^0 transition metals has been taken as a measure of the degree of distortion of the alkylidene ligand (small M–C–H angle) that results from donation of C–H bond density into an empty d or hybrid orbital on an electron-deficient metal.[2a] The J_{CH} values in these complexes are of the same magnitude as those observed in other high-

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(10) Nugent, W. A.; Mayer, J. M., *Metal-Ligand Multiple Bonds*, Wiley: New York, 1988.

(11) (a) Other examples of Re(VII) bridging chloride distances include 2.712 (3) Å in $[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_2]_2(\mu\text{-}Cl)_2$[9b] and 2.673 (4) Å in $\{[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl(ArNH_2)](\mu\text{-}Cl)\}_2$.[11b] (b) Toreki, R.; Davis, W. M. Unpublished results.

Table II. Selected Bond Distances (Å) and Angles (deg) for Re(CH-*t*-Bu)(NAr)(OC$_6$F$_5$)$_3$(THF)[a]

	Bond Distances		
Re–N(1)	1.724 (5)	N(1)–C(5)	1.389 (8)
Re–C(1)	1.905 (7)	C(1)–C(2)	1.49 (1)
Re–O(1)	1.985 (5)	O(1)–C(11)	1.351 (8)
Re–O(2)	1.990 (5)	O(2)–C(21)	1.292 (8)
Re–O(3)	2.012 (5)	O(3)–C(31)	1.307 (8)
Re–O(4)	2.339 (5)		
	Bond Angles		
Re–C(1)–C(2)	140.3 (6)	C(1)–Re–O(1)	98.7 (2)
Re–O(1)–C(11)	128.1 (4)	C(1)–Re–O(2)	91.5 (3)
Re–O(2)–C(21)	154.4 (5)	C(1)–Re–O(3)	101.1 (2)
Re–O(3)–C(31)	141.6 (4)	C(1)–Re–O(4)	173.6 (2)
Re–N(1)–C(51)	173.0 (5)	O(1)–Re–O(2)	82.0 (2)
N(1)–Re–C(1)	98.0 (3)	O(1)–Re–O(3)	156.9 (2)
N(1)–Re–O(1)	96.9 (2)	O(1)–Re–O(4)	77.3 (2)
N(1)–Re–O(2)	170.5 (2)	O(2)–Re–O(3)	85.7 (2)
N(1)–Re–O(3)	92.0 (2)	O(2)–Re–O(4)	83.0 (2)
N(1)–Re–O(4)	87.6 (2)	O(3)–Re–O(4)	81.8 (2)

[a] Atoms are numbered as shown in Figure 2.

Table III. NMR Data for Rhenium Monoimido Alkylidene Complexes[a]

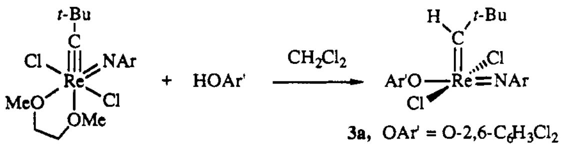
complex	$\delta(H_\alpha)$	$\delta(C_\alpha)$	J_{CH}
Re(CH-*t*-Bu)(NAr)(OC$_6$F$_5$)$_3$ (**1a**)	12.60[b]		
Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$Cl$_2$)$_3$ (**1b**)	12.82[b]	296.5	149
Re(CH-*t*-Bu)(NAr)(OC$_6$Cl$_5$)$_3$ (**1c**)	13.71	296.5	142
Re(CH-*t*-Bu)(NAr)(OC$_6$F$_5$)$_3$(THF) (**2**)	13.60	293.2	146
syn-Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$Cl$_2$)Cl$_2$ (**3a**)	13.58	304.5	140
anti-Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$Cl$_2$)Cl$_2$ (**3a**)	14.45		
Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$Me$_2$)Cl$_2$ (**3b**)	13.48	296.8	143
syn-Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)Cl$_2$ (**3c**)	13.36	296.5	148
anti-Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$-*i*-Pr$_2$)Cl$_2$ (**3c**)	14.15		
Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$(OMe)$_2$)Cl$_2$ (**3d**)	13.26		

[a] Spectra recorded in CD$_2$Cl$_2$ unless noted otherwise. [b] Spectrum recorded in C$_6$D$_6$.

oxidation-state rhenium alkylidene complexes. For example, in Re(NAr)$_2$(CH-*t*-Bu)(CH$_2$-*t*-Bu) J_{CH_α} = 139 Hz.[6c]

None of the five-coordinate alkylidene complexes described thus far will metathesize 1-pentene, *cis*-3-hexene, or even norbornene. Since THF has been shown to exchange with free THF in **2** at room temperature, an olefin should be able to coordinate to the metal center. However, the only coordination site on the metal that is available is trans to the alkylidene ligand; thus, a metallacyclobutane ring cannot form without some rearrangement of the core of the complex.

Preparation of Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ Complexes and Lewis-Acid-Cocatalyzed Olefin Metathesis. Addition of 1 equiv of Ar′OH to Re(NAr)(C-*t*-Bu)Cl$_2$(dme) in dichloromethane affords complexes of the type Re(NAr)(CH-*t*-Bu)(OAr′)Cl$_2$ (eq 2). Proton and carbon NMR data for complexes **3a–d** can be found in Table III. We believe that **3a–d** most likely are isostructural with **1a–c** and **2**. The reaction shown in eq 2 so far has been successful only for phenols; aliphatic and partially fluorinated alcohols (e.g. *t*-BuOH, (CF$_3$)Me$_2$COH, (CF$_3$)$_2$MeCOH, etc.) and thiols (e.g. HSAr) do not react with Re(C-*t*-Bu)(NAr)Cl$_2$(DME).



3a, OAr′ = O-2,6-C$_6$H$_3$Cl$_2$
3b, OAr′ = O-2,6-C$_6$H$_3$Me$_2$
3c, OAr′ = O-2,6-C$_6$H$_3$-*i*-Pr$_2$
3d, OAr′ = O-2,6-C$_6$H$_3$(OMe)$_2$

(2)

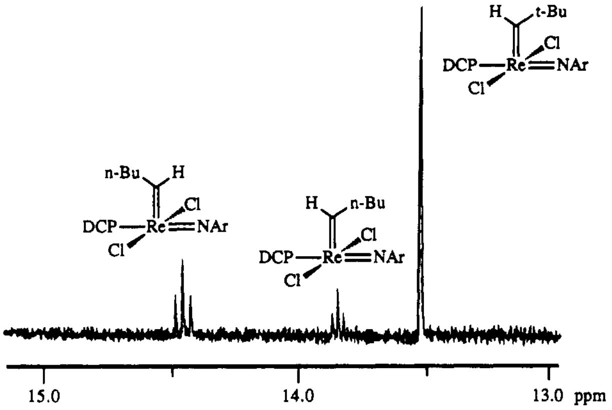


Figure 3. ^{1}H NMR spectrum showing the alkylidene region in a sample of Re(CH-*t*-Bu)(NAr)(O-2,6-C$_6$H$_3$Cl$_2$)Cl$_2$ in CD$_2$Cl$_2$ in the presence of excess 1-hexene and 0.5 equiv of GaCl$_3$.

In Re(CH-*t*-Bu)(NAr)(OAr′)Cl$_2$ complexes, what is believed to be the syn rotamer forms initially, but after 10–12 h in solution, the anti rotamer forms slowly at expense of the syn form. For example, for **3a** H$_\alpha$ resonates at 13.58 ppm for the syn rotamer and 14.45 ppm for the anti rotamer, while for **3c** H$_\alpha$ resonates at 13.38 ppm for the syn rotamer and 14.15 ppm for the anti rotamer. Analogous behavior has been observed for complexes of the type Re(C-*t*-Bu)(CH-*t*-Bu)(OR)$_2$.[8] In both types of rhenium complexes the barrier to alkylidene ligand rotation is significantly larger than it is in complexes of the type M(CH-*t*-Bu)(NAr)(OR)$_2$ (M = Mo, W).[3,12]

Complexes **3a–d** do not react readily with olefins.[13] However, olefins can be metathesized in the presence of a Lewis acid. When 20 mol % of GaBr$_3$ was added to **3a**, **3b**, and **3c**, 1000 equiv (based on GaBr$_3$) of *cis*-3-heptene could be metathesized in 1 min. Approximately 0.8 equiv of 2,2-dimethyl-3-hexene, a primary metathesis product, could be observed by GC. AlCl$_3$, AlBr$_3$, and GaCl$_3$ were much less successful; only very slow metathesis was observed by employing 20% to several equivalents of the Lewis acid. These stronger Lewis acids might be expected to exchange phenoxide ligands for halides, and it is believed that the hypothetical Re(CH-*t*-Bu)(NAr)Cl$_3$, the product of such an exchange, would be unstable.[14] Relatively weak Lewis acids (e.g., SnCl$_4$) did not activate the metal toward metathesis at all.

Efforts to observe new alkylidene complexes by low-temperature proton NMR spectroscopy in the GaBr$_3$ system were not totally successful. New alkylidene proton resonances were observed, but the problem was complicated by Br–Cl exchange. When **3b** was treated with 0.5

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(13) Re(CH-*t*-Bu)(NAr)(DCP)Cl$_2$ (DCP = O-2,6-C$_6$H$_3$Cl$_2$) will metathesize 10 equiv of *cis*-3-heptene 70% of the way to equilibrium in 6 h. However, a proton NMR spectrum of the reaction mixture (in CD$_2$Cl$_2$) shows only Re(CH-*t*-Bu)(NAr)(DCP)Cl$_2$ to be present. The true catalyst in this case is unknown. It may be a trace impurity, a hydrolysis product of the starting alkylidene complex, or simply more reactive Re(CHR)(NAr)(DCP)Cl$_2$ complexes that result from slow initial reaction of Re(CH-*t*-Bu)(NAr)(DCP)Cl$_2$ with heptene.

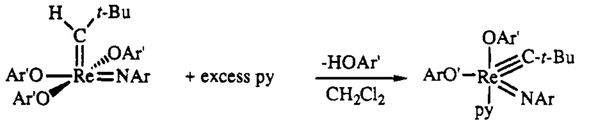
(14) Re(NAr)(CH-*t*-Bu)Cl$_3$ has never been observed, whereas Re(NHAr)(C-*t*-Bu)Cl$_3$ can be isolated as a dimer containing bridging chlorides.[9b]

(15) (a) Burton, J. T.; Puddephatt, R. J.; Jones, N. L.; Ibers, J. A. *Organometallics* 1983, 2, 1487. (b) Miyashita, A.; Takahashi, M.; Takaya, H. *J. Am. Chem. Soc.* 1981, *103*, 6257.

equiv of $GaBr_3$ in CD_2Cl_2 in an NMR tube, a new alkylidene resonance could be observed at 13.35 ppm and another at 13.33 ppm, in addition to the starting alkylidene resonance at 13.38 ppm, a fact that could be explained if Re(CH-*t*-Bu)(NAr)(DCP)ClBr and Re(CH-*t*-Bu)(NAr)(DCP)Br_2 (DCP = O-2,6-$C_6H_3Cl_2$) had formed. Although Re(CH-*t*-Bu)(NAr)(DCP)Cl_2/$GaCl_3$ is not a highly active catalyst combination, addition of 0.5 equiv of $GaCl_3$ to **3a** in the presence of 1.5 equiv of 1-hexene showed two new triplets in the alkylidene region at 13.88 and 14.48 ppm downfield from TMS (Figure 3), in addition to the alkylidene resonance in Re(CH-*t*-Bu)(NAr)(DCP)Cl_2 at 13.58 ppm. The most likely explanation is that a mixture of *syn*- and *anti*-Re(CH-*n*-Bu)(NAr)(DCP)Cl_2 has formed. Rotamers of **3a** have been observed spectroscopically (vide supra), and the difference in chemical shift for the syn and the anti forms is consistent with that observed here. The fact that Re(CH-*t*-Bu)(NAr)Cl_3 has never been observed augurs against it being formed in this circumstance by exchange of DCP by chloride.

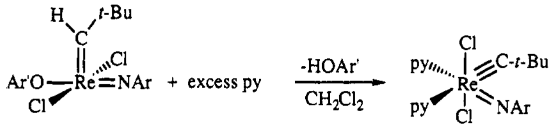
The high activity of many classical catalysts is believed to be the consequence of activation by Lewis acids, and perhaps formation of cationic species.[1] Highly active metathesis catalysts can be generated from five-coordinate tungsten alkylidene complexes by treatment with a Lewis acid,[16d] and a crystal structure of a tungsten alkylidene/gallium bromide adduct has been reported.[16b] Four-coordinate cationic complexes are believed to be the active species in the systems containing the well-characterized five-coordinate tungsten alkylidene complexes.

Deprotonation of Re(CH-*t*-Bu)(NAr)X_3 To Give Imido Neopentylidyne Complexes. Pyridine was added to **1b** and **1c** in an effort to prepare simple base adducts. In each case the orange solution of Re(CH-*t*-Bu)(NAr)(OAr′)$_3$ turned forest green in 15 min and alkylidyne complexes of the type Re(C-*t*-Bu)(NAr)(OAr′)$_2$(py) (py = pyridine; eq 3) could be isolated. Complexes **4a** and **4b** also could be prepared by adding pyridine to four-coordinate imido alkylidyne complexes.[9] The proposed geometry of **4a** and **4b** is consistent with all NMR data. In CD_2Cl_2 **4a** exists in equilibrium with what behaves like the base-free complex ($^{298}K_{eq}$ = 0.27), while **4b** does not lose pyridine to any significant degree at room temperature, presumably because the perchlorophenoxide ligand is the more electron-withdrawing. Treatment of **1b** and **1c** with excess triethylamine or DBU also yields what appear to be base-free Re(C-*t*-Bu)(NAr)(OAr′)$_2$ complexes (by NMR spectroscopy) and 1 equiv of alcohol. Analogous reactions of **3a–d** with pyridine in dichloromethane yield the previously described six-coordinate complex shown in eq 4.[6c] Attempts to employ phenoxides as bases in analogous reactions gave mixed results. For example, reaction of **3a** with potassium 2,6-dichlorophenoxide yielded a mixture of Re(CH-*t*-Bu)(NAr)(OAr′)$_x$Cl$_{3-x}$ (x = 1–3) species. On the other hand, treatment of **3c** with 1 equiv of lithium 2,6-diisopropylphenoxide yielded Re(C-*t*-Bu)(NAr)(OAr)$_2$, Re(CH-*t*-Bu)(NAr)(OAr)Cl_2 (starting material), and ArOH in a 1:1:1 ratio. It is not yet known whether a neopentylidyne complex forms by direct deprotonation of a neopentylidene ligand or whether coordination of the base to the site trans to the alkylidene could crowd the coordination sphere and lead to intramolecular abstraction of the α-hydrogen by a phenoxide ligand.



4a, OAr′ = O-2,6-$C_6H_3Cl_2$
4b, OAr′ = OC_6Cl_5

(3)



(4)

Discussion

There are two major problems with the rhenium imido alkylidene complexes that we have studied here behaving as well-defined olefin metathesis catalysts. The first is that amido alkylidyne complexes also are relatively stable and are formed readily. Only if proton transfer from nitrogen back to carbon were rapid would an alkylidene ligand be available for metathetical reactions. So far there is no evidence that that is the case. The second problem is that the vacant position where an olefin would bind in these five-coordinate species is trans to the alkylidene ligand. It is difficult to form a six-coordinate metallacyclobutane complex for steric reasons alone. Although several six-coordinate metallacyclobutane complexes are known for both late and early transition metals,[15] they are not formed in metathesis-like reactions. In addition, for **1b** and **1c**, an ortho chloride blocks the site trans to the alkylidene ligand, so that in spite of the fact that the chlorinated phenoxides are electron-withdrawing enough to activate the metal as an electrophile, **1b** and **1c** do not react with olefins. The lack of reactivity of **1** and **2** toward olefins should be compared with five-coordinate tungsten alkylidene complexes,[16] which also do not react readily with olefins in the absence of Lewis acids. Stereoelectronic control of this kind also has been invoked to rationalize the low reactivity of trigonal-pyramidal complexes of the type Ta(CH-*t*-Bu)(SR)$_3$ toward olefins[17] and M(C-*t*-Bu)(SR)$_3$ (M = Mo, W) complexes toward acetylenes.[18]

On the basis of the structures of **1b** and **2** one could conclude that the alkylidene ligand shows a considerably greater trans influence than the imido ligand. ("Trans influence" can refer either to "the extent to which the ligand weakens the bond trans to itself"[19] (thermodynamic trans effect) or to the effect a ligand has on the rate of substitution of trans ligands (kinetic trans effect)[20] and has been rationalized both in terms of differences in static π-bonding[21] and in terms of σ-bond polarization.[22]) *If* linearity of the imido ligand can be taken as an indication of at least some tendency to form a second metal–nitrogen π-bond, a linear imido ligand (pseudo triple bond) would be expected to show a *greater* trans influence than the

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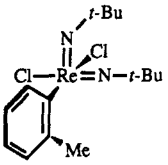
(21) See, for example: Huheey, J. E. *Inorganic Chemistry*, 2nd ed.; Harper and Row: New York, 1983.

(22) Grinberg, A. A. In *An Introduction to the Chemistry of Complex Compounds*, 2nd ed.; Leach, J. R., Busch, D. H., Trimble, R. F., Jr., Eds.; Pergamon: Elmsford, NY, 1962.

neopentylidene ligand. However, the structures of **1b** and **2** can be explained on the basis of the relative σ-bond strengths of the imido and alkylidene ligands. Electronegativity considerations alone would suggest that a given type of σ orbital on carbon is a better base than a given type of σ orbital on nitrogen. Another way of looking at it is that the p and s orbitals on C or N are lower in energy than the d orbitals on Re, but those on carbon are not as low as those on nitrogen.[23] Therefore, a given σ orbital on carbon will be closer in energy to the rhenium d orbitals than one on nitrogen and will form a stronger metal–ligand σ bond.

It is interesting to note that the structure of $Re(N\text{-}t\text{-}Bu)_2(o\text{-tolyl})Cl_2$[24]



is a square pyramid with a bent (150.5 (7)°) imido ligand trans to the vacant site and a linear (176.4 (7)°) imido ligand in a basal coordination position. Arguments analogous to those above also can explain its structure. The (sp hybridized) σ orbital in the *linear* imido ligand should form the *weaker* σ bond (in spite of the higher s content of the sp hybrid), since the dative π bond that is possible in the linear imido ligand leaves the nitrogen atom more positively charged (and a significantly poorer base) than in the bent imido ligand. Therefore, the sp^2-hybridized imido ligand will end up in the apical position.

Data in the literature for "d^0" alkylidene and alkylidyne complexes are consistent with the proposal that covalent bond multiplicity is probably the primary factor in determining the trans effect. (A significant fraction of the effect could be ascribed to the greater s character of the σ bond in a metal–ligand bond of higher multiplicity.) For example, the geometry about the metal in $[W(\text{cyclopentylidene})(OCH_2\text{-}t\text{-}Bu)_2Br_2]_2$ is essentially square pyramidal with a weakly bound μ-bromide trans to the alkylidene ligand, while the structure of $W(\text{cyclopentylidene})(OCH_2\text{-}t\text{-}Bu)_2Br_2(GaBr_3)$ is essentially the same, in which a bromide from $GaBr_3$ occupies the position trans to the alkylidene ligand.[16b] In $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(py)_2I_2$ the Re–py bond trans to the neopentylidyne ligand is marginally longer (2.415 (6) Å) than that trans to the neopentylidene ligand (2.369 (6) Å).[25] In $\{[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)Cl(ArNH_2)](\mu\text{-}Cl)\}_2$[11b] the Re–Cl bond trans to the neopentylidyne ligand is again marginally longer than that trans to the neopentylidene ligand. In $\{[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_2](\mu\text{-}Cl)\}_2$[9b] the Re–Cl(bridging) bond trans to the neopentylidene ligand is longest (2.712 (3) Å), that trans to the planar amido ligand is the next longest (2.407 (3) Å), and that trans to a chloride ligand is the shortest (2.298 (4) Å).

It should be pointed out that the favored approach of an olefin to complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$[26] and an alkyne to complexes of the type $Re(C\text{-}t\text{-}Bu)(NAr)(OR)_2$[9b] appears to be on the C/N/O face trans to what becomes an apical *alkoxide* ligand in a trigonal bipyramid. Base adducts of $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ species that are consistent with this proposal have been structurally characterized, although at least one other type has been observed in solution.[12] The initial metallacyclobutane or metallacyclobutene complexes (respectively) are not observable; they rearrange readily to other types of metallacycles, several of which have been structurally characterized. Since all of the compounds discussed above are six-coordinate or pseudo six-coordinate, we conclude that factors other than the relative trans influence of multiply bound ligands must play an important role in determining the structures of five-coordinate species formed from $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$ or $Re(C\text{-}t\text{-}Bu)(NAr)(OR)_2$ complexes.

The relatively large CH coupling constants in the complexes discussed here are consistent with the trend observed in high-oxidation-state complexes so far as the metal becomes less electropositive overall (core Ta(OH) → W(NR) → Re(CR)).[2a,b,6] Relatively small coupling constants have been attributed to relatively large M–C–C angles and corresponding small M–C–H angles in alkylidene ligands that result from donation of C–H electron density into an empty metal orbital. Such interaction has been studied by theoretical methods in some detail.[27] In the square-pyramidal complexes described here, there is no orbital on rhenium that is available for interacting with the alkylidene $C\text{–}H_\alpha$ bond, and only minimal distortion therefore is possible. At this stage it is unknown which determines the relatively high values for J_{CH_α} for rhenium, the less electropositive nature of rhenium or the decreased distortion of the alkylidene ligand.

Conclusions

A fine balance of steric and electronic factors allow $Re(CH\text{-}t\text{-}Bu)(NAr)(OR)_3$ and $Re(CH\text{-}t\text{-}Bu)(NAr)(OR)Cl_2$ complexes to form in some circumstances instead of imido neopentylidyne complexes. Unfortunately the site where an olefin would bind in the five-coordinate imido neopentylidene species is trans to the alkylidene ligand, which partly explains why they do not react readily with olefins. Addition of Lewis acids to $Re(CH\text{-}t\text{-}Bu)(NAr)(OR)Cl_2$ complexes generates active olefin metathesis catalysts, most likely four-coordinate cationic species. Imido neopentylidene complexes are converted into imido neopentylidyne complexes upon addition of bases.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere is a Vacuum Atmospheres HE43-2 drybox or by using standard Schlenk techniques. Reagent grade diethyl ether, dimethoxyethane (DME), and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl under nitrogen. Reagent grade toluene was distilled from molten sodium under nitrogen. Commercial grade pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade dichloromethane was distilled from calcium hydride prior to use. Pyridine was stirred over potassium hydroxide and distilled from calcium hydride under nitrogen. In general, deuterated NMR solvents were dried by passage through a column of activated alumina and stored over molecular sieves.

Olefins (*cis*-3-heptene, 1-hexene, norbornene) were distilled from sodium sand under nitrogen. HOC_6F_5, $HO\text{-}2,6\text{-}C_6H_3Cl_2$, and $HO\text{-}2,6\text{-}C_6H_3Me_2$ were sublimed prior to use. HOAr was distilled prior to use. All other phenols were used as received. KOC_6F_5, $KO\text{-}2,6\text{-}C_6H_3Cl_2$, and KOC_6Cl_5 were prepared from the appropriate

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phenol and KH in ether. $\mathrm{LiOAr{\cdot}OEt_2}$ was prepared from the parent alcohol and n-BuLi in ether. All other reagents were purchased from commercial sources and purified by standard techniques. Re(C-t-Bu)(NHAr)$\mathrm{Cl_3}$, Re(C-t-Bu)(NHAr)$\mathrm{Cl_3}$(THF), and Re(C-t-Bu)(NAr)$\mathrm{Cl_2}$(DME) were prepared by literature methods.[9b]

^{1}H and ^{13}C NMR data are listed in parts per million downfield from TMS. Coupling constants are quoted in hertz. Obvious multiplicities and routine coupling constants are usually not listed. Spectra were obtained at ca. 25 °C unless otherwise noted. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory (Woodside, NY) or in our own laboratory with use of a Perkin-Elmer PE-2400 microanalyzer.

Olefin Metathesis Studies. In a typical experiment, 10 mg of Re(CH-t-Bu)(NAr)(OAr′)$\mathrm{Cl_2}$ (OAr′ = O-2,6-$\mathrm{C_6H_3Cl_2}$, OAr, or O-2,6-$\mathrm{C_6H_3Me_2}$) was dissolved in 1 mL dichloromethane. In a separate flask, the olefin and toluene (internal standard) were mixed and a small (~100-μL) aliquot of the olefin solution was removed to determine the initial olefin concentration. The rest of the solution was added to the rhenium complex along with the Lewis acid. Samples were then removed at regular intervals, quenched with activated alumina, and analyzed by gas chromatography on a capillary column (Carbowax).

Preparation of Compounds. Re(CH-t-Bu)(NAr)($\mathrm{OC_6F_5}$)$_3$ (1a). $\mathrm{KOC_6F_5}$ (0.079 g, 0.36 mmol) was added to a solution of [Re(C-t-Bu)(NHAr)$\mathrm{Cl_3}$] (0.060 g, 0.11 mmol) in 5 mL of $\mathrm{CH_2Cl_2}$ at −40 °C. The reaction mixture was stirred for 2.5 h and the solvent removed in vacuo. The product was extracted in pentane, and the extract was filtered through Celite and concentrated to give 0.085 g (78%) of a red oil: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 12.60 (s, 1, $\mathrm{C}H\mathrm{CMe_3}$), 6.91 (s, 3, imido H), 3.93 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$, 1.13 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.12 (d, 12, $\mathrm{CH}\mathit{Me}_2$).

Re(CH-t-Bu)(NAr)(O-2,6-$\mathrm{C_6H_3Cl_2}$)$_3$ (1b). To a solution of Re(C-t-Bu)(NHAr)$\mathrm{Cl_3}$ (0.100 g, 0.19 mmol) in 15 mL of $\mathrm{CH_2Cl_2}$ at −40 °C was added KO-2,6-$\mathrm{C_6H_3Cl_2}$ (0.116 g, 0.58 mmol). The mixture was stirred at room temperature for 3 h and the solvent removed in vacuo. The solids were extracted in pentane, and the extract was filtered through Celite and concentrated to dryness, leaving red microcrystals, which were recrystallized from a minimum volume of pentane/$\mathrm{CH_2Cl_2}$ (1:1) to give 0.115 g (67%) of red crystals: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 12.82 (s, 1, $\mathrm{C}H\mathrm{CMe_3}$), 7.37–7.25 (unresolved multiplet, 3, imido H_{Ar}), 7.08 (d, 4, phenoxide H_{o}), 6.88 (d, 2, phenoxide H_{o}), 6.57 (t, 2, phenoxide H_{p}), 6.35 (t, 1, phenoxideH_{p}), 3.86, (sept, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.50 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.07 (d, 12, $\mathrm{CH}\mathit{Me}_2$): ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 293.23 ($C\mathrm{HCMe_3}$), 155.94 (imido C_{i}), 155.45 (phenoxide C_{i}), 155.34 (phenoxide C_{i}), 154.86 (phenoxide C_{o}), 149.08 (phenoxide C_{o}), 132.60, 128.28, 126.77, 126.55, 124.61, 121.03, 120.25 (imido and phenoxide C_{Ar}), 52.77 ($\mathrm{CH}C\mathrm{Me_3}$), 32.05 ($\mathrm{CHC}\mathit{Me}_3$), 28.58 ($C\mathrm{HMe_2}$), 24.40 ($\mathrm{CH}\mathit{Me}_2$). Anal. Calcd for $\mathrm{ReNC_{35}H_{36}O_3Cl_6}$: C, 45.81; H, 3.95; N, 1.53. Found: C, 45.88; H, 3.91; N, 1.38.

Re(CH-t-Bu)(NAr)($\mathrm{OC_6Cl_5}$)$_3$ (1c). $\mathrm{KOC_6Cl_5}$ (0.400 g, 1.31 mmol) was added to a solution of 0.200 g of Re(C-t-Bu)(NHAr)$\mathrm{Cl_3}$ (0.37 mmol) in $\mathrm{CH_2Cl_2}$ (20 mL) at −40 °C. The mixture was stirred for 3 h and filtered through Celite. The solvent was removed in vacuo, leaving a dark red powder. Recrystallization from a minimum volume of $\mathrm{CH_2Cl_2}$ at −40 °C left 0.220 g (48%) of orange crystals: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 13.71 ($\mathrm{C}H\mathrm{CMe_3}$), 7.45 (imido H_{p}), 7.34 (imido H_{m}), 3.78 ($\mathrm{C}H\mathrm{Me_2}$), 1.50 ($\mathrm{CHC}\mathit{Me}_3$), 1.1 ($\mathrm{CH}\mathit{Me}_2$): ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 296.52 ($C\mathrm{HCMe_3}$), 155.42 (imido C_{i}), 148.66 (phenoxide C_{i}), 135.01, 132.84, 131.80, 131.07, 130.75, 126.06, 125.97 (C_{aryl}), 53.96 ($\mathrm{CH}C\mathrm{Me_3}$), 31.68 ($\mathrm{CHC}\mathit{Me}_3$), 28.90 ($\mathrm{C}H\mathrm{Me_2}$), 24.30 ($\mathrm{CH}\mathit{Me}_2$). Three different samples gave different analytical results that were not quite satisfactory. The reasons are not known.

Re(CH-t-Bu)(NAr)($\mathrm{OC_6F_5}$)$_3$(THF) (2). $\mathrm{KOC_6F_5}$ (0.339 g, 1.52 mmol) was added to a purple solution of Re(C-t-Bu)(NHAr)$\mathrm{Cl_3}$(THF) (0.300 g, 0.49 mmol) in 15 mL of $\mathrm{CH_2Cl_2}$ at −40 °C. The mixture was stirred for 2 h while it was warmed to room temperature and filtered through Celite, and the solvent was removed in vacuo from the filtrate to give a red oil. Orange crystals (0.35 g, 68%) were obtained from pentane: ^{1}H NMR ($\mathrm{C_6D_6}$) δ 12.82 ($\mathrm{C}H\mathrm{CMe_3}$), 6.95 (unresolved mult, imido H_{o}, H_{p}), 4.06 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$), 3.86 (br t, 4, *THF*), 1.43 (mult, 4, *THF*), 1.20 ($\mathrm{CHC}\mathit{Me}_3$), 1.17 ($\mathrm{CH}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 299.40 (d, J_{CH} = 149, $C\mathrm{HCMe_3}$), 154.55 (imido C_{i}), 148.47 (phenoxide C_{i}), 143.20 (phenoxide C_{i}), 142.30–123.29 (phenoxide, imido carbons), 68.61 (*THF*), 53.03 ($\mathrm{CH}C\mathrm{Me_3}$), 31.01 ($\mathrm{CHC}\mathit{Me}_3$), 28.60 ($\mathrm{CH}\mathit{Me}_2$), 25.45 (*THF*), 24.21 ($\mathrm{CH}\mathit{Me}_2$). Anal. Calcd for $\mathrm{ReC_{42.5}H_{41}NO_4F_{15}}$: C, 45.73; H, 3.78; N, 1.29. Found: C, 45.92; N, 4.29; H, 1.30. (Half of a molecule of pentane per molecule of Re(CH-t-Bu)(NAr)($\mathrm{OC_6F_5}$)$_3$(THF) was included in the calculated values on the basis of NMR spectra.)

Re(CH-t-Bu)(NAr)(O-2,6-$\mathrm{C_6H_3Cl_2}$)$\mathrm{Cl_2}$ (3a). To a solution of Re(C-t-Bu)(NAr)$\mathrm{Cl_2}$(DME) (1.00 g, 16.9 mmol) in dichloromethane (10 mL) was added HO-2,6-$\mathrm{C_6H_3Cl_2}$ (0.276 g, 16.9 mmol). After 15 min the solution changed from deep red to bright red-orange. Removal of solvent in vacuo left an orange solid, which was washed with pentane (5 mL) and ether (5 mL) to give 1.0 g (90%) of orange microcrystals that were greater than 95% pure by NMR spectroscopy. The product was recrystallized from a minimum amount of ether to give 0.765 g (two crops, 70%) of red-orange crystals: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 13.58 ($\mathrm{C}H\mathrm{CMe_3}$), 7.44–7.31 (mult, 5, imido H_{Ar}, phenoxide H_{m}), 6.80 (t, 1, phenoxide H_{p}), 4.15 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.42 ($\mathrm{CHC}\mathit{Me}_3$), 1.28 (d, 12, $\mathrm{CH}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 306.46 (d, J = 140, $C\mathrm{HCMe_3}$), 157.04 (imido C_{i}), 152.90 (imido C_{o}), 148.35 (phenoxide C_{i}), 133.06 (imido C_{m}), 130.45 (phenoxide C_{o}), 127.13 (phenoxide C_{m}), 124.84 (imido C_{p}), 53.45 ($\mathrm{CH}C\mathrm{Me_3}$), 29.17 ($\mathrm{CHC}\mathit{Me}_3$), 29.00 ($C\mathrm{HMe_2}$), 25.34 ($\mathrm{CHC}\mathit{Me}_2$). Anal. Calcd for $\mathrm{ReC_{23}H_{30}NOCl_4}$: C, 41.57; H, 4.55; N, 2.11. Found: C, 41.91; H, 4.65; N, 2.21.

Re(CH-t-Bu)(NAr)(O-2,6-$\mathrm{C_6H_3Me_2}$)$\mathrm{Cl_2}$ (3b). The preparation of **3b** is analogous to that for **3a** with use of 0.200 g (0.034 mmol) of Re(C-t-Bu)(NAr)$\mathrm{Cl_2}$(DME) and 0.43 g (0.036 mmol) of HO-2,6-$\mathrm{C_6H_3Me_2}$: yield (0.177 g, 78%); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 13.48 ($\mathrm{C}H\mathrm{CMe_3}$), 7.42–7.27 (mult, 3, imido H_{Ar}), 7.08 (d, 2, phenoxide H_{m}), 6.79 (t, 1, phenoxide H_{p}), 4.07 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$) 2.49 (s, 6, $\mathrm{C_6H_3}\mathit{Me}_2$), 1.45 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.30 (d, 12, $\mathrm{CH}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 296.8 (d, J = 143, $C\mathrm{HCMe_3}$), 162.2 (imido C_{i}), 151.1 (phenoxide C_{i}), 148.6 (imido C_{o}), 132.2 (imido C_{m}), 128.1 (phenoxide C_{m}), 127.2 (phenoxide C_{o}), 124.4 (imido C_{p}), 122.6 (phenoxide C_{p}), 52.6 ($\mathrm{CH}C\mathrm{Me_3}$), 29.4 ($\mathrm{CHC}\mathit{Me}_3$), 29.1 (imido $C\mathrm{HMe_2}$), 25.3 (imido $\mathrm{CH}\mathit{Me}_2$). Anal. Calcd for $\mathrm{ReC_{25}H_{36}NOCl_2}$: C, 48.15; H, 5.82; N, 2.25. Found: C, 48.51; H, 5.81; N, 2.06.

Re(CH-t-Bu)(NAr)(OAr)$\mathrm{Cl_2}$ (3c). To a solution of Re(C-t-Bu)(NAr)$\mathrm{Cl_2}$(DME) (0.200 g 0.34 mmol) in dichloromethane (5 mL) was added HOAr (0.063 g, 0.35 mmol). The solution was stirred 15 min and the solvent removed in vacuo, leaving a deep red oil. The product was extracted into pentane (2 mL), and the extract was stored at −40 °C to yield 0.210 g (two crops, 91%) of dark red crystals: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 13.36 ($\mathrm{C}H\mathrm{CMe_3}$), 7.42–7.30 (m, 3, imido H_{Ar}), 7.13 (d, 2, phenoxide H_{m}), 6.92 (t, 1, phenoxide H_{p}), 4.02 (sept, 2, imido $\mathrm{C}H\mathrm{Me_2}$), 3.12 (br, 2, phenoxide $\mathrm{C}H\mathrm{Me_2}$), 1.42 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.30 (d, imido $\mathrm{CH}\mathit{Me}_2$), 1.27 (d, phenoxide ($\mathrm{CH}\mathit{Me}_2$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 296.5 (d, J = 148, $C\mathrm{HCMe_3}$), 159.38 (imido C_{i}), 151.44 (phenoxide C_{i}), 148.72 (imido C_{o}), 137.37 (phenoxide C_{o}), 132.16 (d, imido C_{m}), 124.36 (d, phenoxide C_{m}), 123.37 (d, imido C_{p}), 122.99 (d, phenoxide C_{p}), 52.74 ($\mathrm{CH}C\mathrm{Me_3}$), 29.65 (unresolved doublet, imido $C\mathrm{HMe_2}$), 29.38 (d, phenoxide $C\mathrm{HMe_2}$), 29.05 (q, $\mathrm{CHC}\mathit{Me}_3$), 25.44 (imido $\mathrm{CH}\mathit{Me}_2$), 23.48 (phenoxide $\mathrm{CH}\mathit{Me}_2$). Anal. Calcd for $\mathrm{ReC_{29}H_{44}NOCl_2}$: C, 51.24; H, 6.52; N, 2.06. Found: C, 51.60; H, 6.80; N, 1.93.

Re(CH-t-Bu)(NAr)[O-2,6-$\mathrm{C_6H_3(OMe)_2}$]$\mathrm{Cl_2}$ (3d). To a red-purple solution of Re(C-t-Bu)(NAr)$\mathrm{Cl_2}$(DME) (0.200 g, 0.338 mmol) in 5 mL of $\mathrm{CH_2Cl_2}$ was added HO-2,6-$\mathrm{C_6H_3(OMe)_2}$ (0.052 g, 0.338 mmol). The reaction mixture turned bright red within a few minutes and was stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with 5 mL of ether. The solution was filtered through a glass-fiber filter. Concentration of this solution afforded 0.145 g (65%) of dark red/black microcrystals. An analytically pure sample was recrystallized from ether/pentane (1:1): ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 13.76 ($\mathrm{C}H\mathrm{CMe_3}$), 7.46 (t, 1, imido H_{p}), 7.36 (t, 2, imido H_{m}), 6.73 (t, 1, phenoxide H_{p}), 6.60 (t, 1, phenoxide H_{m}), 4.22 (sept, 2, $\mathrm{CH}\mathit{Me}_2$), 3.85 (s, 6, $\mathrm{C_6H_3(O}\mathit{Me}\mathrm{)_2}$), 1.38 (s, 9, $\mathrm{CHC}\mathit{Me}_3$), 1.24 ($\mathrm{CH}\mathit{Me}_2$). Anal. Calcd for $\mathrm{ReC_{25}H_{36}NO_3}$: C, 45.80; H, 5.53; N, 2.14. Found: C, 46.08; H, 5.76; N, 1.98.

Re(C-t-Bu)(NAr)(O-2,6-$\mathrm{C_6H_3Cl_2}$)$_2$(py) (4a). To a red solution of Re(CH-t-Bu)(NAr)(O-2,6-$\mathrm{C_6H_3Cl_2}$)$_3$ (0.080 g, 0.087 mmol) in 2 mL of dichloromethane was added pyridine (14 μL, 0.17 mmol). After 15 min the solution became forest green. The solution was stirred for 1 h and the solvent removed in vacuo. The product was extracted into a small amount of dichloro-

Table IV. Final Positional Parameters for the Non-Hydrogen Atoms of Re(CH-*t*-Bu)(NAr)(O-2,6-$C_6H_3Cl_2$)$_3$ (1b)

atom	*x*	*y*	*z*
Re	0.28195 (6)	0.09645 (2)	0.19631 (6)
Cl(1)	0.1020 (6)	0.1701 (2)	0.4179 (5)
Cl(2)	−0.0172 (5)	0.1168 (2)	−0.0291 (5)
Cl(3)	0.0728 (5)	0.0220 (2)	0.3097 (5)
Cl(4)	0.4139 (6)	0.1207 (2)	0.5574 (5)
Cl(5)	0.1830 (6)	0.1791 (2)	−0.1571 (5)
Cl(6)	0.3682 (5)	0.1702 (1)	0.3106 (4)
O(2)	0.125 (1)	0.1172 (4)	0.221 (1)
O(3)	0.299 (1)	0.0706 (4)	0.354 (1)
O(4)	0.252 (1)	0.1379 (4)	0.070 (1)
N(1)	0.431 (1)	0.0875 (4)	0.195 (1)
C(1)	0.209 (2)	0.0534 (6)	0.102 (2)
C(2)	0.243 (2)	0.0201 (6)	0.026 (2)
C(3)	0.197 (3)	−0.022 (1)	0.067 (3)
C(4)	0.373 (2)	0.0139 (9)	0.029 (2)
C(5)	0.176 (3)	0.025 (1)	−0.099 (3)
C(51)	0.703 (3)	0.201 (1)	0.354 (4)
C(52)	0.721 (3)	0.190 (1)	0.475 (3)
C(53)	0.811 (3)	0.165 (1)	0.534 (3)
C(54)	0.826 (3)	0.156 (1)	0.649 (4)
C(55)	0.748 (4)	0.174 (1)	0.710 (4)
C(56)	0.657 (4)	0.193 (1)	0.653 (4)
C(57)	0.642 (3)	0.210 (1)	0.537 (3)
C(21)	0.060 (2)	0.1507 (5)	0.189 (2)
C(22)	0.046 (2)	0.1809 (6)	0.272 (2)
C(23)	−0.015 (2)	0.2162 (8)	0.235 (2)
C(24)	−0.061 (3)	0.222 (1)	0.115 (3)
C(25)	−0.064 (2)	0.1938 (8)	0.034 (2)
C(26)	−0.007 (2)	0.1566 (6)	0.075 (2)
C(31)	0.234 (1)	0.0740 (5)	0.437 (1)
C(32)	0.127 (2)	0.0516 (6)	0.430 (2)
C(33)	0.063 (2)	0.0547 (7)	0.518 (2)
C(34)	0.107 (2)	0.0779 (8)	0.620 (2)
C(35)	0.216 (2)	0.0985 (7)	0.628 (2)
C(36)	0.277 (2)	0.0953 (6)	0.539 (2)
C(41)	0.275 (2)	0.1782 (5)	0.078 (2)
C(42)	0.248 (2)	0.2029 (7)	−0.024 (2)
C(43)	0.271 (2)	0.2429 (8)	−0.023 (2)
C(44)	0.322 (2)	0.2614 (7)	0.083 (2)
C(45)	0.354 (2)	0.2406 (6)	0.186 (2)
C(46)	0.331 (2)	0.1989 (6)	0.179 (2)
C(11)	0.552 (2)	0.0887 (5)	0.201 (2)
C(12)	0.631 (2)	0.0723 (7)	0.293 (2)
C(13)	0.756 (2)	0.0712 (7)	0.297 (2)
C(14)	0.797 (2)	0.0909 (6)	0.210 (2)
C(15)	0.721 (2)	0.1100 (7)	0.118 (2)
C(16)	0.597 (2)	0.1080 (6)	0.111 (2)
C(121)	0.587 (2)	0.0462 (7)	0.388 (2)
C(122)	0.659 (3)	0.0578 (9)	0.512 (3)
C(123)	0.597 (3)	0.0006 (9)	0.367 (3)
C(161)	0.517 (2)	0.1296 (7)	0.003 (2)
C(162)	0.530 (3)	0.1072 (9)	−0.112 (3)
C(163)	0.547 (2)	0.1760 (8)	0.001 (2)

methane, and the extract was filtered through a glass-fiber filter, concentrated to ca. 1 mL, and stored at −40 °C to yield 0.049 g (84% yield) of green needles: ^{1}H NMR (C_6D_6) δ 8.8 (d, 2, pyridine H_o), 7.74 (t, 2, pyridine H_m), 4.41 ($\mathrm{C}H\mathrm{Me_AMe_B}$), 1.15 (d, 6, $\mathrm{CH}Me_A\mathrm{Me_B}$), 1.06 (d, 6, $\mathrm{CHMe_A}Me_B$), 0.72 (s, 9, $\mathrm{C}CMe_3$). Anal. Calcd for $ReC_{34}H_{37}N_2O_2Cl_4$: C, 48.98; H, 4.47; N, 3.36. Found: C, 48.63; H, 4.68; N, 3.56.

Re(C-*t*-Bu)(NAr)(OC_6Cl_5)$_2$(py) (4b). From Re(CH-*t*-Bu)(NAr)(OC_6Cl_5)$_3$. To a red-orange solution of 0.100 g (0.081 mmol) of Re(CH-*t*-Bu)(NAr)(O-C_6Cl_5)$_3$ in dichloromethane (5 mL) was added 33 μL (0.41 mmol) of pyridine. The solution slowly became forest green. After 1 h, the solvent was removed in vacuo, the resulting green solid was extracted with 1 mL of dichloromethane, and the extract was filtered and stored at −40 °C overnight to yield 0.080 g (94%) of dark green needles: ^{1}H NMR (CD_2Cl_2) δ 8.84 (d, 2, pyridine H_o), 7.90 (t, 1, pyridine H_m), 7.40 (t, 2, pyridine H_p), 7.33 (d, 2, imido H_m), 7.18 (t, 1, imido H_p), 4.27 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.15 (d, 6, $\mathrm{CH}Me_A\mathrm{Me_B}$), 1.05 (d, 6, $\mathrm{CHMe_A}Me_B$), 0.98 (s, 9, $\mathrm{C}CMe_3$). Anal. Calcd for $ReC_{34}H_{31}N_2O_2Cl_{10}$: C, 39.25; H, 3.00; N, 2.69. Found: C, 39.28; H, 2.88; N, 2.29.

Table V. Final Positional Parameters for the Non-Hydrogen Atoms of Re(CH-*t*-Bu)(NAr)(OC_6F_5)$_3$(THF) (2)

atom	*x*	*y*	*z*
Re	0.36383 (3)	0.24645 (2)	0.20295 (2)
F(12)	0.4527 (5)	0.4561 (3)	0.1752 (5)
F(13)	0.3842 (7)	0.5863 (3)	0.2696 (7)
F(14)	0.3124 (5)	0.5907 (3)	0.5028 (7)
F(15)	0.3067 (5)	0.4622 (4)	0.6355 (5)
F(16)	0.3732 (5)	0.3322 (3)	0.5439 (4)
F(22)	0.0735 (5)	0.3055 (3)	0.3911 (4)
F(23)	−0.1067 (5)	0.2425 (4)	0.5214 (5)
F(24)	−0.0906 (5)	0.1002 (4)	0.6118 (5)
F(25)	0.1084 (5)	0.0239 (3)	0.5772 (5)
F(26)	0.2857 (4)	0.0839 (3)	0.4433 (4)
F(32)	0.0538 (4)	0.1883 (2)	0.1670 (4)
F(33)	−0.1326 (4)	0.0841 (3)	0.1671 (5)
F(34)	−0.0971 (5)	−0.0665 (3)	0.1469 (5)
F(35)	0.1322 (5)	−0.1106 (3)	0.1296 (5)
F(36)	0.3239 (4)	−0.0078 (3)	0.1385 (5)
O(1)	0.4537 (4)	0.3259 (3)	0.3094 (4)
O(2)	0.2721 (4)	0.2287 (3)	0.3513 (5)
O(3)	0.2979 (4)	0.1411 (3)	0.1514 (5)
O(4)	0.5091 (4)	0.1785 (3)	0.3121 (4)
N(1)	0.4603 (5)	0.2522 (3)	0.0858 (4)
C(1)	0.2407 (7)	0.3057 (4)	0.1313 (6)
C(2)	0.2068 (7)	0.3436 (4)	0.0145 (7)
C(3)	0.144 (1)	0.4166 (5)	0.047 (1)
C(4)	0.113 91)	0.2891 (7)	−0.057 (1)
C(5)	0.3117 (9)	0.3652 (5)	−0.646 (8)
C(6)	1.037 (1)	0.558 (1)	0.296 (1)
C(7)	1.026 (2)	0.497 (1)	0.371 (2)
C(8)	1.0000	$^1/_2$	$^1/_2$
C(9A)	1.012 (3)	0.558 (2)	0.421 (2)
C(11)	0.4117 (6)	0.3897 (4)	0.3540 (6)
C(12)	0.4131 (7)	0.4558 (5)	0.2888 (7)
C(13)	0.3804 (8)	0.5230 (5)	0.338 (1)
C(14)	0.3436 (8)	0.5237 (6)	0.456 (1)
C(15)	0.3406 (8)	0.4604 (6)	0.5209 (8)
C(16)	0.3735 (7)	0.3942 (5)	0.4710 (7)
C(21)	0.1861 (6)	0.1973 (4)	0.4120 (6)
C(22)	0.0841 (7)	0.2348 (5)	0.4359 (6)
C(23)	−0.0082 (7)	0.2034 (5)	0.5013 (7)
C(24)	−0.0005 (7)	0.1322 (5)	0.5488 (7)
C(25)	0.0978 (7)	0.0937 (5)	0.5279 (7)
C(26)	0.1892 (7)	0.1252 (4)	0.4608 (6)
C(31)	0.2000 (6)	0.0950 (4)	0.1529 (6)
C(32)	0.0795 (6)	0.1148 (4)	0.1601 (6)
C(33)	−0.0192 (6)	0.0619 (4)	0.1598 (6)
C(34)	−0.0007 (7)	−0.0143 (4)	0.1502 (7)
C(35)	0.1146 (8)	−0.0369 (4)	0.1406 (7)
C(36)	0.2114 (7)	0.0174 (4)	0.1446 (7)
C(41)	0.5560 (9)	0.1108 (5)	0.2670 (8)
C(42)	0.647 (1)	0.0871 (7)	0.3654 (8)
C(43)	0.601 (1)	0.1174 (6)	0.4794 (8)
C(44)	0.5515 (8)	0.1926 (5)	0.4383 (7)
C(51)	0.5451 (6)	0.2496 (4)	−0.0016 (6)
C(52)	0.5137 (6)	0.2071 (4)	−0.1105 (6)
C(53)	0.6010 (8)	0.2080 (5)	−0.1962 (7)
C(54)	0.7111 (8)	0.2486 (5)	−0.1780 (8)
C(55)	0.7394 (7)	0.2889 (4)	−0.0702 (7)
C(56)	0.6593 (6)	0.2909 (4)	0.0196 (6)
C(57)	0.6916 (7)	0.3344 (5)	0.1373 (7)
C(58)	0.790 (1)	0.2948 (9)	0.215 (1)
C(59)	0.735 (1)	0.4172 (5)	0.114 (1)
C(510)	0.3931 (7)	0.1604 (4)	−0.1320 (6)
C(511)	0.332 (1)	0.1747 (7)	−0.2580 (8)
C(512)	0.414 (1)	0.0769 (5)	−0.114 (1)

From Re(C-*t*-Bu)(NAr)(OC_6Cl_5)$_2$. To a red solution of 0.05 g (0.052 mmol) of Re(C-*t*-Bu)(NAr)(OC_6Cl_5)$_2$ in 2 mL of dichloromethane was added 21 μL (0.26 mmol) of pyridine. The solution was stirred for 1 h and the solvent removed in vacuo. The resulting product was extracted into 0.5 mL of dichloromethane, and the extract was cooled to −40 °C to give 0.043 g (80%) of green needles identical with the compound described above.

Re(C-*t*-Bu)(NAr)(O-2,6-$C_6H_3Cl_2$)$_2$. KO-2,6-$C_6H_3Cl_2$ (0.072 g, 0.35 mmol) was added to a purple solution of Re(C-*t*-Bu)-

(NAr)$\mathrm{Cl_2}$(DME) (0.100 g, 0.17 mmol) in 10 mL of $\mathrm{CH_2Cl_2}$ at −40 °C. The solution immediately turned deep red. The reaction mixture was stirred at room temperature for 2 h and the solvent removed in vacuo. The solids were extracted with pentane, and the extract was filtered through Celite and concentrated in vacuo to give a deep red oil. The oil was extracted with 1–2 mL of pentane, and the extract was cooled to −40 °C to yield deep red prisms: yield 0.112 g (88%); ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.33 (d, 4, phenoxide H_m), 7.16 (d, 2, imido H_m), 6.95 (t, 1, imido H_p), 6.85 (t, 2, phenoxide H_p), 3.09 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.03 (d, 12, $\mathrm{CH}Me_2$), 0.77 (s, 9, $\mathrm{CHC}Me_3$); ^{13}C NMR δ 311.59 (C_α–$\mathrm{CMe_3}$), 160.31 (phenoxide C_i), 156.50 (imido C_i), 139.59 (imido C_o), 128.42 (phenoxide C_o), 127.02 (imido, C_m) 125.55 (imido, C_p), 122.22 (phenoxide, C_m), 122.04 (phenoxide C_p), 54.64 ($\mathrm{C}C\mathrm{Me_3}$), 29.59 ($\mathrm{CH}Me_2$), 28.31 ($C\mathrm{HMe_2}$), 23.17 ($\mathrm{CC}Me_3$).

Re(C-*t*-Bu)(NAr)($\mathbf{OC_6Cl_5}$)$_\mathbf{2}$. $\mathrm{KOC_6Cl_5}$ (0.105 g, 0.35 mmol) was added to a solution of Re(C-*t*-Bu)(NAr)$\mathrm{Cl_2}$(DME) (0.100 g, 0.17 mmol) in 10 mL of cold (−40 °C) $\mathrm{CH_2Cl_2}$. The mixture was stirred at ambient temperature for 3 h, during which time the color became orange/yellow. The solvent was removed in vacuo and the product extracted in ether. The extract was filtered through Celite, concentrated to 4 mL, and cooled to −40 °C to give 0.105 g (65%) of red/orange crystals: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 7.18 (d, 2, imido C_m), 6.97 (t, 1, imido C_p), 2.97 (sept, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.03 (d, 12, $\mathrm{CH}Me_2$), 0.80 (s, 9, $\mathrm{CC}Me_3$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 314.60 ($C\mathrm{CMe_3}$), 160.00 (phenoxide C_i), 155.73 (imido C_i), 139.49 (phenoxide C_o), 131.37 (imido, C_o), 128.00 (d, imido C_m), 125.66 (phenoxide C_m), 124.20 (phenoxide C_p), 122.20 (d, imido C_p), 55.31 ($\mathrm{C}C\mathrm{Me_3}$), 29.69 ($\mathrm{CH}Me_2$), 28.38 ($C\mathrm{HMe_2}$), 23.24 ($\mathrm{CC}Me_3$).

Observation of Re(C-*t*-Bu)(NAr)Cl$_\mathbf{2}$(py)$_\mathbf{2}$. To a solution of Re(C-*t*-Bu)(NAr)$\mathrm{Cl_2}$(DME) (0.05 g, 0.073 mmol) in 5 mL of $\mathrm{CH_2Cl_2}$ was added pyridine (30 μL, 0.36 mmol). The solution was stirred for 30 min and the solvent removed in vacuo. The product was extracted into $\mathrm{CD_2Cl_2}$. Proton NMR spectroscopy revealed that Re(C-*t*-Bu)(NAr)$\mathrm{Cl_2(py)_2}$ and 2,6-diisopropylphenol were formed quantitatively: ^{1}H NMR ($\mathrm{CD_2Cl_2}$) δ 9.68 (d, 4, pyridine H_o), 7.70 (tt, 4, pyridine H_p) 7.30 (mult, 2, pyridine H_m), 7.12 (d, 2, imido H_m), 6.79 (t, 1, imido H_p), 3.27 (mult, 2, $\mathrm{C}H\mathrm{Me_2}$), 1.09 (d, 12, $\mathrm{CH}Me_2$), 1.01 (s, 9, $\mathrm{CC}Me_3$).

General Crystallography. All measurements were made on a Rigaku AFC6R diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71079 Å). The intensities of three representative reflections, which were measured after every 150 reflections, remained constant throughout the data collection time, indicating crystal and electronic stability (no decay correction was applied). All calculations were performed with use of the TEXSAN crystallographic software package of Molecular Structure Corp.[28]

Crystal Structure of Re(CH-*t*-Bu)(NAr)(O-2,6-C$_\mathbf{6}$H$_\mathbf{3}$Cl$_\mathbf{2}$)$_\mathbf{3}$ (1b). An orange prismatic crystal of Re(CH-*t*-Bu)(NAr)(O-2,6-$\mathrm{C_6H_3Cl_2)_3}$ was mounted on a glass fiber under a stream of cold nitrogen. The data were collected at −72 ± 1 °C with use of the ω-scan technique to a maximum 2θ value of 55.0°. Of the 10468 reflections that were collected, 9991 were unique (R_int = 0.192). Of the reflections with $I > 10\sigma(I)$, two were removed: [1,4,−1] and [2,8,−2]. An empirical absorption correction, from the program DIFABS,[29] was applied, which resulted in transmission factors ranging from 0.92 to 1.03.

The position of the rhenium atom was determined by the Patterson method. Subsequent atoms were located from successive difference maps. The unit cell was found to contain toluene (one molecule per asymmetric unit). All carbon atoms were refined isotropically, while rhenium, oxygen, chlorine, and nitrogen were refined anisotropically. All hydrogen atoms were included in the structure factor calculation in idealized positions ($d_\mathrm{C-H}$ = 0.95 Å). The final cycle of full-matrix least-squares refinement was based on 6061 observed reflections ($I > 3.00\sigma(I)$) and 268 variable parameters and converged (largest parameter shift was 0.29 times its esd) with unweighted and weighted agreement factors of R = 0.074 and R_w = 0.130.

Crystal Structure of Re(CH-*t*-Bu)(NAr)(OC$_\mathbf{6}$F$_\mathbf{5}$)$_\mathbf{3}$(THF) (2). An orange prismatic crystal of Re(CH-*t*-Bu)(NAr)($\mathrm{OC_6F_5)_3}$(THF) was mounted on a glass fiber under a stream of cold nitrogen. The data were collected at 3 ± 1 °C with use of the ω–2θ scan technique to a maximum 2θ value of 55.0°. Of the 10275 reflections that were collected, 9763 were unique (R_int = 0.048); equivalent reflections were merged. An empirical absorption correction, from the program DIFABS, was applied, which resulted in transmission factors ranging from 0.87 to 1.07.

The position of rhenium was determined by the Patterson method. Subsequent atoms were located from successive difference maps. The unit cell was found to contain pentane (half of a molecule per asymmetric unit). C(3) of the pentane was found on a special position (1, 1, 0.5), and the chain was disordered by an inversion through this special position. The resulting structure was refined for two different molecules of pentane, each sharing C(3), and the occupancy for each carbon was set so that the total occupancy was consistent with half of a pentane per unit cell. Hydrogens for each pentane fragment were generated in ATOMED, and the occupancy for each was set accordingly. The carbons in the chain were refined isotropically. With the exception of the alkylidene hydrogen, which was located in a difference map, all hydrogen atoms were included in the structure factor calculation in idealized positions ($d_\mathrm{C-H}$ = 0.95 Å). The final cycle of full-matrix least-squares refinement was based on 6493 observed reflections ($I > 3.00\sigma(I)$) and 694 variable parameters and converged (largest parameter shift was 0.18 times its esd) with unweighted and weighted agreement factors of R = 0.038 and R_w = 0.050.

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Supplementary Material Available: Fully labeled ORTEP drawings and tables of final positional parameters and final thermal parameters for 1b and 2 (23 pages); tables of final observed and calculated structure factors (107 pages). Ordering information is given on any current masthead page.

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[28] TEXSAN is the TEXRAY structure analysis package of the Molecular Structure Corp. (1985).

[29] DIFABS: Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158–166.