Multiple metal-carbon bonds. 32. Rhenium(VII) neopentylidene and neopentylidyne complexes and the x-ray structure of Re(CCMe3)(CHCMe3)(C5H5N)2

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Rhenium(VII) Neopentylidene and Neopentylidyne Complexes and the X-ray Structure of $\mathrm{Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2}$[1]

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Addition of 4 equiv of HCl to $\mathrm{Re(NCMe_3)_3(OSiMe_3)}$ yields orange $\mathrm{Re(NCMe_3)_2Cl_3}$ in >85% yield. Analogous alkyl complexes $\mathrm{Re(NCMe_3)_2R_3}$ (R = Me, $\mathrm{CH_2Ph}$, $\mathrm{CH_2SiMe_3}$) can be prepared by using the appropriate alkylating agent, but attempts to prepare $\mathrm{Re(NCMe_3)_2(CH_2CMe_3)_3}$ yielded $\mathrm{Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)}$, a yellow-orange oil, in >70% yield. Irradiation of $\mathrm{Re(NCMe_3)_2(CH_2SiMe_3)_3}$ with a medium-pressure mercury lamp produces yellow, crystalline $\mathrm{Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)}$ quantitatively. Protonation of $\mathrm{Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)}$ with 3 equiv of 2,4-lutidine hydrochloride yields $\mathrm{[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2}$. Use of pyridine hydrochloride produces intermediate $\mathrm{Re(CCMe_3)(CH_2CMe_3)(NHCMe_3)(py)Cl_2}$ that decomposes to give $\mathrm{[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2}$. Deuterium labeling studies show that one imido ligand is first deuterated and then (most likely) a neopentylidyne ligand is formed by migration of a hydrogen atom from the neopentylidene α-carbon atom to the other imido nitrogen atom. Derivatives of $\mathrm{[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2}$ such as $\mathrm{Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2}$, $\mathrm{Re(CCMe_3)(CHCMe_3)(OCMe_3)_2}$, and $\mathrm{Re(CCMe_3)(CHCMe_3)py_2I_2}$ were also prepared. $\mathrm{Re(CCMe_3)(CHCMe_3)py_2I_2}$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 9.7682$ (25) Å, $b = 14.7250$ (41) Å, $c = 17.4070$ (44) Å, $\beta = 110.821$ (21)°, and $Z = 4$. Diffraction data were collected with a Syntex $\mathrm{P2_1}$ diffractometer, and the structure was refined to $R_F = 3.7\%$ for all 3076 data with 2θ 4.5–45.0° (Mo Kα). The complex has mutually trans iodide and mutually cis pyridine ligands. The rhenium–neopentylidyne system is defined by $\mathrm{Re{\equiv}C(11)} = 1.742$ (9) Å and $\mathrm{Re{\equiv}C(11){-}C(12)} = 174.8$ (7)°; the rhenium–neopentylidene system has $\mathrm{Re{=}C(16)} = 1.873$ (9) Å and $\mathrm{Re{=}C(16){-}C(17)} = 150.3$ (7)°. Addition of HCl to $\mathrm{Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2}$ yields trigonal-bipyramidal $\mathrm{Re(CCMe_3)(CH_2CMe_3)_3Cl}$, the third member of a series of related molecules that includes $\mathrm{Ta(CH_2CMe_3)_3Cl_2}$ and $\mathrm{W(NPh)(CH_2CMe_3)_3Cl}$.

Introduction

It has been known for more than 15 years that heterogeneous catalysts containing rhenium will metathesize olefins.[3] More recently, rhenium has been found to be one of the best catalysts (in combination with a tin reagent) for the metathesis of some functionalized olefins.[4] Since it has been shown fairly conclusively that olefins are metathesized by tungsten(VI) alkylidene complexes,[5] one might suspect that rhenium olefin metathesis catalysts contain Re(VII). Therefore, we set out to prepare some rhenium(VII) alkylidene complexes under the assumption that the principles of α-hydrogen atom abstraction, which have now been shown to extend to molybdenum(VI)[6] and tungsten(VI),[7] also extend to rhenium(VII). Since initial attempts to prepare rhenium(VII) oxo alkyl complexes were not successful, we proceeded to study the chemistry of analogous rhenium(VII) imido complexes. Imido ligands are more bulky than an oxo ligand and less likely to bridge between two or more metals.[8,9] In this paper we report the results of these studies, some of which have appeared in a preliminary communication.[10]

Results and Discussion

Bis(*tert*-butylimido) Halo, Alkyl, and Alkylidene Complexes. Addition of 4 equiv of HCl to $\mathrm{Re(NCMe_3)_3(OSiMe_3)}$[9] in dichloromethane produces 1 equiv of $\mathrm{Me_3CNH_3Cl}$ and orange $\mathrm{Re(NCMe_3)_2Cl_3}$ in >85% yield. The *tert*-butyl groups are equivalent in $\mathrm{Re(NCMe_3)_2Cl_3}$ by both ^{1}H and ^{13}C NMR, and it is a monomer in dichloromethane. We propose that it is a trigonal-bipyramidal molecule with the two imido ligands in equatorial positions. The analogous bromide complex is best prepared by reacting $\mathrm{Re(NCMe_3)_2Cl_3}$ with $\mathrm{Me_3SiBr}$ in toluene.

Trialkyl complexes can be prepared by addition of the appropriate alkylating agent to $\mathrm{Re(NCMe_3)_2Cl_3}$, $\mathrm{Re(NCMe_3)_2Me_3}$, a colorless liquid (mp ~10 °C), by adding 3 equiv of $\mathrm{AlMe_3}$ in toluene, orange, crystalline $\mathrm{Re(NCMe_3)_2(CH_2Ph)_3}$ by adding 3 equiv of $\mathrm{PhCH_2MgCl}$ in ether, and yellow, light-sensitive $\mathrm{Re(NCMe_3)_2(CH_2SiMe_3)_3}$ by adding 1.5 equiv of $\mathrm{Zn(CH_2SiMe_3)_2}$ in the presence of 1.5 equiv of $\mathrm{NEt_4Cl}$ in dichloromethane. NMR spectra of the $\mathrm{Re(NCMe_3)_2R_3}$ complexes show two different types of alkyl ligands, but only one type of imido ligand. In the case of the $\mathrm{CH_2R'}$ complexes (R′ = Ph or $\mathrm{SiMe_3}$) the α protons in any given alkyl ligand are equivalent. These data together suggest that these molecules also are trigonal bipyramids with the two imido ligands located in the equatorial plane. Note that this proposal differs from that concerning the structure of $\mathrm{ReO_2Me_3}$, where axial and equatorial oxo ligands were postulated.[11] It seems more

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[1] Multiple Metal–Carbon Bonds 32. For part 31 see ref 19.

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likely now that ReO_2Me_3 also contains equatorial oxo ligands. Two other five-coordinate d^0 complexes that are known through X-ray studies to contain the π-bonding ligands in the equatorial plane are $Ta(CHCMe_3)_2(mesityl)(PMe_3)_2$[12] and $W(O)(CHCMe_3)(PEt_3)Cl_2$.[13]

It is possible to prepare some mixed alkyl/halide complexes (eq 1 and 2). In each complex the two alkyl groups are equivalent and are presumed to occupy axial positions in a trigonal-bipyramidal molecule.

$$2\,Re(NCMe_3)_2Me_3 + Re(NCMe_3)_2Cl_3 \longrightarrow 3\,Re(NCMe_3)_2Me_2Cl \qquad (1)$$

$$Re(NCMe_3)_2Cl_3 + Zn(CH_2SiMe_3)_2 \xrightarrow[Et_4NCl]{CH_2Cl_2} Re(NCMe_3)_2(CH_2SiMe_3)_2Cl \qquad (2)$$

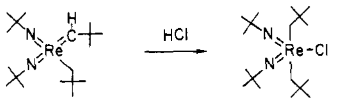
All attempts to prepare $Re(NCMe_3)_2(CH_2CMe_3)_3$ have failed. Instead, the product of the reaction between $Re(NCMe_3)_2Cl_3$ and Me_3CCH_2MgCl is a distillable yellow-orange oil (>70% yield, doubly distilled) with the formula $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$. The signal for the alkylidene α-carbon atom is found at 262.2 ppm in the ^{13}C NMR spectrum. The fact that $J_{CH} = 134$ Hz suggests that the metal is not withdrawing electron density from the $CH(\alpha)$ bond of the alkylidene ligand,[14] as has been observed in a d^0 tantalum complex[15] and a "d^2" tungsten complex,[16] but not in d^0 tungsten alkylidene complexes containing other π-bonding ligands.[13,17] If one includes the π-electron pair on each imido ligand, the electron count is in fact 18, and no further electron density should be attracted to the metal, especially that as relatively inaccessible (at least compared to an electron pair in an imido ligand) as the bonding CH_α electron pair. For this reason, as well as for steric reasons, the molecule is likely to be monomeric (cf. $Ta(CHCMe_3)(CH_2CMe_3)_3$,[18] $W(CCMe_3)(CH_2CMe_3)_3$,[19] and $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$ below). In that case it is notable that the α protons in the neopentyl group are diastereotopic and four different *tert*-butyl groups are observed in the high-field ^{13}C NMR spectrum. Evidently the neopentylidene ligand is first, not freely rotating about the Re=C bond and, second, oriented so that there is no plane of symmetry through the molecule.

It seems likely that $Re(NCMe_3)_2(CH_2CMe_3)_3$ is the intermediate in the reaction which gives $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$. Therefore, we examined the available $Re(NCMe_3)_2R_3$ species for any evidence that an intramolecular, controlled α-hydrogen abstraction reaction could be induced by heat or light. Photolysis of $Re(NCMe_3)_2(CH_2SiMe_3)_3$ in pentane through Pyrex with a medium-pressure mercury lamp yields yellow, crystalline, monomeric $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$ virtually quantitatively. This result is surprising since although it has been known for several years that light will accelerate a thermal α-hydrogen abstraction reaction,[20] reactions involving cleavage of a metal–carbon bond to give alkyl radicals in general appear to compete with the α-hydrogen abstraction reaction. In each system studied (qualitatively) to date, however, the two alkyl groups can attain a mutually trans orientation, a situation that is much more likely to result in metal reduction rather than α abstraction. In $Re(NCMe_3)_2(CH_2SiMe_3)_3$, however, two alkyl ligands are always mutually cis. This may in part explain why α abstraction is favored over reduction of Re(VII) to Re(VI) through loss of a (trimethylsilyl)methyl radical, especially if it is the equatorial alkyl group that leaves. These results suggest that $Re(NCMe_3)_2(CH_2CMe_3)_3$ could be the intermediate in the reaction to give $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$, although more complex reaction pathways are certainly possible (cf. formation of $Ta(CHCMe_3)(CH_2CMe_3)_3$[18]). If $Re(NCMe_3)_2(CH_2CMe_3)_3$ is the precursor to $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$, then as we have postulated for related Ta[21] and W[7] α-hydrogen abstraction reactions, α abstraction from a neopentyl group by a neopentyl group is easier than from a (trimethylsilyl)methyl group by a (trimethylsilyl)methyl group.

Photolysis of $Re(NCMe_3)_2(CH_2Ph)_3$ produces a complex mixture of products, one of which contains a benzylidene ligand ($H(\alpha)$ at 12.4 ppm). Most likely this product is $Re(NCMe_3)_2(CHPh)(CH_2Ph)$. At least one reason for believing so is the fact that this product is not stable under the reaction conditions. It is well-known that d^0 benzylidene complexes in general are less stable toward bimolecular decomposition reactions to give stilbenes[21] than are neopentylidene or (trimethylsilyl)methylidene complexes.

Finally, photolysis of $Re(NCMe_3)_2Me_3$ is even more complex than that of $Re(NCMe_3)_2(CH_2Ph)_3$. There is no indication, other than evolution of methane, that $Re(NCMe_3)_2(CH_2)Me$ forms. Even if it does, it is not likely to be stable. Methylene complexes are the most unstable of all the simple d^0 alkylidene complexes in which the alkylidene ligand lacks a β-hydrogen atom with respect to, among other things, bimolecular decomposition reactions;[21] $Ta(\eta^5\text{-}C_5H_5)_2(CH_2)(CH_3)$[22] and $W(O)(CH_2)(PMe_3)_2Cl_2$[5a] are the only known isolable species.

Protonation of $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$. On the basis of previous work with tantalum[18] and tungsten[7] neopentylidene complexes, we expected that HCl would add to the neopentylidene ligand to give an analogue of the complexes shown in eq 1 and 2 (eq 3). In spite of the fact that the neopentyl ligands would probably be trans as shown, a reasonably well-behaved α-hydrogen abstraction reaction to give $Re(NCMe_3)_2(CHCMe_3)Cl$ might be possible after isomerization to a cis form. Since we were not able to make $Re(NCMe_3)_2(CH_2CMe_3)_2Cl$ by using routes analogous to those used to make $Re(NCMe_3)_2Me_2Cl$ and $Re(NCMe_3)_2(CH_2SiMe_3)_2Cl$, the possible preparative route shown in eq 3 would be valuable. The major difficulty with the proposal in eq 3 is that the imido ligands might be protonated more rapidly than the neopentylidene ligand. This turned out to be the case.



(3)

The reaction between $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$ in pentane at −78 °C and 3 equiv of gaseous

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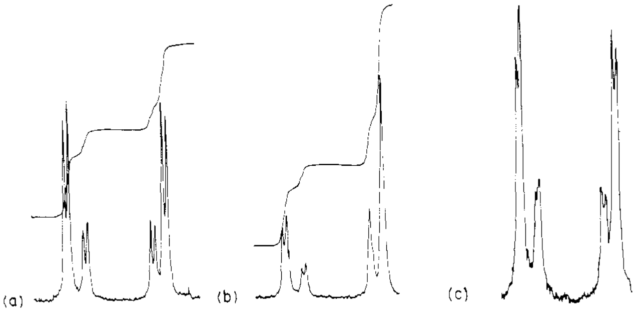
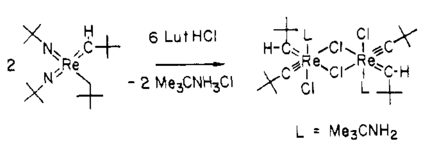


Figure 1. The 250-MHz ^{1}H NMR spectrum of the amine protons in (a) [Re(CCMe$_3$)(CHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$]$_2$ isomers, (b) a mixture of isomers obtained upon treatment of Re(NCMe$_3$)$_2$(CHCMe$_3$)(CH$_2$CMe$_3$) with 3 equiv of 2,4-lutidine–deuterium chloride, and (c) a mixture of isomers obtained upon treatment of Re(NCMe$_3$)$_2$(CHCMe$_3$)(CH$_2$CMe$_3$) with 3 equiv of DCl in pentane at −78 °C.

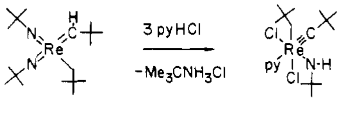
HCl produces an insoluble orange powder in ~60% yield. The same product is obtained in high yield if 3 equiv of 2,4-lutidine hydrochloride in dichloromethane are used (eq 4). Two isomers with similar symmetries are observed,



(4)

most likely those in which the two π-bonding ligands are cis to one another and the neopentylidene ligand lies in the C≡Re=C plane. Since we have only rarely observed what we believe to be isomers derived from two possible orientations of a neopentylidene ligand cis to another π-bonding ligand, we prefer the proposal that the other isomer has the same orientation of the neopentylidene ligand relative to the neopentylidyne ligand, but a cisoid instead of transoid arrangement of *tert*-butylamine ligands about the Re$_2$Cl$_2$ core. Two features of the NMR spectra of this compound are worth noting; the *tert*-butylamine protons are diastereotopic (Figure 1a), but more surprisingly, the signal for the neopentylidyne α-carbon atom is found *upfield* (by 4–5 ppm) of that for the neopentylidene α-carbon atom in each isomer. This latter finding caused some concern initially since although there is a significant degree of overlap of the regions in which neopentylidyne and neopentylidene α-carbon signals are found,[14b] this is the first example where the normal order is reversed in a given compound.

If pyridine hydrochloride is employed instead of lutidine hydrochloride, an unstable *tert*-butylamido complex can be isolated (eq 5). It is logical to assume that the *tert*-butylamido ligand will be located cis to the neopentylidyne ligand in order to allow for maximum donation of the amido lone pair to the metal and that the C–N–H plane coincides with the N—Re≡C plane. (Tungsten amido neopentylidyne complexes are known as well as the results of an X-ray structure of a tungsten phenylphosphido neopentylidyne complex.[23]) Since the neopentyl α protons are inequivalent the neopentyl ligand must be located cis to the neopentylidyne and amido ligands. The disposition of the remaining two chloride ligands and the pyridine ligand as shown are a reasonable possibility. As in the dimeric compound above, two similar isomers are observed. Again we would expect the *tert*-butylamido ligand to be oriented the same way in each isomer. We suspect that the pyridine ligand is trans to the neopentylidyne ligand in one isomer and trans to the *tert*-butylamido ligand in the other. When Re(CCMe$_3$)(NHCMe$_3$)(CH$_2$CMe$_3$)(py)Cl$_2$ decomposes, it produces [Re(CCMe$_3$)(CHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$]$_2$ (both isomers) in moderate yield. It is interesting to note that the amido hydrogen atom does not transfer to the neopentylidyne ligand (eq 6), a result one might have expected on the basis of the finding that W(CCMe$_3$)(NHPh)(PMe$_3$)$_2$Cl$_2$ decomposes cleanly to W(CHCMe$_3$)(NPh)(PMe$_3$)$_2$Cl$_2$.[23] These results suggest that in general a system might be driven toward the compound with the maximum number of *covalent* π bonds (three in [Re(CCMe$_3$)(CHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$]$_2$ vs. two in Re(CCMe$_3$)(NHCMe$_3$)(CH$_2$CMe$_3$)(py)Cl$_2$ and Re(CHCMe$_3$)(NCMe$_3$)(CH$_2$CMe$_3$)(py)Cl$_2$) if such a compound can be formed.



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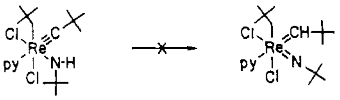
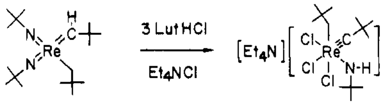


(6)

A complex related to Re(CCMe$_3$)(NHCMe$_3$)(CH$_2$CMe$_3$)(py)Cl$_2$ can be obtained by the reaction shown in eq 7. Only one isomer is present, presumably that shown (or that in which the amido *tert*-butyl group points toward the neopentylidyne ligand) since the α protons in the neopentyl group are again diastereotopic. [Et$_4$N][Re(CCMe$_3$)(NHCMe$_3$)(CH$_2$CMe$_3$)Cl$_3$] is stable in dichloromethane at 25 °C toward loss of Et$_4$NCl to give [Re(CCMe$_3$)(CHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$]$_2$. Although it reacts with ZnCl$_2$, a chloride scavenger, again little or no dimer is produced. However, [Et$_4$N][Re(CCMe$_3$)(NHCMe$_3$)(CH$_2$CMe$_3$)Cl$_3$] does yield Et$_4$NCl and [Re(CCMe$_3$)(CHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$]$_2$ quantitatively in dichloromethane in 1 h when treated with 3 equiv of 2,4-lutidine or 0.1 equiv of gaseous HCl. The former is not surprising since Re(CCMe$_3$)(NHCMe$_3$)(CH$_2$CMe$_3$)(py)Cl$_2$ is not stable. The latter, however, suggests that an acid-catalyzed proton transfer is possible, most likely via formation of Re(CCMe$_3$)(NH$_2$CMe$_3$)(CH$_2$CMe$_3$)Cl$_3$ (see also next section).



(7)

Deuteration Studies. When Re(NCMe$_3$)$_2$(CHCMe$_3$)(CH$_2$CMe$_3$) is treated with 3 equiv of lutidine–deuterium chloride (~95% D), the rhenium-containing product is a mixture of dimers (two isomers of each, as before) formed from one part of Re(CCMe$_3$)(CHCMe$_3$)(NH$_2$CMe$_3$)Cl$_2$ and one part of Re(CCMe$_3$)(CHCMe$_3$)(NHDCMe$_3$)Cl$_2$, as shown by the ^{1}H pattern (and the integration thereof) for the amine α protons in Figure 1b (cf. Figure 1a). Note that a signal for only one diastereomeric N*H*DCMe$_3$ proton is found. The *tert*-butylammonium chloride formed in the reaction was converted into the dichloromethane-soluble BF$_4^-$ salt by treatment with AgBF$_4$ overnight in dichloromethane. A ^{1}H NMR spectrum in CD$_2$Cl$_2$ revealed a broad multiplet of relative area 0.5 at ~6.8 ppm, consistent with the original salt being a 1:1 mixture of Me$_3$CND$_3$Cl and Me$_3$CND$_2$HCl; more likely HD scrambling results in a mixture containing some Me$_3$CNH$_2$DCl and a trace of Me$_3$CNH$_3$Cl.

The above result can be explained by the mechanism shown in Scheme I, one which differs in an important way

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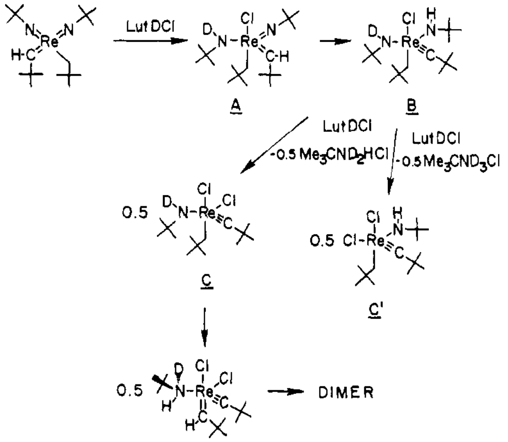
[23] Rocklage, S. M.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *Organometallics* **1982**, *1*, 1332.

Scheme I



from the mechanism we proposed initially.[10] We cannot be certain of the geometries of the intermediates or that lutidine does not coordinate to the metal at some point, but the conclusions we come to here do not depend upon such details. A crucial feature is that the neopentylidyne ligand is formed in the second step (A → B) by transfer of a neopentylidene α proton to the imido nitrogen at a rate which is much greater than the rate at which LutDCl can deuterate the $NDCMe_3$ ligand. The neopentylidyne complex B is then deuterated to give the analogous chloride complexes C and C′ and the amines Me_3CNDH and Me_3CND_2, respectively (possibly still coordinated to Re). The amines are then removed from the reaction as the ammonium salts. Proton transfer from the neopentyl α-carbon atom to the amido nitrogen atom completes the reaction sequence. Since C (as well as likely alternative intermediates) is chiral, the chirality at the nitrogen of the resulting $NHDCMe_3$ complex is determined by the chirality at the metal, as long as the amine does not dissociate. Therefore only one diastereomeric $N\mathit{H}DCMe_3$ proton will be observed.

The proposal shown in Scheme I is of course also supported by the fact that $Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)(py)Cl_2$ (eq 5) and $[Et_4N][Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)Cl_3]$ (eq 7) can be observed. Therefore we were interested in whether one of the analogous deuterium-labeled compounds could also be transformed into a product containing only one diastereomeric $NHDCMe_3$ proton. In the presence of Et_4NCl the reaction shown in Scheme I yielded chloride adducts of C and C′, which, when treated with 3 equiv of 2,4-lutidine, produced a product with an ^1H NMR spectrum identical with that shown in Figure 1b.

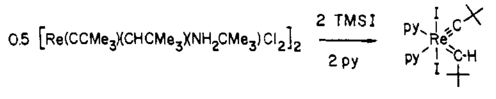
Of the many possible variations of the mechanism shown in Scheme I, one alternative that deserves mention is formation of $Re(CHCMe_3)_2(NDCMe_3)(NHCMe_3)Cl$ instead of B and formation the *neopentylidyne* ligand in the last step. This explanation seems less likely to us because bis(neopentylidene) complexes are not known for Mo, W, or Re, while several neopentyl/neopentylidyne complexes are known. (See later in this paper for a Re example.) Therefore, we can propose that the C—M≡C combination is preferred when the metal is Mo, W, or Re, while in at least two types of Nb and Ta complexes,[12,24] the C=M=C combination is found instead of the C—M≡C combination.

The reaction of $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$ with 3 equiv of DCl in pentane at −78 °C yields a product which still contains only 25% deuterium in the amine ligand. However, it is clear from the ^1H NMR pattern (Figure 1c) that the proton is now no longer found in only one diastereomeric position in the $NHDCMe_3$ complex. In fact, there is now some uncertainty that the product is a mixture of dimers formed from only one part of $Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2$ and one part $Re(CCMe_3)(CHCMe_3)(NHDCMe_3)Cl_2$. If 15 equiv of DCl are used instead of 3 equiv, the product contains only ~30% amine protons instead of 75%; i.e., there is a means of exchanging D for H at some stage. It is possible that conversion of the neopentylidene complex A to the neopentylidyne complex B (Scheme I) is no longer faster than deuteration; i.e., an entirely different mechanism is operating. Alternatively, and the explanation we prefer, is that C (and C′) are deuterated at the amide nitrogen and a neopentyl α proton is then lost to solution. This explanation would account for the loss of stereospecificity as well as the incorporation of D at the expense of H.

Derivatives of $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$. It was partly in an effort to find suitable crystals of a compound consisting of only a single isomer that we prepared some derivatives of $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$.

Treatment of $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ with lithium *tert*-butoxide, lithium trimethylsiloxide, or lithium neopentyl produced the monomeric complexes $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$, $Re(CCMe_3)(CHCMe_3)(OSiMe_3)_2$, and $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$, respectively. The alkoxide derivatives are extremely volatile, water- and oxygen-sensitive yellow crystalline materials while the neopentyl derivative is a somewhat less volatile but equally sensitive yellow oil. In each compound the signal for the neopentylidyne α-carbon atom is found downfield of the signal for the neopentylidene α-carbon atom, the normal order.[14b] $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$ is an especially interesting species in the sense that it fills out the series of four-coordinate compounds starting with $Ta(CHCMe_3)(CH_2CMe_3)_3$ and including $W(CCMe_3)(CH_2CMe_3)_3$. Note that a plausible tautomer of $W(CCMe_3)(CH_2CMe_3)_3$ would be $W(CHCMe_3)_2(CH_2CMe_3)_2$ (cf. $W(NCMe_3)_2R_2$[25]), while a plausible tautomer of $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$ would be $Re(CHCMe_3)_3(CH_2CMe_3)$ (cf. ReO_3Me[26]). As we noted earlier, bis(neopentylidene) complexes have been observed so far only for Nb and Ta.[12,24] Apparently tungsten and rhenium prefer to form triple bonds to carbon.

Although $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ does not readily react with excess pyridine or *N,N,N′,N′*-tetramethylethylenediamine to give monomeric species, a monomeric diiodo bis(pyridine) complex (and the analogous TMEDA complex) can be prepared as shown in eq 8. In each compound the signal for the neopentylidyne α-carbon atom is again found at higher field than that for the neopentylidene α-carbon atom, but only one isomer of each is present. The reaction between TMSI and $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$ in toluene yields an insoluble orange powder that reacts readily with pyridine to give the bis(pyridine) complex shown in eq 8. This insoluble compound is likely to be $[Re(CCMe_3)(CHCMe_3)I_2]_x$. Interestingly, in ether an analogous reaction yields an orange solution from which $[Re(CCMe_3)$-



$$0.5\,[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2 \xrightarrow[2\,py]{2\,TMSI} ReI_2(py)_2(CCMe_3)(CHCMe_3) \quad (8)$$

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[24] Fellmann, J. D.; Rupprecht, G. A.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 5964.

[25] Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759.

[26] Beattie, I. R.; Jones, P. J. *Inorg. Chem.* **1979**, *18*, 2318.

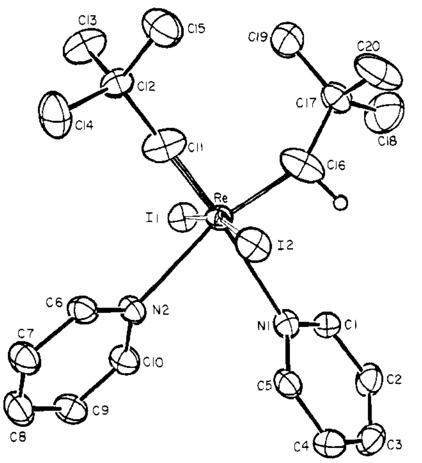
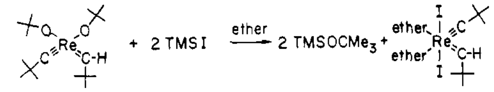


Figure 2. Molecular geometry and labeling of non-hydrogen atoms in the $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$ molecule (ORTEP-II diagram; 30% probability ellipsoids).

$(CHCMe_3)I_2]_x$ deposits only relatively slowly, but more rapidly if the solution is concentrated. We propose that in ether a weakly solvated bis(ether) complex is formed (eq 9).



(9)

X-ray Structure of $Re(CCMe_3)(CHCMe_3)py_2I_2$. The collection of diffraction data and the solution and refinement of the structure are described in the Experimental Section. $Re(CCMe_3)(CHCMe_3)py_2I_2$ exists in the crystal as discrete molecular units; there are no abnormally short intermolecular contacts. The molecule is illustrated in Figure 2. Interatomic distances and their estimated standard deviations (esd's) are listed in Table III; interatomic angles (with esd's) are given in Table IV.

The molecule consists of a formal rhenium(VII) atom with a rather distorted octahedral coordination geometry, consisting of mutually trans iodide ligands, mutually cis pyridine ligands, and mutually cis neopentylidyne and neopentylidene ligands. Most of the distortion may be ascribed to repulsion between the electron density in the $Re\equiv C$ and $Re=C$ bonds and between the iodides and the electron density in the $Re\equiv C$ and $Re=$ bonds. Thus, C(11)–Re–C(16) = 98.11 (42)°, I(1)–Re–I(2) = 170.09 (2)°, N(1)–Re–C(11) = 173.99 (33)°, and N(2)–Re–C(16) = 164.34 (33)°. The tendency for cis ligands multiply bonded to a metal to repel one another and to repel ligands that are mutually cis to them has been observed before in $W(O)(CHCMe_3)(PMe_3)_2Cl_2$,[17] $W(O)(CHCMe_3)(PEt_3)Cl_2$,[13] $Ta(CHCMe_3)_2(mesityl)(PMe_3)_2$,[12] and $W(CCMe_3)(PHPh)(PMe_3)_2Cl_2$.[23]

The two rhenium–pyridine linkages are inequivalent. That trans to the neopentylidyne ligand (Re–N(1) = 2.415 (6) Å is ca. 0.05 Å longer than that trans to the neopentylidene ligand (Re–N(2) = 2.369 (6) Å). It was noted in the structural study of $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$[27] that the W–P bond trans to the neopentylidene ligand was substantially longer than that trans to the neopentyl ligand (2.577 (3) vs. 2.450 (3) Å). The structural study of $W(CCMe_3)(PHPh)(PMe_3)_2Cl_2$[23] also revealed a relatively long W–Cl bond trans to the neopentylidyne ligand (2.578 (2) Å) compared to the W–Cl bond trans to the phosphido ligand (2.456 (2) Å). Thus it is now fairly well established that in general a metal–carbon triple bond lengthens the bond trans to it more than a metal–carbon (or metal–phosphido, -oxo, etc.) double bond lengthens the bond trans to it and likewise for a metal–ligand double bond vs. a metal–ligand single bond.

The rhenium–neopentylidyne linkage (Re(1)–C(11) = 1.742 (9) Å) is significantly shorter than the rhenium–neopentylidene linkage (Re(1)–C(16) = 1.873 (9) Å), as expected. The difference of 0.131 (13) Å is comparable to that of 0.157 (12) Å between the $W\equiv C$ and $W=C$ linkages in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$. But it is worth noting that the rhenium neopentylidyne C(α) bond length is one of the shortest, if not the shortest, known. For example, in $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(dmpe)$ it is 1.785 (8) Å,[27] in $Ta(\eta^5\text{-}C_5Me_5)(CPh)(PMe_3)_2Cl$ it is 1.849 (8) Å,[28] in $W(CCMe_3)(PHPh)(PMe_3)_2Cl_2$ it is 1.808 (6) Å,[23] and in $[W(CMe)(OCMe_3)_3]_2$ it is 1.759 (6) Å.[29] The shorter metal–ligand bonds probably result from the fact that the covalent radius of rhenium(VII) is necessarily less than that of tantalum(V) or tungsten(VI). The rhenium–neopentylidene bond length is also a relatively short one, at least for undistorted neopentylidene ligands. As has been demonstrated in several cases (see below), alkylidene ligands can be severely distorted toward a nearly linear $M=C(\alpha)-C(\beta)$ angle, resulting in a severe shortening of the metal–carbon double bond to a degree that one would expect for a (protonated) metal–carbon triple bond.

The $Re-C(\alpha)-C(\beta)$ angles are $Re\equiv C(11)-C(12)$ = 174.7 (7)° and $Re=C(16)-C(17)$ = 150.3 (7)°. The latter is comparable to some of the smallest of the $M=C(\alpha)-C(\beta)$ angles known for neopentylidene complexes of tantalum and tungsten. For example, $Ta=C(\alpha)-C(\beta)$ angles range from 150.4 (5)° in $Ta(\eta^5\text{-}C_5H_5)_2(CHCMe_3)Cl$[30] through 170.2 (2)° in $Ta(\eta^5\text{-}C_5Me_5)(CHCMe_3)(\eta^2\text{-}C_2H_4)(PMe_3)$,[15] while $W=C(\alpha)-C(\beta)$ angles range from 140.6 (11)° in $W(O)(CHCMe_3)(PEt_3)Cl_2$[13] through 168.7 (3)° in $W(CHCMe_3)(CO)(PMe_3)_2Cl_2$.[16] Large $M=C(\alpha)-C(\beta)$ angles are typically found in reduced alkylidene complexes (e.g., $W(CHCMe_3)(CO)(PMe_3)_2Cl_2$) or d^0 species in which no other good π-electron-donating ligands are present. The minimum $M=C(\alpha)-C(\beta)$ angle, perhaps for steric reasons, is likely to be around 140°. Therefore, we can say that the neopentylidene ligand in $Re(CCMe_3)(CHCMe_3)py_2I_2$ is relatively undistorted, as one would expect on the basis of the fact that the neopentylidyne ligand, probably more so than an oxo or imido ligand, is an excellent π-bonding ligand, thereby decreasing the metal's need for more electron density from the CH(α) bond of the neopentylidene ligand.

Protonation of $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$. It is known that $Ta(CHCMe_3)(CH_2CMe_3)_3$ reacts with HCl to give $Ta(CH_2CMe_3)_4Cl$[18] and that $W(NPh)(CHCMe_3)(CH_2CMe_3)_2$ reacts with HCl to give $W(NPh)(CH_2CMe_3)_3Cl$.[7] Although the structure of neither complex has been determined by X-ray studies, all the evidence in hand suggests that each is a trigonal-bipyramidal molecule with three neopentyl groups in the equatorial plane.

Addition of HCl to $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$ yields yellow, crystalline $Re(CCMe_3)(CH_2CMe_3)_3Cl$ quantitatively. An analogous reaction employing HI yields $Re(CCMe_3)(CH_2CMe_3)_3(I)$ while $Re(CCMe_3)(CH_2CMe_3)_3(OTf)$ can be made by reacting $Re(CCMe_3)(CH_2CMe_3)_3Cl$ with TMSOTf in toluene (OTf = triflate). All three $Re(CCMe_3)(CH_2CMe_3)_3X$ species are believed to

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(27) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 2454.

(28) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171.

(29) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.*, in press.

(30) Churchill, M. R.; Hollander, F. J. *Inorg. Chem.* **1978**, *17*, 1957.

have the same type of structure, a trigonal bipyramid with the three neopentyl groups located in the equatorial positions. The triflate ligand is likely to be only monodentate in this sterically rather crowded molecule. $Re(CCMe_3)(CH_2CMe_3)_3Cl$, like $W(NPh)(CH_2CMe_3)_3Cl$ and $Ta(CH_2CMe_3)_3Cl_2$, is a highly crystalline, thermally stable molecule that does not react readily with HCl gas. In contrast, $Ta(CH_2CMe_3)_4Cl$[18] reacts readily with HCl to give $Ta(CH_2CMe_3)_3Cl_2$ and decomposes below room temperature to give thermally unstable $Ta(CHCMe_3)(CH_2CMe_3)_2Cl$.

On Metal–Ligand Multiple Bonds. One of the most surprising features of this chemistry is the apparent preference of rhenium to form multiple bonds to carbon vs. multiple bonds to nitrogen. We do not know at this time whether it is a thermodynamic or a kinetic preference. There is, however, some reason for believing it may be thermodynamic. In general, the metal in a d^0 complex containing several oxo ligands is likely to be more positively charged than in the analogue containing the same number of isoelectronic, but less electronegative, imido ligands. Likewise, the metal in the analogue containing the same number of alkylidene ligands is likely to be least positively charged, i.e., in the lowest of the three "oxidation states". Now if the d^0 metal with some oxo or halide ligands is known to be a strong oxidant (e.g., Cr(VI), Re(VII), Os(VIII)), then replacement of an oxo ligand by an alkylidene ligand should be exothermic. Some support for this claim comes in the form of recent calculations by Goddard;[31] the reaction of MO_2Cl_2 complexes with ethylene to give $MO(CH_2)Cl_2$ complexes is exothermic for M = Cr ($\Delta G = -3$ kcal mol^{-1}) but *endothermic* for M = Mo ($\Delta G = 4$ kcal mol^{-1}). We might speculate then that (for example) $Cr(CCMe_3)(CH_2CMe_3)_3$ and $Os(CCMe_3)(CHCMe_3)(CH_2CMe_3)_3$ will be isolable species. The problem, of course, is that finding a synthetic route becomes increasingly difficult due to the high redox potential of readily available d^0 starting materials. Most likely such d^0 alkylidene and alkylidyne complexes must be prepared by a route involving oxidation of a d^2 or d^3 complex at the appropriate stage. That an "oxidation" can occur even under reducing conditions is evident in the preparation of $W(CCMe_3)(CH_2CMe_3)_3$ from WCl_6 and 6 equiv of $LiCH_2CMe_3$ where 3 equiv of $LiCH_2CMe_3$ are consumed in the reduction of W(VI) to W(III).[19]

Experimental Section

All experiments were performed under a nitrogen atmosphere by either Schlenk techniques or in a Vacuum Atmospheres HE43-2 drybox at room temperature (unless otherwise noted). Solvents were purified under N_2 by standard techniques and transferred to the drybox without exposure to air. Organic reagents were degassed with nitrogen and, where applicable, dried by passing through alumina. Re_2O_7 (Pressure Chemical) was used as received. $Re(NCMe_3)_3(OSiMe_3)$[9] was prepared by Nugent's method.

Collection of X-ray Diffraction Data for $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$. A number of purple-red crystals of $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$ were sealed in thin-walled glass capillary tubes under an inert atmosphere (Ar). Quality was checked by means of rotation and axial photographs. The crystal selected for the diffraction study had dimensions of 0.2 × 0.2 × 0.4 mm. It was mounted along its extended direction. Crystal alignment, determination of the orientation matrix and unit cell parameters, and data collection were carried out on a Syntex $P2_1$ automated four-circle diffractometer at SUNY/Buffalo, using techniques described previously.[32] Details appear in Table I.

Table I. Experimental Data for the X-ray Diffraction Study of $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$

(A) Crystal Parameters at 24 °C

cryst system: monoclinic
space group: $P2_1/c$
$a = 9.7682\ (25)$ Å
$b = 14.7250\ (41)$ Å
$c = 17.4070\ (44)$ Å
$\beta = 110.821\ (21)$ Å
$V = 2340.3\ (11)$ Å^3
$Z = 4$
mol wt 737.5
ρ(calcd) = 2.09 g/cm^3

(B) Intensity Data

radiation: Mo $K\overline{\alpha}$ (λ = 0.710 730 Å)
2θ limits, deg: 4.5–45.0
scan width, deg: $[2\theta(K\alpha_1) - 1.0]$–$[2\theta(K\alpha_2) + 1.0]$
scan speed, deg min^{-1}: 2.50
scan type: coupled θ(crystal)–2θ(counter)
reflctns measd: $+h, +k, \pm l$
reflctns collected: 3285 total yielding 3076 unique data
abs coeff, cm^{-1}: 81.7

Table II. Atomic Coordinates for $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$

atom	*x*	*y*	*z*
Re	0.37592 (3)	0.74509 (2)	0.38651 (2)
I(1)	0.54620 (6)	0.88702 (3)	0.36615 (3)
I(2)	0.25157 (6)	0.59004 (3)	0.42320 (4)
N(1)	0.5200 (6)	0.7516 (4)	0.5315 (4)
N(2)	0.5804 (6)	0.6527 (4)	0.3972 (4)
C(1)	0.5479 (8)	0.8320 (5)	0.5709 (5)
C(2)	0.6187 (9)	0.8392 (6)	0.6540 (5)
C(3)	0.6662 (9)	0.7614 (7)	0.6994 (5)
C(4)	0.6430 (9)	0.6795 (6)	0.6611 (5)
C(5)	0.5712 (9)	0.6768 (5)	0.5777 (5)
C(6)	0.5595 (8)	0.5735 (5)	0.3561 (5)
C(7)	0.6724 (9)	0.5209 (5)	0.3519 (5)
C(8)	0.8125 (10)	0.5481 (6)	0.3928 (6)
C(9)	0.8367 (8)	0.6279 (6)	0.4372 (5)
C(10)	0.7201 (8)	0.6783 (5)	0.4372 (5)
C(11)	0.2802 (10)	0.7293 (5)	0.2819 (6)
C(12)	0.1927 (8)	0.7084 (5)	0.1948 (5)
C(13)	0.2171 (11)	0.7800 (7)	0.1388 (6)
C(14)	0.2429 (12)	0.6148 (7)	0.1749 (7)
C(15)	0.0303 (10)	0.7006 (7)	0.1831 (7)
C(16)	0.2458 (9)	0.8262 (6)	0.4076 (7)
C(17)	0.1200 (8)	0.8903 (5)	0.3777 (5)
C(18)	0.1599 (13)	0.9722 (7)	0.4325 (7)
C(19)	0.0873 (11)	0.9226 (7)	0.2912 (6)
C(20)	−0.0114 (10)	0.8431 (7)	0.3838 (7)

All data were corrected for absorption ($\mu = 81.7$ cm^{-1}) and for Lorentz and polarization factors. Data were reduced to $|F_o|$ values. Any reflection with I(net) < 0 was assigned a value of $|F_o| = 0$.

Solution and Refinement of the Structure. The structure was solved by direct methods, using the program MULTAN76[33] on the CDC Cyber 173 computer at SUNY/Buffalo. (A minor complication was that the iodine atom peaks were initially of greater peak height (e Å^{-3}) than the rhenium peak.)

All subsequent calculations were performed using the Syntex XTL system (Nova 1200 computer with parallel floating-point hardware and disk unit) as modified at SUNY/Buffalo. Difference Fourier and full-matrix least-squares refinement (anisotropic thermal parameters for all 25 non-hydrogen atoms) led smoothly to convergence with[34] $R_F = 3.7\%$ and $R_{wF} = 3.3\%$ for 226 parameters refined against all 3076 independent data ($R_F = 3.0\%$ and $R_{wF} = 1.8\%$ for those 2748 data with $|F_o| > 3\sigma(|F_o|)$). Final positional parameters for all nonhydrogen atoms appear in Table II. The positions of all hydrogens (calculated with d(C–H) = 0.95 Å,[35] and the appropriate planar (sp^2) or staggered tetrahedral (sp^3) geometry are deposited in Table I-S.[36] Anisotropic thermal

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[31] Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 448.

[32] Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

[33] Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A* **1971**, *A27*, 368.

[34] $R_F(\%) = 100\,[\sum||F_o| - |F_c||/\sum|F_o|]$; $R_{wF}(\%) = 100[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

[35] Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

[36] See paragraph at end regarding supplementary material.

Table III. Interatomic Distances (Å) and Esd's for $\mathrm{Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2}$

(A) Distances from the Rhenium Atom			
Re–I(1)	2.771 (1)	Re–C(11)	1.742 (9)
Re–I(2)	2.765 (1)	Re–C(16)	1.873 (9)
Re–N(1)	2.415 (6)	Re···H(16)	2.34
Re–N(2)	2.369 (6)		
(B) Distances within the Pyridine Ligands			
N(1)–C(1)	1.348 (10)	N(2)–C(6)	1.345 (9)
C(1)–C(2)	1.368 (12)	C(6)–C(7)	1.371 (12)
C(2)–C(3)	1.376 (13)	C(7)–C(8)	1.359 (14)
C(3)–C(4)	1.358 (13)	C(8)–C(9)	1.380 (12)
C(4)–C(5)	1.370 (12)	C(9)–C(10)	1.359 (12)
C(5)–N(1)	1.350 (10)	C(10)–N(2)	1.347 (11)
(C) Distances within the Neopentylidene Ligand			
C(16)–C(17)	1.489 (12)	C(17)–C(19)	1.501 (13)
C(17)–C(18)	1.501 (14)	C(17)–C(20)	1.497 (14)
(D) Distances within the Neopentylidyne Ligand			
C(11)–C(12)	1.484 (12)	C(12)–C(14)	1.543 (14)
C(12)–C(13)	1.512 (12)	C(12)–C(15)	1.529 (13)

parameters are listed in Table II-S.[36]

The analytical forms of the scattering factors of the neutral atoms were corrected for both the $\Delta f'$ and $\Delta f''$ terms.[37] The function minimized was $\sum w(|F_o| - |F_c|)^2$, where w is based upon counting statistics, modified by an ignorance factor of $p = 0.015$.

Preparations. $\mathrm{Re(NCMe_3)_2Cl_3}$. Excess HCl was bubbled into a yellow solution of $\mathrm{Re(NCMe_3)_3(OSiMe_3)}$ (3.60 g, 7.37 mmol) in dichloromethane at −78 °C. The resulting deep red solution was allowed to warm to room temperature. Over a 3-h period, white $\mathrm{[Me_3CNH_3][Cl]}$ crystallized from solution as the color lightened to orange. The solution was filtered and stripped to dryness in vacuo. The orange residue was recrystallized from ether by adding pentane and cooling the sample to −40 °C for 1 day. The yield of orange, crystalline $\mathrm{Re(NCMe_3)_2Cl_3}$ was 2.66 g (83%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.12 (s, 18, NCMe$_3$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 78.5 (s, N*C*Me$_3$), 28.1 (q, J_{CH} = 125 Hz, NC*Me*$_3$); mol wt (differential vapor pressure, $\mathrm{CH_2Cl_2}$, 0 °C) calcd 435, found 509 at 5.3×10^{-2} M. Anal. Calcd for $\mathrm{ReC_8H_{18}Cl_3N_2}$: C, 22.09; H, 4.17. Found: C, 22.15; H, 4.11.

$\mathrm{Re(NCMe_3)_2Br_3}$. Three equivalents of $\mathrm{Me_3SiBr}$ (0.27 g, 1.7 mmol) was added to an orange solution of $\mathrm{Re(NCMe_3)_2Cl_3}$ (0.25 g, 0.58 mmol) in toluene (10 mL). The solution immediately turned cherry red. After 12 h the solvent was removed in vacuo, leaving a mixture of orange and red crystals. The mixture was dissolved in minimal ether, excess $\mathrm{Me_3SiBr}$ was added (another ~3 equiv), and the solution was cooled to −40 °C to give red crystals of $\mathrm{Re(NCMe_3)_2Br_3}$ (0.26 g, 80%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.09 (s, 18, NCMe$_3$). Anal. Calcd for $\mathrm{ReC_8H_{18}N_2Br_3}$: C, 16.91; H, 3.19. Found: C, 17.10; H, 3.24.

$\mathrm{Re(NCMe_3)_2(CH_2SiMe_3)_3}$. Since the product is quite photosensitive, all reactions and workups were performed in subdued light. An orange solution of $\mathrm{Re(NCMe_3)_2Cl_3}$ (0.50 g, 1.2 mmol) in dichloromethane (15 mL) was cooled to −40 °C, and a solution of $\mathrm{Zn(CH_2SiMe_3)_2}$ (0.42 g, 1.7 mmol) in 5 mL of pentane was added rapidly. The solution lightened immediately to yellow. After the solution was stirred at room temperature for ~5 min, $\mathrm{NEt_4Cl}$ (0.38 g, 2.3 mmol) was added as a solid and the reaction mixture was stirred for another 15 min. The mixture was filtered and the solvent removed in vacuo. The yellow, oily residue was extracted with 25 mL of pentane. The solution was filtered through Celite, and the solvent was removed from the filtrate in vacuo to give 0.5 g (70%) of a yellow, fluffy solid. $\mathrm{Re(NCMe_3)_2(CH_2SiMe_3)_3}$ was crystallized from ether by adding acetonitrile and cooling the solution to −40 °C (0.35 g after two crops, 50%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.54 (s, 4, C*H*$_2$SiMe$_3$ ax), 1.37 (s, 2, C*H*$_2$SiMe$_3$ eq), 1.24 (s, 18, NCMe$_3$), 0.38 (s, 9, CH$_2$Si*Me*$_3$ eq), 0.33 (s, 9, CH$_2$Si*Me*$_3$ ax); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 71.2 (s, N*C*Me$_3$), 34.4 (t, J_{CH} = 117 Hz, *C*H$_2$SiMe$_3$ eq), 30.5 (q, J_{CH} = 132 Hz, NC*Me*$_3$), 14.8 (t, J_{CH} = 118 Hz, *C*H$_2$SiMe$_3$ ax), 3.7 (q, J_{CH} = 117 Hz, CH$_2$Si*Me*$_3$ ax), 3.2 (q, J_{CH} = 120 Hz, CH$_2$Si*Me*$_3$ eq). Anal. Calcd for $\mathrm{ReC_{20}H_{51}N_2Si_3}$: C, 40.70; H, 7.83. Found: C, 40.94; H, 7.99.

$\mathrm{Re(NCMe_3)_2(CH_2Ph)_3}$. $\mathrm{Re(NCMe_3)_2Cl_3}$ (0.75 g, 1.7 mmol) was suspended in ether (50 mL) which had been cooled to −78 °C, and $\mathrm{PhCH_2MgCl}$ (6.5 mL, 0.80 M in ether) was added dropwise. The resulting deep red-violet solution was allowed to warm to room temperature over 2 h. The orange-brown solution was treated with activated charcoal three times. The solvent was removed from the filtrate, leaving an orange powder which was recrystallized from pentane at −40 °C as orange nuggets (three crops, yield 0.73 g, 70%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 7.15–7.00 (m, 15, CH$_2$*Ph*), 3.99 (s, 4, C*H*$_2$Ph ax), 3.33 (s, 2, C*H*$_2$Ph eq), 1.05 (s, 18, NCMe$_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 148.6 (s, CH$_2$*Ph* ipso, eq), 147.7 (s, CH$_2$*Ph* ipso, ax), 129.1–121.6 (m, CH$_2$*Ph*), 70.3 (s, N*C*Me$_3$), 54.2 (t, J_{CH} = 129 Hz, *C*H$_2$Ph eq), 38.0 (t, J_{CH} = 134 Hz, *C*H$_2$Ph ax), 27.6 (q, J_{CH} = 127 Hz, NC*Me*$_3$). Anal. Calcd for $\mathrm{ReC_{29}H_{39}N_2}$: C, 57.86; H, 6,53. Found: C, 58.35; H, 6.59.

$\mathrm{Re(NCMe_3)_2Me_3}$. Three equiv of $\mathrm{AlMe_3}$ (0.20 mL, 2.1 mmol) was added to an orange solution of $\mathrm{Re(NCMe_3)_2Cl_3}$ (0.31 g, 0.71 mmol) in toluene (15 mL) at −40 °C. The solution lightened immediately to yellow. After 30 min 1.5 equiv of TMEDA (0.16 mL, 1.1 mmol) was added by syringe. After another 30 min the volatile components were removed in vacuo. The oily yellow residue was extracted with two 10-mL portions of pentane. The pentane extract was filtered through Celite and the solvent removed from the filtrate, leaving a yellow oil. The oil was sublimed (<1 μm) onto a dry ice cooled probe as a pale yellow solid which melted to a yellow oil at room temperature (yield 0.24 g, 90%): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 1.81 (s, 6, CH$_3$ ax), 1.62 (s, 3, CH$_3$ eq), 1.17 (s, 18, NCMe$_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 70.0 (s, N*C*Me$_3$), 30.1 (q, J_{CH} = 128 Hz, NC*Me*$_3$), 29.0 (q, J_{CH} = 130 Hz, CH$_3$ eq), 9.7 (q, J_{CH} = 130 Hz, CH$_3$ ax).

$\mathrm{Re(NCMe_3)_2Me_2Cl}$. Orange, crystalline $\mathrm{Re(NCMe_3)_2Cl_3}$ (0.19 g, 0.44 mmol) was added to a pale yellow solution of $\mathrm{Re(NCMe_3)_2Me_3}$ (0.33 g, 0.88 mmol) in ether. After 24 h the ether was removed in vacuo, leaving an orange oil. Crystals were obtained from minimal pentane at −40 °C (0.50 g, 86%): ^{1}H NMR (tol-d_8) δ 2.03 (s, 6, Me), 1.10 (s, 18, NCMe$_3$); ^{13}C NMR ($\mathrm{CD_2Cl_2}$) δ 72.2 (s, N*C*Me$_3$), 29.5 (q, J_{CH} = 132 Hz, NC*Me*$_3$), 21.2 (q, J_{CH} = 133 Hz, Me). Anal. Calcd for $\mathrm{ReC_{10}H_{24}ClN_2}$: C, 30.48; H, 6.14. Found: C, 30.59; H, 6.29.

$\mathrm{Re(NCMe_3)_2(CH_2SiMe_3)_2Cl}$. A solution of $\mathrm{Zn(CH_2SiMe_3)_2}$ in dichloromethane (~2 mL) was added to a solution of $\mathrm{Re(NCMe_3)_2Cl_3}$ (1.00 g, 2.30 mmol) in dichloromethane (10 mL) at −30 °C. The solution was allowed to warm to room temperature where it lightened to yellow after ~5 min. $\mathrm{Et_4NCl}$ (0.38 g, 2.30 mmol) was added and the $\mathrm{Et_4NZnCl_3}$ filtered off after ~5 min. The solvent was removed from the filtrate in vacuo to give a yellow, oily solid which was recrystallized from pentane at −30 °C (yield 1.10 g, 90%): ^{1}H NMR ($\mathrm{C_6H_6}$) δ 1.29 (s, 4, C*H*$_2$SiMe$_3$), 1.20 (s, 18, NCMe$_3$), 0.38 (s, 18, CH$_2$Si*Me*$_3$); ^{13}C NMR ($\mathrm{CDCl_3}$) δ 72.0 (s, N*C*Me$_3$), 29.3 (q, J_{CH} = 127 Hz, NC*Me*$_3$), 28.8 (t, J_{CH} = 122 Hz, *C*H$_2$SiMe$_3$), 2.4 (q, J_{CH} = 118 Hz, CH$_2$Si*Me*$_3$). Anal. Calcd for $\mathrm{ReC_{16}H_{40}ClN_2Si_2}$: C, 35.69; H, 7.49. Found: C, 35.54; H, 7.50.

$\mathrm{Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)}$. A solution of $\mathrm{Re(NCMe_3)_2Cl_3}$ (7.00 g, 16.1 mmol) in 300 mL of ether was cooled to −78 °C at which point most of the $\mathrm{Re(NCMe_3)_2Cl_3}$ precipitated from solution. The mixture was stirred vigorously as 3 equiv of $\mathrm{Me_3CCH_2MgCl}$ (1.4 M in ether) were added dropwise. As the intense purple solution warmed to room temperature, the magnesium salts precipitated and the color turned brown. After 3 h the mixture was filtered through Celite, and the magnesium salts were washed thoroughly with ether. The solvent was removed from the filtrate in vacuo leaving a dark brown oily solid. The dark brown oil was distilled twice at ~80 °C and 1 μm through a short-path distillation apparatus to give $\mathrm{Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)}$ as a yellow oil (5.15 g, 68%): ^{1}H NMR (tol-d_8) δ 11.95 (s, 1, C*H*CMe$_3$), 2.83 (d, 1, $^2J_{\mathrm{H_AH_B}}$ = 13.2 Hz, C*H*$_\mathrm{A}$H$_\mathrm{B}$CMe$_3$), 2.62 (d, 1, $^2J_{\mathrm{H_BH_A}}$ = 13.2 Hz, CH$_\mathrm{A}$*H*$_\mathrm{B}$CMe$_3$), 1.37 (s, 18, NC*Me*$_3$), 1.26 (s, 9, CMe$_3$), 1.15 (s, 9, CMe$_3$); ^{13}C NMR ($\mathrm{C_6D_6}$) δ 262.2 (d, J_{CH} = 134 Hz, *C*HCMe$_3$), 69.5 (s, N*C*Me$_3$), 44.1 (s, CH*C*Me$_3$), 34.5 (t, J_{CH} = 128 Hz, *C*H$_2$CMe$_3$), 34.0 (q, J_{CH} = 126 Hz, C*Me*$_3$), 32.7 (q, J_{CH} = 128 Hz, C*Me*$_3$), 32.5 (q, J_{CH} = 125 Hz, C*Me*$_3$), 32.4 (q, J_{CH} = 131 Hz, C*Me*$_3$), 31.4 (s, CH$_2$*C*Me$_3$); mass spectrum (40 eV), parent ions at *m*/*e* (relative intensity) 468 (^{185}Re,

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(37) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. 4, pp 99–101 and 149–150.

Table IV. Interatomic Angles (deg) with Esd's for $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$

(A) Angles about the Rhenium Atom

I(1)-Re-I(2)	170.09 (2)	N(1)-Re-C(11)	173.99 (33)	I(2)-Re-N(2)	86.27 (15)
I(1)-Re-N(1)	87.17 (14)	N(1)-Re-C(16)	87.34 (33)	I(2)-Re-C(11)	90.84 (30)
I(1)-Re-N(2)	85.16 (15)	C(11)-Re-C(16)	98.11 (42)	I(2)-Re-C(16)	95.53 (30)
I(1)-Re-C(11)	95.19 (30)	N(1)-Re-N(2)	77.24 (21)	N(2)-Re-C(11)	97.42 (33)
I(1)-Re-C(16)	91.41 (30)	I(2)-Re-N(1)	86.09 (14)	N(2)-Re-C(16)	164.34 (33)

(B) Angles within the Pyridine Rings

C(1)-N(1)-C(5)	116.66 (66)	C(5)-C(4)-C(3)	118.60 (84)	C(8)-C(7)-C(6)	119.01 (80)
C(2)-C(1)-N(1)	122.74 (74)	N(1)-C(5)-C(4)	123.37 (78)	C(9)-C(8)-C(7)	118.99 (85)
C(3)-C(2)-C(1)	118.92 (83)	C(6)-N(2)-C(10)	116.90 (65)	C(10)-C(9)-C(8)	119.18 (80)
C(4)-C(3)-C(2)	119.64 (86)	C(7)-C(6)-N(2)	123.02 (72)	N(2)-C(10)-C(9)	122.84 (74)

(C) Angles within the Neopentylidene Ligand

Re-C(16)-C(17)	150.27 (72)	C(16)-C(17)-C(20)	107.59 (76)	C(18)-C(17)-C(20)	111.28 (81)
C(16)-C(17)-C(18)	106.96 (78)	C(18)-C(17)-C(19)	107.32 (79)	C(19)-C(17)-C(20)	109.68 (79)
C(16)-C(17)-C(18)	114.03 (77)				

(D) Angles within the Neopentylidyne Ligand

Re-C(11)-C(12)	174.77 (71)	C(11)-C(12)-C(15)	110.25 (71)	C(13)-C(12)-C(15)	111.09 (72)
C(11)-C(12)-C(13)	110.39 (71)	C(13)-C(12)-C(14)	109.98 (74)	C(14)-C(12)-C(15)	107.50 (73)
C(11)-C(12)-C(14)	107.53 (72)				

37.5%) and 470 (^{187}Re, 62.5%). Anal. Calcd for $ReC_{18}H_{39}N_2$: C, 46.03; H, 8.39. Found: C, 46.12; H, 8.31.

$Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$. $Re(NCMe_3)_2(CH_2SiMe_3)_3$ can be photolyzed in C_6D_6 by a medium-pressure Hg lamp to give $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$ virtually quantitatively, as determined by ^{1}H NMR. The most efficient method of preparing $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$ avoids isolation of $Re(NCMe_3)_2(CH_2SiMe_3)_3$. $Re(NCMe_3)_2Cl_3$ (1.00 g, 2.30 mmol) in 20 mL of dichloromethane was treated with 1.5 equiv of $Zn(CH_2SiMe_3)_2$ (0.83 g, 3.4 mmol), and 1.5 equiv of NEt_4Cl (0.57 g, 3.5 mmol) was subsequently added to give a yellow solution of $Re(NCMe_3)_2(CH_2SiMe_3)_3$. The dichloromethane was removed in vacuo, and the pentane extract of the residue was photolyzed with a medium pressure mercury lamp for 30 min (3 × 10 min to prevent overheating). The solvent was removed in vacuo, leaving an oily yellow-orange solid. The residue was sublimed at 50 °C (0.1 μm) to give $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$ as a flaky, yellow solid which can be recrystallized from ether by adding acetonitrile and cooling to −40 °C (0.85 g, 75% based on $Re(NCMe_3)_2Cl_3$): ^{1}H NMR ($CDCl_3$) δ 12.09 (s, 1, C*H*SiMe$_3$), 1.38 (s, 9, NCMe$_3$), 1.37 (s, 9, NCMe$_3$), 1.04 (d, 1, $^2J_{H_AH_B}$ = 13 Hz, C*H*$_A$H$_B$SiMe$_3$), 0.90 (d, 1, $^2J_{H_BH_A}$ = 13 Hz, CH$_A$*H*$_B$SiMe$_3$), 0.13 (s, 9, SiMe$_3$), −0.06 (s, 9, SiMe$_3$); ^{13}C NMR (C_6D_6) δ 237.5 (d, J_{CH} = 128 Hz, *C*HSiMe$_3$), 69.6 (s, N*C*Me$_3$), 69.5 (s, N*C*Me$_3$), 32.6 (q, J_{CH} = 122 Hz, NC*Me*$_3$), 32.0 (q, J_{CH} = 125 Hz, NC*Me*$_3$), 1.8 (q, J_{CH} = 118 Hz, SiMe$_3$), 1.5 (t, J_{CH} = 116 Hz, *C*H$_2$SiMe$_3$), 1.0 (q, J_{CH} = 116 Hz, SiMe$_3$); mass spectrum (40 eV), parent ions at *m/e* (relative intensity) 500 (^{185}Re, 37.5%), and 502 (^{187}Re, 62.5%). Anal. Calcd for $ReC_{16}H_{39}N_2Si_2$: C, 38.28; H, 7.83. Found: C, 38.65; H, 7.99.

$[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$. A solution of $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$ (2.00 g, 4.26 mmol) in dichloromethane (15 mL) was cooled to −40 °C, and 2,4-lutidine hydrochloride (1.84 g, 12.8 mmol) was added as a solid. The solution turned orange immediately. The *tert*-butylammonium chloride was filtered off after ~5 h and the solvent removed from the filtrate in vacuo, leaving 1.88 g (94%) of a pale orange powder that was pure $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ by ^{1}H NMR. $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ can be crystallized from dichloromethane by addition of pentane at −40 °C or more easily from mixtures of THF and pentane at −40 °C. The compound crystallizes with one THF of crystallization per dimer (as determined by ^{1}H NMR integration) which can be removed at 1 μm after 48 h at 25 °C: ^{1}H NMR ($CDCl_3$) major isomer δ 13.63 (s, 2, C*H*CMe$_3$), 5.33 (d, 2, $^2J_{H_AH_B}$ = 13.5 Hz, N*H*$_A$H$_B$CMe$_3$), 4.23 (d, 2, $^2J_{H_BH_A}$ = 13.5 Hz, NH$_A$*H*$_B$CMe$_3$), 1.39 (s, 18, CMe$_3$), 1.29 (s, 18, CMe$_3$), 1.17 (s, 18, CMe$_3$), minor isomer δ 13.58 (s, 2, C*H*CMe$_3$), 5.12 (d, 2, $^2J_{H_AH_B}$ = 13.5 Hz, N*H*$_A$H$_B$CMe$_3$), 4.37 (d, 2, $^2J_{H_BH_A}$ = 13.5 Hz, NH$_A$*H*$_B$CMe$_3$), 1.39 (s, 18, CMe$_3$), 1.27 (s, 18, CMe$_3$), 1.18 (s, 18, CMe$_3$); ^{13}C NMR ($CDCl_3$, THF solvate) major isomer δ 298.4 (d, J_{CH} = 128 Hz, *C*HCMe$_3$), 294.3 (s, *C*CMe$_3$), 53.5 (s, *C*Me$_3$), 52.9 (s, *C*Me$_3$), 48.1 (s, NH$_2$*C*Me$_3$), 29.7 (q, C*Me*$_3$), 29.5 (q, C*Me*$_3$), 28.2 (q, C*Me*$_3$), minor isomer δ 299.2 (d, J_{CH} = 125 Hz, *C*HCMe$_3$), 293.7 (s, *C*CMe$_3$), all other peaks coincident with those of the major isomer. Anal. Calcd for $Re_2C_{28}H_{60}Cl_4N_2$: C, 35.82; H, 6.44; N, 2.98. Found: C, 35.66; H, 6.52; N, 3.29.

The compound may be prepared by using gaseous HCl as follows: A yellow pentane solution (25 mL) of $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$ (0.25 g, 0.53 mmol) was cooled to −78 °C and gaseous HCl (36 mL, 1.6 mmol) introduced via syringe. A light yellow precipitate formed immediately. The yellow solid redissolved when the reaction mixture was warmed to room temperature. After 12 h a pale orange precipitate formed. The precipitate was isolated by filtration, washed with 2 × 10 mL of pentane, and extracted with 10 mL of THF. Cooling of the yellow THF extract to −40 °C for 12 h afforded orange crystals of $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2(THF)$ (0.15 g, 56%).

$Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)(py)Cl_2$. Solid pyridine hydrochloride (0.37 g, 3.2 mmol) was added to a yellow solution of $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$ (0.50 g, 1.1 mmol) in dichloromethane (20 mL) at −40 °C. The solution immediately turned orange. After 12 h the mixture was filtered and the solvent was removed in vacuo, leaving an orange oil. The oil was triturated with cold pentane (5 mL) to give an orange powder which was recrystallized from minimal ether (~50 mL) by adding pentane and cooling the solution to −40 °C for 12 h (yield 0.46 g, 80%): ^{1}H NMR ($CDCl_3$, 243 K) major isomer δ 14.94 (s, 1, N*H*CMe$_3$), 9.32 (d, 2, ^3J = 6 Hz, py$_{ortho}$), 7.79 (t, 1, ^3J = 7 Hz, py$_{para}$), 7.36 (t, 2, ^3J = 7 Hz, py$_{metal}$), 3.77 (d, 1, $^2J_{H_AH_B}$ = 12.0 Hz, C*H*$_A$H$_B$CMe$_3$), 3.55 (d, 1, $^2J_{H_BH_A}$ = 12.0 Hz, CH$_A$*H*$_B$CMe$_3$), 1.54 (s, 9, CMe$_3$), 1.44 (s, 9, CMe$_3$), 0.95 (s, 9, CH$_2$C*Me*$_3$), minor isomer δ 14.64 (s, 1, N*H*CMe$_3$), 9.16 (d, 2, ^3J = 6 Hz, py$_{ortho}$), 7.79 (t, 1, ^3J = 7 Hz, py$_{para}$), 7.36 (t, 2, ^3J = 7 Hz, py$_{meta}$), 3.35 (d, 1, $^2J_{H_AH_B}$ = 12.0 Hz, C*H*$_A$H$_B$CMe$_3$), 3.20 (d, 1, $^2J_{H_BH_A}$ = 12.0 Hz, CH$_A$*H*$_B$CMe$_3$), 1.48 (s, 9, CMe$_3$), 1.40 (s, 9, CMe$_3$), 0.98 (s, 9, CH$_2$C*Me*$_3$); ^{13}C NMR ($CDCl_3$, 243 K) major isomer δ 304.4 (s, *C*CMe$_3$), 153.9 (d, J_{CH} = 183 Hz, py$_{ortho}$), 138.2 (d, J_{CH} = 165 Hz, py$_{para}$), 123.7 (d, J_{CH} = 168 Hz, py$_{meta}$), 74.3 (t, J_{CH} = 128 Hz, *C*H$_2$CMe$_3$), 66.9 (s, NH*C*Me$_3$), 52.4 (s, C*C*Me$_3$), 35.1 (s, CH$_2$*C*Me$_3$), 32.7 (q, J_{CH} = 128 Hz, NC*Me*$_3$), 29.4 (q, J_{CH} = 128 Hz, C*Me*$_3$), 28.3 (q, J_{CH} = 128 Hz, C*Me*$_3$), minor isomer δ 305.0 (s, *C*CMe$_3$), 153.9 (d, J_{CH} = 183 Hz, py$_{ortho}$), 139.0 (d, J_{CH} = 165 Hz, py$_{para}$), 124.0 (d, J_{CH} = 168 Hz, py$_{meta}$), 68.6 (t, J_{CH} = 129 Hz, *C*H$_2$CMe$_3$), 67.2 (s, NH*C*Me$_3$), 52.4 (s, C*C*Me$_3$), 35.1 (s, CH$_2$*C*Me$_3$), 33.0 (q, J_{CH} = 129 Hz, C*Me*$_3$), 28.8 (q, J_{CH} = 128 Hz, C*Me*$_3$), 28.1 (q, J_{CH} = 128 Hz, C*Me*$_3$).

$[NEt_4][Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)Cl_3]$. Solid 2,4-lutidine hydrochloride (0.46 g, 3.2 mmol) was added to a mixture of $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$ (0.50 g, 1.1 mmol) and Et_4NCl (0.18 g, 1.1 mmol) in dichloromethane (15 mL) at −40 °C. After 5 h, the solution was orange. The flocculent *tert*-butylamine hydrochloride was filtered off at 25 °C and the solvent removed from the filtrate in vacuo, leaving an orange powder. The powder was washed with pentane (2 × 10 mL) and then dissolved with THF (10 mL). The solution was filtered through Celite and the product crystallized at −40 °C after adding pentane (yield 0.51 g, 76%): ^{1}H NMR ($CDCl_3$) δ 14.46 (s, 1, N*H*CMe$_3$), 3.38 (q, 8,

J_{HH} = 7.0 Hz, NCH_2CH_3), 3.29 (d, 1, $^2J_{H_AH_B}$ = 11.7 Hz, $CH_AH_BCMe_3$), 3.17 (d, 1, $^2J_{H_BH_A}$ = 11.7 Hz, $CH_AH_BCMe_3$), 1.42 (s, 18, CMe_3), peaks for $CCMe_3$ and $NHCMe_3$ coincident at 25 °C, 1.29 (t, 12, J_{HH} = 7.0 Hz, NCH_2CH_3), 0.91 (s, 9, CH_2CMe_3); ^{13}C NMR ($CDCl_3$) δ 303.1 (s, $CCMe_3$), 70.9 (t, J_{CH} = 131 Hz, CH_2CMe_3), 65.5 (s, $NHCMe_3$), 51.8 (t, NCH_2CH_3), 51.2 (s, $CCMe_3$), 33.7 (s, CH_2CMe_3), 32.9 (q, CMe_3), 28.4 (q, CMe_3), 27.6 (q, CMe_3), 8.1 (q, NCH_2CH_3). Anal. Calcd for $ReC_{22}H_{50}Cl_3N_2$: C, 41.60; H, 7.93. Found: C, 41.06; H, 8.23.

$Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$. Solid $LiOCMe_3$ (0.23 g, 2.85 mmol) was added to a suspension of pale orange $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2(THF)$ (0.72 g, 0.71 mmol) in 15 mL of THF at −40 °C. The mixture was stirred at room temperature until all solids had dissolved and the color was bright yellow (~30 min). The solvent was removed in vacuo, and the residue was extracted with pentane (20 mL), leaving the white lithium salts. The extract was filtered through Celite and the solvent removed in vacuo until the flask returned to room temperature. (The product is extremely volatile!) The resulting bright yellow oily solids were sublimed onto a probe cooled to 0 °C in a static (1 μm) vacuum (yield 0.46 g, 69%). $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$ melts at ~30 °C. It is extremely sensitive to water and oxygen and also extremely soluble in common organic solvents. Therefore, it can only be handled as a solid in the highest quality, inert atmosphere: ^1H NMR (C_6D_6) δ 10.15 (s, 1, $CHCMe_3$), 1.37 (s, 9, CMe_3), 1.36 (s, 9, CMe_3), 1.21 (s, 18, $OCMe_3$); ^{13}C NMR (C_6D_6) δ 287.4 (s, $CCMe_3$), 229.9 (d, J_{CH} = 126 Hz, $CHCMe_3$), 77.5 (s, $OCMe_3$), 52.9 (s, $CCMe_3$), 43.6 (s, $CHCMe_3$), 33.5 (q, CMe_3), 32.1 (q, $OCMe_3$), 30.9 (q, CMe_3).

$Re(CCMe_3)(CHCMe_3)(OSiMe_3)_2$. In a manner analogous to the preparation of $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$ above, $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2(THF)$ (0.25 g, 0.25 mmol) was treated with solid $LiOSiMe_3$ (0.10 g, 1.0 mmol) to yield yellow, low-melting $Re(CCMe_3)(CHCMe_3)(OSiMe_3)_2$ (0.18 g, 73%): ^1H NMR (C_6D_6) δ 10.10 (s, 1, $CHCMe_3$), 1.31 (s, 18, $CCMe_3$ coincident with $CHCMe_3$), 0.12 (s, 18, $OSiMe_3$); ^{13}C NMR (C_6D_6) δ 290.5 (s, $CCMe_3$), 231.3 (d, J_{CH} = 121 Hz, $CHCMe_3$), 53.4 (s, $CCMe_3$), 43.8 (s, $CHCMe_3$), 33.1 (q, J_{CH} = 126 Hz, CMe_3), 30.8 (q, J_{CH} = 128 Hz, CMe_3), 1.9 (q, J_{CH} = 118 Hz, $OSiMe_3$).

$Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$. $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2(THF)$ (0.50 g, 0.50 mmol) was dissolved in 15 mL of THF and the solution was cooled to −40 °C. Me_3CCH_2MgCl (1.4 mL, 1.4 M in ether) was added by syringe. The orange solution changed to yellow. After 0.5 h the solvent was removed in vacuo, and the oily, solid residue was extracted with 20 mL of pentane. The yellow-orange extract was filtered through Celite and the solvent removed from the filtrate in vacuo. The resulting yellow-orange oil was sublimed at 0.1 μm onto a cold finger cooled to −78 °C. $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$ (0.42 g, 90%) was collected as a yellow-orange oil as it melted off the cold finger: ^1H NMR (C_6D_6) δ 7.65 (s, 1, $CHCMe_3$), 1.89 (d, 2, $^2J_{H_AH_B}$ = 12.4 Hz, $CH_AH_BCMe_3$), 1.55 (d, 2, $^2J_{H_BH_A}$ = 12.4 Hz, $CH_AH_BCMe_3$), 1.38 (s, 9, CMe_3), 1.27 (s, 9, CMe_3), 1.11 (s, 18, CH_2CMe_3); ^{13}C NMR (C_6D_6) δ 295.1 (s, $CCMe_3$), 224.6 (d, J_{CH} = 121 Hz, $CHCMe_3$), 78.6 (t, J_{CH} = 115 Hz, CH_2CMe_3), 52.7 (s, $CCMe_3$), 43.3 (s, $CHCMe_3$), 34.6 (q, J_{CH} = 120 Hz, CH_2CMe_3), 32.5 (q, J_{CH} = 127 Hz, CMe_3), 29.8 (q, J_{CH} = 123 Hz, CMe_3). Anal. Calcd for $ReC_{20}H_{41}$: C, 51.36; H, 8.84. Found: C, 51.30; H, 8.84.

$Re(CCMe_3)(CHCMe_3)py_2I_2$. $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ (0.50 g, 0.53 mmol) was suspended in 30 mL of toluene and pyridine (0.18 mL, 2.2 mmol) and Me_3SiI (0.31 mL, 2.2 mmol) added via syringe. The reaction mixture was stirred at room temperature for a minimum of 2 days or until no starting material remained. The resulting deep red solution was filtered through Celite. Pentane was added to the filtrate until it became slightly cloudy, and the solution was cooled to −40 °C to give dark red crystals of $Re(CCMe_3)(CHCMe_3)py_2I_2$ (0.59 g, 75%): ^1H NMR ($CDCl_3$) δ 14.06 (s, 1, $CHCMe_3$), 9.19 (br d, 4, $J_{HH} \approx$ 3 Hz, py_{ortho}), 7.76 (t, 2, J_{HH} = 8 Hz, py_{para}), 7.27 (br m, 4, py_{meta}), 1.37 (s, 9, CMe_3), 1.34 (s, 9, CMe_3); ^{13}C NMR (CD_2Cl_2) δ 307.1 (d, J_{CH} = 123 Hz, $CHCMe_3$), 299.5 (s, $CCMe_3$), 155.5 (d, J_{CH} = 183 Hz, py_{ortho}), 138.3 (d, J_{CH} = 162 Hz, py_{para}), 124.4 (d, J_{CH} = 165 Hz, py_{meta}), 55.6 (s, $CCMe_3$), 49.7 (s, $CHCMe_3$), 29.6 (q, J_{CH} = 122 Hz, $CCMe_3$), 27.4 (q, J_{CH} = 126 Hz, CMe_3). Anal. Calcd for $ReC_{20}H_{29}I_2N_2$: C, 32.57; H, 3.96. Found: C, 33.01; H, 4.16.

$Re(CCMe_3)(CH_2CMe_3)_3Cl$. A pentane solution (20 mL) of $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$ (0.35 g, 0.75 mmol) was cooled to −78 °C, and 1 equiv of HCl gas was added via syringe. The color changed from yellow-orange to yellow, and a yellow solid precipitated. After the solution was warmed to room temperature, the solvent was removed in vacuo and the yellow residue extracted with minimal pentane. The extract was filtered, concentrated, and cooled to −40 °C to give yellow crystals of $Re(CCMe_3)(CH_2CMe_3)_3Cl$ (0.31 g, 82%): ^1H NMR (C_6D_6) δ 3.01 (s, 6, CH_2CMe_3), 1.24 (s, 9, $CCMe_3$), 1.12 (s, 27, CH_2CMe_3); ^{13}C NMR (C_6D_6) δ 278.2 (s, $CCMe_3$), 72.2 (t, J_{CH} = 128 Hz, CH_2CMe_3), 50.5 (s, $CCMe_3$), 35.5 (s, CH_2CMe_3), 33.7 (q, J_{CH} = 125 Hz, CH_2CMe_3), 26.7 (q, J_{CH} = 128 Hz, $CCMe_3$). Anal. Calcd for $ReC_{20}H_{42}Cl$: C, 47.64; H, 8.40. Found: C, 47.72; H, 8.48.

$Re(CCMe_3)(CH_2CMe_3)_3I$. The reaction was performed as in the preparation above using gaseous HI. The product was crystallized from pentane at −40 °C as flaky yellow crystals (83% yield): ^1H NMR (C_6D_6) δ 3.38 (s, 6, CH_2CMe_3), 1.21 (s, 9, $CCMe_3$), 1.16 (s, 27, CH_2CMe_3).

$Re(CCMe_3)(CH_2CMe_3)_3(O_3SCF_3)$. $Re(CCMe_3)(CH_2CMe_3)_3Cl$ (0.10 g, 0.20 mmol) was dissolved in 10 mL of pentane, and the solution was stirred while 1 equiv of $Me_3SiO_3SCF_3$ (0.045 g, 0.20 mmol) was added. After 24 h the solution color had changed from yellow to yellow-orange. The solvent was removed in vacuo, leaving a light yellow solid. The solid was recrystallized from pentane at −40 °C to yield flaky, yellow crystals of $Re(CCMe_3)(CH_2CMe_3)_3(O_3SCF_3)$ (0.11 g, 90%): ^1H NMR (C_6D_6) δ 2.79 (s, 6, CH_2CMe_3), 1.13 (s, 9, $CCMe_3$), 1.02 (s, 27, CH_2CMe_3); ^{13}C NMR (C_6D_6) δ 296.3 (s, $CCMe_3$), 125.3 (q, J_{CF} = 320 Hz, CF_3SO_3), 80.7 (t, J_{CH} = 127 Hz, CH_2CMe_3), 53.2 (s, $CCMe_3$), 37.1 (s, CH_2CMe_3), 32.8 (q, J_{CH} = 125 Hz, CH_2CMe_3), 26.8 (q, J_{CH} = 128 Hz, $CCMe_3$); ^{19}F NMR (C_6D_6) δ 250.5 (s, CF_3SO_3). Anal. Calcd for $ReC_{21}H_{42}F_3O_3S$: C, 40.83; H, 6,85. Found: C, 41.43; H, 7.04.

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Registry No. $Re(NCMe_3)_2Cl_3$, 83487-31-4; $Re(NCMe_3)_2Br_3$, 86823-31-6; $Re(NCMe_3)_2(CH_2SiMe_3)_3$, 83487-30-3; $Re(NCMe_3)_2(CH_2Ph)_3$, 83487-29-0; $Re(NCMe_3)_2Me_3$, 83487-28-9; $Re(NCMe_3)_2Me_2Cl$, 86823-32-7; $Re(NCMe_3)_2(CH_2SiMe_3)_2Cl$, 86823-33-8; $Re(NCMe_3)_2(CHCMe_3)(CH_2CMe_3)$, 83487-27-8; $Re(NCMe_3)_2(CHSiMe_3)(CH_2SiMe_3)$, 83487-33-6; $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ (isomer 1), 86851-96-9; $[Re(CCMe_3)(CHCMe_3)(NH_2CMe_3)Cl_2]_2$ (isomer 2), 86851-99-2; $Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)(py)Cl_2$ (isomer 1), 86851-97-0; $Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)(py)Cl_2$ (isomer 2), 86852-56-4; $[NEt_4][Re(CCMe_3)(NHCMe_3)(CH_2CMe_3)Cl_3]$, 86823-30-5; $Re(CCMe_3)(CHCMe_3)(OCMe_3)_2$, 83487-35-8; $Re(CCMe_3)(CHCMe_3)OSiMe_3)_2$, 86823-34-9; $Re(CCMe_3)(CHCMe_3)(CH_2CMe_3)_2$, 86823-35-0; $Re(CCMe_3)(CHCMe_3)Py_2I_2$, 86851-98-1; $Re(CCMe_3)(CH_2CMe_3)_3Cl$, 86823-36-1; $Re(CCMe_3)(CH_2CMe_3)_3I$, 86823-37-2; $Re(CCMe_3)(CH_2CMe_3)_3(OTF)$, 86834-32-4; $Re(NCMe_3)_3(OSiMe_3)$, 73321-57-0.

Supplementary Material Available: Calculated hydrogen positions, anisotropic thermal parameters, and observed and calculated structure factors for $Re(CCMe_3)(CHCMe_3)(C_5H_5N)_2I_2$ (16 pages). Ordering information is given on any current masthead page.