Rhenium(VII) Monoimido Alkylidyne Complexes. The Importance of Face Selectivity in the Metathesis of Acetylenes via Rhenacyclobutadiene Intermediates

I. A. Weinstock, R. R. Schrock,* and William M. Davis

Contribution from the Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received April 30, 1990*

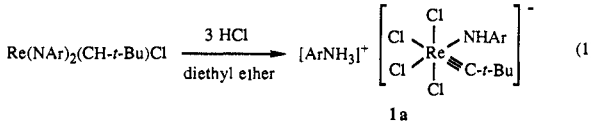
Abstract: $Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$ (Ar = 2,6-C_6H_3-*i*-Pr_2) reacts with 3 equiv of HCl in diethyl ether to give $[ArNH_3][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (**1a**) as an insoluble orange powder. $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (**1b**) can be prepared from **1a** by cation exchange. Addition of $ZnCl_2$ to **1b** yields $[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3]_2$ (**2a**), an X-ray study of which shows it to be a dimer in which each Re is a square pyramid with the neopentylidyne α-carbon atom in the apical position and a weakly bound bridging chloride ligand trans to it (space group $P2_1/c$, a = 9.953 (4) Å, b = 12.398 (9) Å, c = 19.720 (6) Å, β = 93.08 (3)°, V = 2430 (2) Å^3, Z = 4, ρ = 1.473 g/cm^3, R = 0.050, R_w = 0.084). Adducts of the type $Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(L)$ (L = THF, py) can be prepared from **2a**. Addition of DBU to $Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(py)$ in the presence of pyridine gives $Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(py)_2$ (**4a**). A more useful analogue, $Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(DME)$ (**4b**), can be prepared by adding $ZnCl_2$ to **1b** followed by NEt_3 in DME. Complexes of the type $Re(C\text{-}t\text{-}Bu)(NAr)(OR)_2$ (OR = O-*t*-Bu (**5a**), $OCMe_2(CF_3)$ (**5b**), O-2,6-C_6H_3-*i*-Pr_2 (**5c**), $OC(CF_3)_2Me$ (**5d**), or $OC(CF_3)_2H$ (as a diethyl ether adduct, **5e**)) can be prepared from **1b** or **4b**. Reactions of **5d** and **5e** with symmetric internal acetylenes give fluxional rhenacyclobutadiene complexes, $Re(NAr)(C_3R_3)[OC(CF_3)_2Me]_2$ and $Re(NAr)(C_3R_3)[OC(CF_3)_2H]_2$ for R = Et, *n*-Pr, *i*-Bu, and *i*-Pr. Crystals of $Re(NAr)(C_3Et_3)[OC(CF_3)_2Me]_2$ belong to the space group $P2_1/a$ with a = 19.553 (8) Å, b = 9.225 (4) Å, c = 20.246 (8) Å, β = 117.36 (3)°, V = 3243 (2) Å^3, Z = 4, ρ_{calcd} = 1.73 g/cm^3, μ = 40.70 cm^{-1}. The core structure is roughly a trigonal bipyramid containing axial carbon and oxygen atoms. The rhenacyclobutadiene ring is bent and asymmetric with Re–C_α bond lengths of 1.88 (1) and 2.09 (1) Å and C_α–C_β bond lengths of 1.33 (2) and 1.46 (1) Å. All but one of the rhenacycles have analogous structures (type 1) according to NMR studies and are stable toward loss of an acetylene or further reactions with an internal acetylene for hours at 25 °C. The exception is $Re(NAr)(C_3\text{-}i\text{-}Pr_3)[OC(CF_3)_2Me]_2$, a significantly different rhenacycle (type 2) that readily loses *i*-PrC≡C-*i*-Pr to give $Re(C\text{-}i\text{-}Pr)(NAr)[OC(CF_3)_2Me]_2$. It is proposed that rhenacycles of type 2 are the ones that are active for metathesis of internal acetylenes, that rhenacycles of type 2 form when an acetylene attacks a C/O/O face in $Re(CR')(NAr)(OR)_2$, and that inactive rhenacycles of type 1 form when an acetylene attacks a C/N/O face in $Re(CR')(NAr)(OR)_2$. Only acetylenes containing bulky groups are metathesized and only complexes that contain $OC(CF_3)_2Me$ ligands are active. The ultimate fate of Re(VII) metallacyclobutadiene complexes over a period of hours to days is reduction to yield Re(V) complexes.

Introduction

Metathesis of acetylenes by "d^0" molybdenum and tungsten alkylidyne complexes of the type $M(CR')(OR)_3$ (R′ is alkyl, R is alkyl, fluoroalkyl, or aryl)[1] and of olefins (mostly cyclic[2]) by tungsten[3] and molybdenum[4] alkylidene complexes of the type $M(CHR')(NAr)(OR)_2$ (Ar = 2,6-C_6H_3-*i*-Pr_2) has been established in the last few years. In contrast, although classical rhenium metathesis catalysts have been known for more than two decades,[5] all are heterogeneous and the oxidation state and coordination geometry of the metal are unknown. Several years ago we began to explore the organometallic chemistry of Re(VII) with the intent of preparing well-characterized metathesis catalysts.[6] More recently we have developed an entry into Re(VII) organometallic chemistry that employs 2,6-disubstituted arylimido ligands as protecting and stabilizing groups for the Re(VII) complexes[7] and are now in a position to explore in a systematic fashion the synthesis of Re(VII) alkylidyne and alkylidene complexes and their potential as catalysts for metathesis reactions. In a preliminary communication we reported several monoimido neopentylidyne complexes and the metathesis of internal acetylenes by one of the bisalkoxide derivatives.[8] Here we report the full version of these and related studies, including elucidation of the chemistry that limits the longevity of acetylene metathesis. We have found that acetylene metathesis is limited by formation of a relatively stable rhenacyclobutadiene complex, the one that we believed originally to be part of the catalytic cycle, and have been able to identify the type of metallacycle that is active for metathesis of internal acetylenes, but which is not observable under most circumstances.

Results

Preparation of Amido Neopentylidyne Complexes. $Re(NAr)_2(CH_2\text{-}t\text{-}Bu)Cl_2$ can be prepared in high yield in three steps from Re_2O_7 and can be dehydrohalogenated to give $Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$.[7] Addition of 3 equiv of HCl to $Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$ gives **1a** quantitatively as an insoluble orange powder (eq 1). A more tractable tetraethylammonium salt (**1b**) can be



(1)

1a

(1) (a) Schrock, R. R. *Acc. Chem. Res.* **1986**, *19*, 342. (b) Murdzek, J. S.; Schrock, R. R. In *Carbyne Complexes*; Verlag Chemie: Weinheim, New York, 1988.

(2) (a) Schrock, R. R. *Acc. Chem. Res.* **1990**, *24*, 158. (b) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C. *Polym. Commun.* **1989**, *30*, 258. (c) Swager, T. M.; Dougherty, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 2973. (d) Klavetter, F. L.; Grubbs, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 7807.

(3) (a) Feldman, J.; DePue, R. T.; Schaverien, C. J.; Davis, W. M.; Schrock, R. R. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; Kluwer Academic Publishers: Boston, 1989. (b) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.; Park, L.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (c) Schrock, R. R.; Krouse, S. A.; Knoll, K.; Feldman, J.; Murdzek, J. S.; Yang, D. C. *J. Mol. Catal.* **1988**, *46*, 243. (d) Schrock, R. R.; DePue, R.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (e) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 5384.

(4) (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373. (b) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(5) (a) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (b) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: New York, 1982; Vol. 8. (c) Dragutan, V.; Balaban, A. T.; Dimonie, M. *Olefin Metathesis and Ring-opening Polymerization of Cyclo-Olefins*, 2nd ed.; Wiley-Interscience: New York, 1985.

(6) Edwards, D. S.; Biondi, L. V.; Ziller, J. W.; Churchill, M. R.; Schrock, R. R. *Organometallics* **1983**, *2*, 1505.

(7) Horton, A. D.; Schrock, R. R. *Polyhedron* **1988**, *7*, 1841.

(8) Schrock, R. R.; Weinstock, I. A.; Horton, A. D.; Liu, A. H.; Schofield, M. H. *J. Am. Chem. Soc.* **1988**, *110*, 2686.

0002-7863/91/1513-135$02.50/0

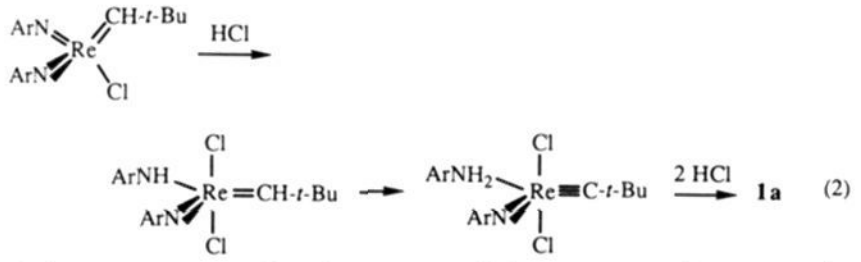
Table I. Selected Bond Distances (Å) and Angles (deg) in $[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3]_2$ (**2a**)

Re–Cl(1)	2.407 (3)	Re–Cl(2)	2.429 (3)	Re–N	1.901 (9)
Re–Cl(1)′	2.712 (3)	Re–Cl(3)	2.298 (4)	Re–C(1)	1.75 (1)

Cl(1)–Re–Cl(1)′	80.5 (1)	Cl(1)–Re–N	89.8 (3)
Cl(1)–Re–Cl(2)	80.0 (1)	Cl(1)–Re–C(1)	97.2 (6)
Cl(1)–Re–Cl(3)	158.9 (1)	Cl(1)′–Re–Cl(2)	87.1 (1)
Cl(3)–Re–N	101.5 (3)	Cl(1)′–Re–Cl(3)	83.0 (1)
Cl(3)–Re–C(1)	99.5 (6)	Cl(1)′–Re–N	83.5 (3)
N–Re–C(1)	95.2 (5)	Cl(1)–Re–C(1)	177.4 (6)
Re–Cl(1)–Re	99.5 (1)	Cl(2)–Re–Cl(3)	86.0 (1)
Re–N–C(12)	130.7 (8)	Cl(2)–Re–N	167.2
Re–C(1)–C(2)	165 (1)	Cl(2)–Re–C(1)	93.8 (4)

prepared by cation exchange. In the ^1H NMR spectrum of **1b** in CD_2Cl_2 the ArN*H* resonance is observed at 16.93 ppm and the neopentylidyne C_α resonance is found at 315.9 ppm. The cis structure shown for the anion in eq 1 is the most plausible one, since the π bonds in the neopentylidyne ligand and the likely dative π bond in the amido ligand thereby do not compete with one another. In theory two isomers would be possible, a syn isomer in which the Ar group points toward the neopentylidyne ligand, and an anti isomer in which the Ar group points away from the neopentylidyne ligand; only one isomer is observed.

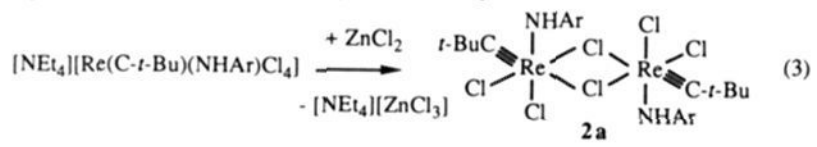
The process of converting $Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$ into **1a** is believed to be related to the reaction between $Re(N\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ and 3 equiv of HCl to give $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(NH_2\text{-}t\text{-}Bu)Cl_2]_2$,[6] the key feature in that case being initial protonation of the imido ligand followed by transfer of the neopentylidene α proton to an imido or amido nitrogen atom. One of several plausible sequences for forming **1a** is shown in eq 2.



(2)

It is not necessary that the neopentylidene proton migrates to the imido nitrogen atom intramolecularly. For example, further protonation of the amido ligand to give the aniline (perhaps in a cationic complex) followed by loss of H_α in the neopentylidene ligand to some extramolecular base is equally plausible.

Addition of $ZnCl_2$ to **1b** in methylene chloride yields red **2a** (eq 3). Proton NMR spectra of **2a** in CD_2Cl_2 suggest that it is in equilibrium with a closely related species (**2b**), but at a rate



(3)

slower than the NMR time scale. At 220 K in CD_2Cl_2 only resonances for **2a** are observed, while at room temperature both **2a** and **2b** are observed. Resonances for **2a** are broad; those for **2b** are sharp. A plausible scenario is that **2b** is a dimer that is relatively stable to cleavage while **2a** breaks up readily and rapidly at room temperature to form a dichloromethane adduct.[9] An example of what **2b** might be is a species with a different relative arrangement of metal cores at each end (e.g., cisoid alkylidyne ligands) or one in which the amido ligand is a different rotamer. Crystalline samples do not contain dichloromethane, according to elemental analysis.

An X-ray study of **2a** shows it to have the structure shown in eq 3 (Figure 1; important bond distances and angles can be found in Table I). Each rhenium is best described as a square pyramid with a neopentylidyne α-carbon atom in the apical position and a weakly bridging chloride ligand (Re–Cl(1)′ = 2.712 (3) Å) trans

(9) Newbound, T. D.; Colsman, M. R.; Miller, M. M.; Wulfsberg, G. P.; Anderson, O. P.; Strauss, S. H. *J. Am. Chem. Soc.* **1989**, *111*, 3762.

(10) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Reide, J. *Organometallics* **1990**, *9*, 1434.

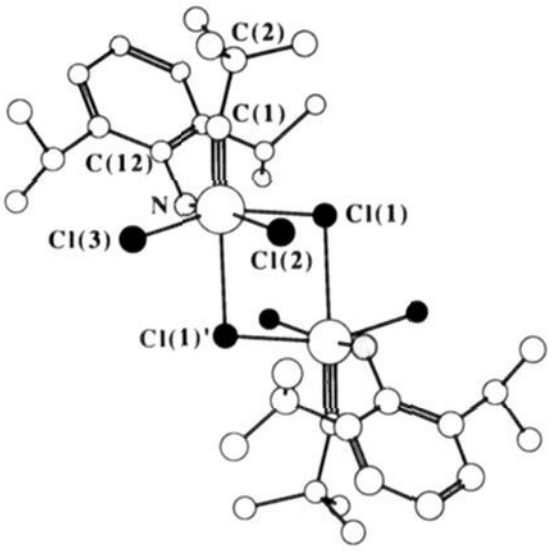


Figure 1. A view of the structure of $[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3]_2$ (**2a**).

to it. (The C(1)–Re–L_{basal} angles are all in the range 94–99° while the Cl(1)′–Re–L_{basal} angles are all in the range 80–87°.) The Re–C(1) distance is typical of M≡C bonds in high oxidation state alkylidyne complexes[1] and should be compared with Re≡C bond lengths of 1.742 (9) Å in $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(py)_2I_2$[6] and 1.755 (6) Å in $Re(\eta^5\text{-}C_5Me_5)(C\text{-}t\text{-}Bu)Br_3$.[10] The Re≡C(1)—C(2) angle (165 (1)°) should be compared to the Re≡C—C angles of 175° and 179° in the above two compounds (respectively). The phenyl ring of the amido ligand is tipped up toward C(1) (the "syn" conformation) and the *tert*-butyl group of the neopentylidyne ligand is tipped toward Cl(2). The relatively short Re–N bond (1.901 (9) Å) is consistent with a significant amount of Re–N π bonding. Since C(12) lies in the N/Re/C(1) plane N must be sp^2 hybridized and pseudo doubly bound to rhenium with the d_{xy} orbital in the basal plane.

Pyridine (**3a**) and THF (**3b**) adducts of $Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3$ can be prepared as shown in eqs 4 and 5. Resonances in the proton NMR spectrum of **3a** are broad, and addition of pyridine results

$$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4] \xrightarrow[\text{2. pyridine}]{\text{1. } ZnCl_2 \text{ in } CH_2Cl_2} Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(py) \quad (4)$$

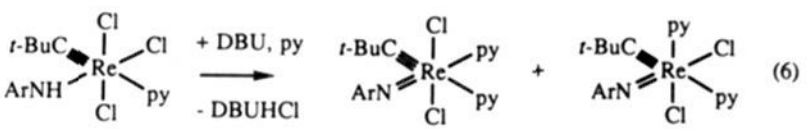
3a

$$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4] \xrightarrow[THF]{ZnCl_2} Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(THF) \quad (5)$$

3b

in an averaged pyridine resonance. Proton NMR spectra at 253 K are consistent with a structure having mer chloride ligands in which rotation about the N–C_{ipso} bond of the amido ligand is slow or a structure having fac chloride ligands in which rotation about the N–C_{ipso} bond is still rapid at 253 K. At low temperatures in CD_2Cl_2 two isomers of **3b** are observed in roughly a 1:1 ratio, and a trace of **2b** is observed. At room temperature the two isomers of **3b** interconvert readily, but they do not interconvert readily with **2b**. The isomers of **3b** probably are analogous to those proposed for **3a**.

Preparation of Imido Neopentylidyne Complexes. DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) reacts with $Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(py)$ in tetrahydrofuran at −40 °C in the presence of pyridine to give dark blue $Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(py)_2$ (**4a**; eq 6)



(6)

as a mixture of isomers in which added pyridine exchanges rapidly with coordinated pyridine. NMR spectra are consistent with the structures shown. In the minor isomer a pyridine could be trans to the imido ligand instead of the neopentylidyne ligand. Note that the electron count in $Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(py)_2$ is 18 if the electron pair on the imido ligand is *not* included.

Synthesis of a more versatile precursor to imido alkylidyne complexes, an analogue of $M(NAr)(CH\text{-}t\text{-}Bu)Cl_2(DME)$ (M =

Table II. Chemical Shifts (ppm) of C_α Resonances in Monoimido Neopentylidyne Complexes

$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (**1b**)	315.9[b]
$Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(dme)$ (**4b**)	312.1[a]
$Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(py)_2$ (**4a**)	318.7[a]
$Re(C\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (**5a**)	291.0[a]
$Re(C\text{-}t\text{-}Bu)(NAr)[OC(CF_3)Me_2]_2$ (**5b**)	297.5[a]
$Re(C\text{-}t\text{-}Bu)(NAr)(OAr)_2$ (**5c**)	304.4[b]
$Re(C\text{-}t\text{-}Bu)(NAr)[OC(CF_3)_2Me]_2$ (**5d**)	304.6[a]
$Re(C\text{-}t\text{-}Bu)(NAr)[OC(CF_3)_2H]_2(THF)$ (**5e**)	308.5[a]

[a] C_6D_6. [b] CD_2Cl_2.

Mo or W) complexes that have proven so useful for the preparation of complexes of the type $M(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$,[3,4] can be achieved as shown in eq 7. **4b** is soluble and stable in pentane, diethyl ether, methylene chloride, and toluene. It is very sensitive to water. Proton NMR studies show that added DME exchanges with coordinated DME. At 253 K NMR spectra are consistent with a molecule having the structure shown in eq 7. ($Mo(CH\text{-}t\text{-}Bu)(NAr)(triflate)_2(DME)$ has a structure in which DME is bound trans to the neopentylidene and imido ligands.[4b]) Note that the total electron count again is 18 if the imido electron pair is not counted.

$$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4] \xrightarrow[DME]{+\ ZnCl_2 -\ [NEt_4][ZnCl_3]} \text{"}Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(DME)\text{"} \xrightarrow[DME]{+\ NEt_3 -\ NEt_3HCl} \textbf{4b} \quad (7)$$

Bisalkoxide complexes can be prepared as shown in eq 8. Complexes **5a–d** also may be prepared from **4b**. Addition of 3 equiv of $LiOC(CF_3)_2H$ to **4b** at −40 °C in diethyl ether gave red crystalline $[Li(DME)]\{Re(C\text{-}t\text{-}Bu)(NAr)[OC(CF_3)_2H]_3\}$ instead of $Re(C\text{-}t\text{-}Bu)(NAr)[OC(CF_3)_2H]_2$. However, a THF derivative of this compound could be prepared by removing an alkoxide with zinc chloride as shown in eq 9.

$$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4] \xrightarrow[-NEt_4Cl\ -\ 3\ LiCl\ -\ ROH]{+\ 3\ LiOR\ in\ CH_2Cl_2} \textbf{5} \quad (8)$$

OR = O-*t*-Bu (**5a**), $OC(CF_3)Me_2$ (**5b**), O-2,6-C_6H_3-i-Pr_2 (DIPP) (**5c**), $OC(CF_3)_2Me$ (**5d**)

$$[Li(DME)]\{Re(C\text{-}t\text{-}Bu)(NAr)(OR)_3\} \xrightarrow[THF]{ZnCl_2} Re(C\text{-}t\text{-}Bu)(NAr)(OR)_2(THF)\ (\textbf{5e}) \quad (9)$$
$$OR = OC(CF_3)_2H$$

NMR spectra of neopentylidyne alkoxide complexes are straightforward. The chemical shift of the neopentylidyne α-carbon atom (Table II) correlates with the electron-withdrawing power of the alkoxide, although the entire range of chemical shifts is only ~20 ppm.

Reactions of Imido Neopentylidyne Complexes with Symmetrical Internal Acetylenes. Since $Re(C\text{-}t\text{-}Bu)(NAr)(OR)_2$ complexes are Re(VII) alkylidyne analogues of olefin metathesis catalysts of the type $W(CH\text{-}t\text{-}Bu)(NAr)(OR)_2$, one might expect them to react with acetylenes. Complexes containing O-*t*-Bu, DIPP, or $OC(CF_3)Me_2$ groups do not react with internal acetylenes at room temperature over a period of hours, but **5d** and **5e** do react to give rhenacyclobutadiene complexes. Examples are shown in eqs 10 and 11. 2,2-Dimethyl-3-hexyne must be lost rapidly from the

$$\textbf{5d} \xrightarrow[-\ t\text{-}BuC{\equiv}CEt]{+\ 2\ EtC{\equiv}CEt} \textbf{6a} \quad (10)$$
OR = $OC(CF_3)_2Me$; Et

$$\textbf{5e} \xrightarrow[-\ t\text{-}BuC{\equiv}CEt\ -\ THF]{+\ 2\ EtC{\equiv}CEt} \textbf{7a} \quad (11)$$
OR = $OC(CF_3)_2H$; Et

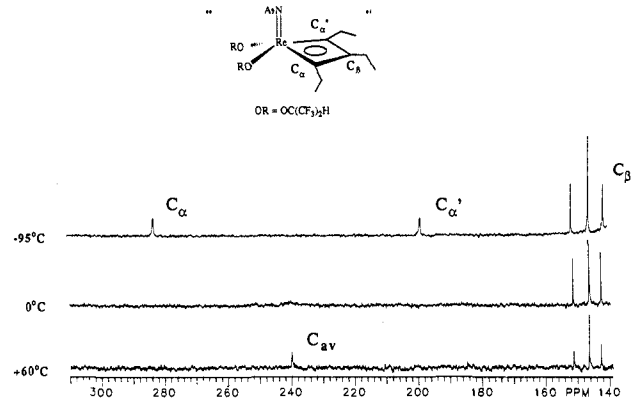


Figure 2. Variable-temperature ^{13}C NMR spectrum of $Re(NAr)(C_3\text{-}i\text{-}Pr_3)[OC(CF_3)_2H]_2$ (**7a**).

Table III. Chemical Shifts (ppm) of C_α, C_α', and C_β in Rhenacyclobutadiene Complexes[a]

compd	C_α	C_α'	C_β	T, K
$Re(NAr)(C_3Et_3)[OC(CF_3)_2Me]_2$ (**6a**)	277.9	199.7	141.9	293
$Re(NAr)(C_3\text{-}n\text{-}Pr_3)[OC(CF_3)_2Me]_2$ (**6b**)	276.6	199.5	142.0	193
$Re(NAr)(C_3\text{-}i\text{-}Bu_3)[OC(CF_3)_2Me]_2$ (**6c**)	282.1	201.7	150.0	203
$Re(NAr)(C_3\text{-}i\text{-}Pr_3)[OC(CF_3)_2Me]_2$ (**6d**)	257.5	255.7	107	187
$Re(NAr)[C(t\text{-}Bu)CHC(i\text{-}Bu)][OC(CF_3)_2H]_2$ (**7e**)	288.0	204.6	120.4	295
$Re(NAr)(C_3Et_3)[OC(CF_3)_2H]_2$ (**7a**)	282.6	198.1	141	183
$Re(NAr)(C_3\text{-}i\text{-}Pr_3)[OC(CF_3)_2H]_2$ (**7d**)	287.4	194.7	140.6	193

[a] Solvent = toluene-d_8. ^{13}C NMR studies of $Re(NAr)(C_3\text{-}n\text{-}Pr_3)[OC(CF_3)_2H]_2$ (**7b**; observed in situ) were not completed. The spectrum of $Re(NAr)(C_3\text{-}i\text{-}Bu_3)[OC(CF_3)_2H]_2$ (**7c**) was still broad at 273 K.

Table IV. Selected Bond Distances (Å) and Angles (deg) in $Re(NAr)(C_3Et_3)[OC(CF_3)_2Me]_2$ (**6a**)

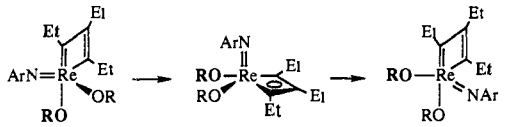
Re–C(41)	1.88 (1)	Re–O(3)	1.958 (7)
Re–C(43)	2.09 (1)	C(41)–C(42)	1.46 (1)
Re–N	1.72 (1)	C(42)–C(43)	1.33 (2)
Re–O(2)	2.034 (7)		
O(2)–Re–N	109.6 (4)	O(2)–Re–C(41)	141.8 (4)
O(3)–Re–N	119.1 (4)	O(2)–Re–O(3)	83.2 (3)
N–Re–C(43)	119.8 (4)	O(3)–Re–C(41)	105.5 (4)
N–Re–C(41)	98.6 (4)	C(43)–Re–C(41)	65.3 (4)
Re–N–C(11)	173.1 (8)	C941)–C(411)–C(412)	115 (1)
C(43)–Re–O(3)	121.1 (4)		

initially formed α-*tert*-butyl-substituted metallacycles in each case since 1 equiv of 3-hexyne consumes only 0.5 equiv of **5d** or **5e**. Although **6a** decomposes slowly in solution, **7a** is unchanged after 24 h. Variable-temperature NMR studies show that in the static structures for **6a** and **7a** (Figure 2) the α-carbon resonances are significantly different (Table III). Typically only a single broad α-carbon resonance is observed near room temperature. The primary difference between the low-temperature NMR behavior of **6a** and **7a** is that slightly lower temperatures are required to freeze out the structure of **7a**.

An X-ray study showed that **6a** (Figure 3) can be described roughly as a trigonal bipyramid in which N, O(3), and C(43) are located in equatorial positions with N–Re–O(3), N–Re–C(43), and C(43)–Re–O(3) angles of 119.1 (4)°, 119.8 (4)°, and 121.1 (4)°, respectively. (Important bond distances and angles can be found in Table IV.) The large O(2)–Re–C(41) angle (141.8 (4)°) suggests that a square-pyramidal description (with N at the apex) also may be appropriate, but we shall discuss the structure as a TBP. The ReC_3 ring is bent (the dihedral angle between the C(41)/Re/C(43) and C(41)/C(42)/C(43) planes is 34°) and unsymmetrically bound between "axial" (C(41)) and "equatorial" (C(43)) positions. The two Re–C_α bond lengths (Re–C(41) = 1.88 (1) Å; Re–C(43) = 2.09 Å) differ by an amount well beyond 3σ, as do the C_α–C_β bond lengths (C(42)–C(43) = 1.33 (2) Å; C(41)–C(42) = 1.46 (1) Å), i.e., the double bonds in the ReC_3

ring are localized as shown. These values should be compared with those for a bent ring in a tungstacyclobutadiene complex (W–C_α = 1.943 (5) and 2.132 (5) Å, C_α–C_β = 1.382 (8) and 1.4485 (7) Å, dihedral angle = 58°).[11] The short Re–C_α bond distance (Re–C(41) = 1.88 (1) Å) is almost identical with that of the formal rhenium–carbon double bond in Re(C-*t*-Bu)(CH-*t*-Bu)I_2(py) (Re–C_α = 1.873 (9) Å).[6] The imido ligand is almost linear (Re–N(1)–C(11) = 173.1 (8)°) and the Re–N bond distance (1.72 (1) Å) is relatively short. The large (~80 ppm) difference in chemical shift between C_α and C_α' in the low-temperature ^{13}C NMR spectrum of **6a** is consistent with the different bond orders for the two rhenium–carbon bonds, the lower field resonance presumably being that associated with the axial carbon that is formally doubly bound to Re. This type of rhenacycle will be called type 1.

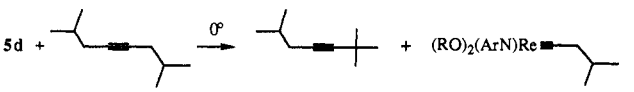
Interconversion of C_α and C_α' (and the two alkoxide ligands) in rhenacycles of type 1 can be explained by a pseudorotation about the equatorial nitrogen atom as shown in eq 12. If the intermediate symmetrical square pyramid does not build up to any significant concentration, then the chemical shift for C_β should change little during equilibration of C_{axial} and $C_{equatorial}$, consistent with what is observed.



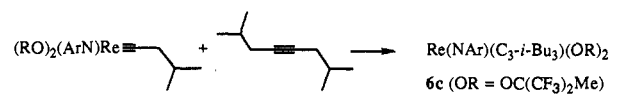
(12)

Reactions of **5d** and **5e** with 2.5 equiv of 4-octyne proceed analogously to give fluxional type 1 rhenacycles, Re(NAr)(C_3Pr_3)[$OC(CF_3)_2Me$]$_2$ (**6b**) and Re(NAr)(C_3Pr_3)[$OC(CF_3)_2H$]$_2$ (**7b**).

2,7-Dimethyl-4-octyne slowly reacts with **5d** in toluene-d_8 at 0 °C as shown in eq 13 (OR = $OC(CF_3)_2Me$). After the mixture is warmed to room temperature, the isopentylidyne complex reacts further to give **6c** (eq 14), a type 1 rhenacycle (Table III). No



(13)



(14)

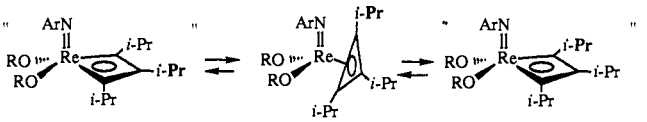
Re(C-*i*-Bu)(NAr)[$OC(CF_3)_2Me$]$_2$ is observed when **6c** is dissolved in C_6D_6 at room temperature, and when 1 equiv of 3-hexyne is added to **6c**, no new rhenacycle or alkylidyne resonances are observed after several hours at room temperature. A feature of the reaction to give **6c** that is different from reactions described so far is that a dark green crystalline product is also formed. It will be described later.

An analogous reaction between **5e** and 3 equiv of 2,7-dimethyl-4-octyne gave Re(NAr)(C_3-*i*-Bu_3)[$OC(CF_3)_2H$]$_2$ (**7c**) as large dark purple crystals in high yield. (No green decomposition product was observed.) The room temperature proton and carbon NMR spectra of this complex are similar to those of **6c** (δC_α = 238 ppm, δC_β = 145.6 ppm), characteristic of a type 1 rhenacycle, but the low-temperature limit could not be reached at 173 K.

Addition of 2.5 equiv of 2,5-dimethyl-3-hexyne to **5e** yields dark red **7d** (eq 15), a type 1 rhenacycle. Above room temperature

$$\text{Re(C-}t\text{-Bu)(NAr)[OC(CF}_3)_2\text{H]}_2\text{(THF)} \xrightarrow[-t\text{-BuC}\equiv\text{C-}i\text{-Pr}]{+2\ i\text{-PrC}\equiv\text{C-}i\text{-Pr}} \xrightarrow[-\text{THF}]{} \underset{\mathbf{7d}}{\text{Re(NAr)(C}_3\text{-}i\text{-Pr}_3\text{)[OC(CF}_3)_2\text{H]}_2} \quad (15)$$

proton and carbon resonances associated with $C_\alpha CHMe_2$ and $C_\beta CHMe_2$ in **7d** broaden significantly, in contrast to the sharp spectrum for **7a** at high temperature. After a sample of **7d** containing 3 equiv of 3-hexyne had been heated for 1 h at 70 °C in toluene-d_8, no new resonances were observed in a subsequent spectrum at 25 °C, consistent with the stability of type 1 rhenacycles. When the resonance for $C_\beta CHMe_2$ at 2.26 ppm in a room temperature sample of **7d** was irradiated, the intensity of the $C_\alpha CHMe_2$ resonance at 4.27 ppm decreased; at +60 °C in a similar experiment the $C_\alpha CHMe_2$ septet disappeared completely. We conclude that the three carbon atoms of the ReC_3 ring of **7d** exchange *without* loss of acetylene. A rhenacyclopropenyl intermediate (eq 16; a symmetric rhenacycle is shown for simplicity) is a good possibility since such species have been observed and structurally characterized in d^0 tungsten systems.[11,12]



(16)

The isopropyl system containing the more bulky $OC(CF_3)_2Me$ ligand is strikingly different from any discussed so far. Addition of 2 equiv of 2,5-dimethyl-3-hexyne to **5d** yields the equilibrium mixture shown in eq 17. At room temperature, *no metallacyclic species are observed.* At 298 K in C_6D_6, K_{eq} for the equilibrium shown in eq 17 is 4.0 ± 0.5. If a large excess of 2,5-dimethyl-3-hexyne is added, Re(C-*i*-Pr)(NAr)[$OC(CF_3)_2Me$]$_2$ can be isolated. If a pentane solution containing **5d** and 5 equiv of 2,5-dimethyl-3-hexyne is cooled to −40 °C overnight, red-orange

$$\text{Re(C-}t\text{-Bu)(NAr)[OC(CF}_3)_2\text{Me]}_2 \underset{+\ t\text{-BuC}\equiv\text{C-}i\text{-Pr}}{\overset{+\ i\text{-PrC}\equiv\text{C-}i\text{-Pr}}{\rightleftharpoons}} \text{Re(C-}i\text{-Pr)(NAr)[OC(CF}_3)_2\text{Me]}_2 \quad (17)$$

crystals are obtained and may be isolated at low temperature. However, at room temperature an approximately one-to-one mixture of Re(C-*i*-Pr)(NAr)[$OC(CF_3)_2Me$]$_2$ and 2,5-dimethyl-3-hexyne is observed by proton NMR. Upon cooling this solution resonances appear that can be assigned to a rhenacyclobutadiene complex, Re(NAr)(C_3-*i*-Pr_3)[$OC(CF_3)_2Me$]$_2$ (**6d**; Table III). Upon returning to room temperature, only the one-to-one mixture of Re(C-*i*-Pr)(NAr)[$OC(CF_3)_2Me$]$_2$ and 2,5-dimethyl-3-hexyne is observed. At 228 K, the ^{13}C NMR spectrum of **6d** shows an averaged resonance for C_α and C_α' at 256 ppm and a signal assigned to C_β at 107.1 ppm, a rather different chemical shift for C_β than in other metallacycles mentioned so far. At 187 K two C_α and C_α' resonances can be observed, but their chemical shifts are very nearly the same (257.5 and 255.7 ppm). On this basis we propose that **6d** is not a type 1 metallacycle but one that contains an almost symmetric ring in which the electronic environments of C_α and C_α' are nearly identical. The fact that this metallacycle forms and breaks up relatively rapidly also contrasts strongly with observations concerning metallacycles of type 1, which do not break up readily. We shall call **6d** a rhenacyclobutadiene complex of type 2.

A preliminary X-ray study of **6d** suggests that it is a trigonal bipyramid in which the ring and the imido ligand are located in the equatorial plane. Although the study is incomplete owing to difficulties arising from possible disorder in the peripheral fluorine atoms and the fact that the molecule is in an acentric space group, the core has been identified unambiguously. This molecule is structurally analogous to W(C_3Et_3)[O-2,6-C_6H_3-*i*-Pr_2]$_3$[13] and W(C_3Et_3)[$OCH(CF_3)_2$]$_3$.[14] Interestingly, the equatorial alkoxide in the tungsten complexes is displaced to one side by a small angle

(11) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046.

(12) (a) Churchill, M. R.; Ziller, J. W.; Pedersen, S. F.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1984**, 485. (b) Churchill, M. R.; Fettinger, J. C.; McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3356.

(13) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554.

(14) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563.

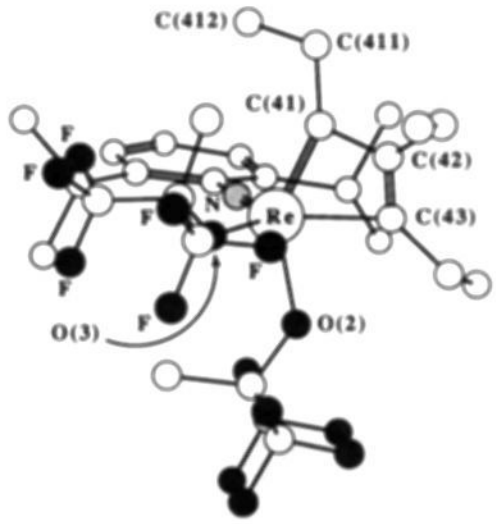
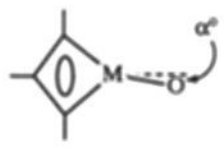


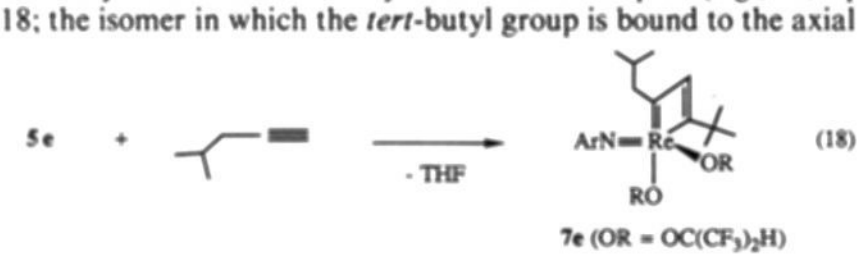
Figure 3. A view of the structure of $Re(NAr)(C_3Et_3)[OC(CF_3)_2Me]_2$ (**6a**).

α (see below), even though the C_3R_3 rings are symmetric within experimental error in the solid state and on the NMR time scale



at low temperatures. If the imido ligand in **6d** more rigidly enforces a slight asymmetry in an essentially symmetric ring at low temperatures, then the C_α's would be slightly different, as observed.

Whereas **5d** reacts with 4-methyl-1-pentyne to give a complex mixture of decomposition products, **5e** reacts with slightly more than 1 equiv of 4-methyl-1-pentyne to give an observable α-*tert*-butyl-substituted rhenacyclobutadiene complex (e.g., **7e**, eq 18; the isomer in which the *tert*-butyl group is bound to the axial

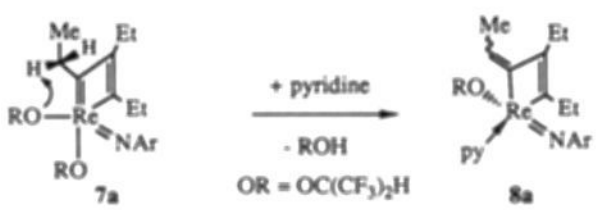


(18)

carbon atom would be indistinguishable.) Although **7e** could not be separated from unreacted **5e**, its NMR spectra leave little room for doubt that it is a metallacycle of type 1. Unlike the rhenacyclobutadiene complexes of type 1 that have been described so far, **7e** is not fluxional at room temperature. This fact probably can be ascribed to the significantly different steric properties of the ring substituents. Repulsion between the *tert*-butyl and isobutyl groups presumably is why an α,α'-disubstituted rhenacycle is formed rather than an α,β-disubstituted rhenacycle. α,α'-Disubstitution in tungsten and molybdacyclobutadiene complexes is also preferred.[1]

In summary we find that rhenacyclobutadiene complexes of type 1 (Figure 3) ultimately form in reactions between acetylenes and alkylidyne complexes in which OR = $OC(CF_3)_2Me$ or $OC(CF_3)_2H$, but they do *not* lose an acetylene readily. In contrast $Re(NAr)(C_3\text{-}i\text{-}Pr_3)[OC(CF_3)_2Me]_2$ (**6d**), a trigonal-bipyramidal rhenacyclobutadiene complex containing an equatorial ring system and imido ligand ("type 2"), readily loses diisopropylacetylene to give $Re(C\text{-}i\text{-}Pr)(NAr)[OC(CF_3)_2Me]_2$. These findings are of fundamental importance to understanding the results concerning acetylene metathesis to be presented later.

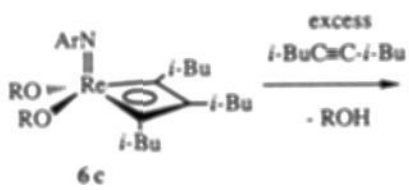
Formation of Reduced Rhenacyclobutene and Related Complexes. The reaction between **7a** and 1.5 equiv of pyridine yields yellow-green **8a** (eq 19). Several structures for unsymmetrical



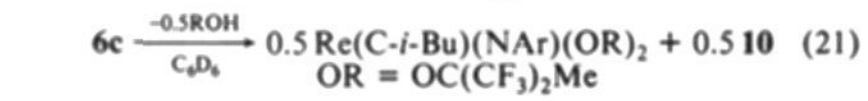
(19)

8a can be imagined on the basis of NMR data, the most significant features of which are a quartet integrating as one proton at 6.27 ppm and a doublet integrating as three protons at 2.05 ppm that we assign to a vinylic proton and methyl group coupled to it, respectively. (The vinylic C–H stretch is observed by IR at 3078 cm^{-1}.) The ^{13}C NMR spectrum contains singlet resonances at 163.6 and 160.9 ppm that we assign to C_α and C_α' (both sp^2 hybridized and singly bound to rhenium(V)) and a doublet (J_{CH} = 149 Hz) at 115.3 ppm that we assign to the vinylic carbon atom of the exocyclic propenyl group. Only one geometry about the double bond of the propenyl group is observed. Bound pyridine in **8a** exchanges rapidly with added pyridine. An analogous complex (**8b**) can be obtained by treating **7c** with pyridine. Addition of pyridine to **7d** results in loss of hexafluoroisopropyl alcohol and conversion to a reduced rhenacyclobutene complex containing an exocyclic isopropenyl group, but this product could not be isolated. Similar reactions of **6a** and **6c** give respectively **9a** and **9b** (OR = $OC(CF_3)_2Me$) that probably are closely analogous to **8a** and **8b**, according to proton NMR spectra, but they also could not be isolated cleanly.

Let us now return to the dark green material recovered in a large-scale synthesis of **6c**. Three hours after adding 10 equiv of 2,7-dimethyl-4-octyne to a pentane solution of Re(C-*t*-Bu)(NAr)$[OC(CF_3)_2Me]_2$ (**5d**), the pentane was removed in vacuo, and the remaining solution, now in neat alkyne, was cooled overnight to −40 °C to give 0.27 g of dark red microcrystalline **6c**. Removal of the remaining alkyne in vacuo and recrystallization of the resultant solid from cold pentane gave 0.73 g of dark green **10**. Proton NMR spectra of **10** are complex, but it is clear that two isomers are present in a ratio of ~3:1. Each isomer contains a doublet resonance assignable to a vinylic proton (at 5.60 and 4.12 ppm, J_{HH} = ~12 Hz). A vinylic C–H stretch is observed by IR at 3080 cm^{-1}. Although the ^{13}C NMR spectrum is also complex, low-field resonances associated with metal–carbon multiple bonds are absent, and two vinylic carbon resonances (106.1 and 94.0 ppm, J_{CH} = 151 Hz) are observed. We propose that **10** is a rhenacyclobutene complex analogous to **8a** and **8b**, one that contains a bound acetylene in place of pyridine (eq 20; OR = $OC(CF_3)_2Me$). A weak IR absorption observed at 1730 cm^{-1} can be assigned to the carbon–carbon bond of the coordinated alkyne. The two isomers may arise from *E* and *Z* configurations about the exocyclic carbon–carbon double bond. **10** was also observed when **6c** (50 mg in 0.5 mL of C_6D_6) was allowed to decompose over a 4-day period (eq 21).

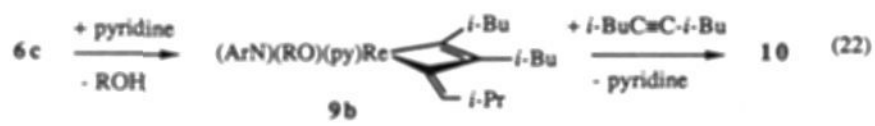


(20)



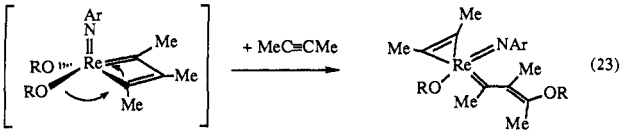
(21)

Additional evidence for the proposed structure of **10** is shown in eq 22 (OR = $OC(CF_3)_2Me$). In this case predominantly *one* isomer (~90%) of **10** was formed. The main point is that over a period of *days* one ultimate fate of a rhenacyclobutadiene complex of type 1 is reduction to Re(V) by loss of ROH.



(22)

5d reacts with 3 equiv of 2-butyne to give orange crystalline **11** (eq 23). The proposed mechanism is initial metathesis to give 4,4-dimethyl-2-pentyne (confirmed by proton NMR) followed by reaction of two more equivalents of 2-butyne with incipient Re(CMe)(NAr)$[OC(CF_3)_2Me]_2$. The most distinctive features of the carbon NMR spectrum of **11** are a resonance at 259.9 ppm, characteristic of a carbon atom multiply bound to rhenium, and



(23)

11

at 233 K two sharp singlets at 184.0 and 167.0 ppm ascribable to the acetylenic carbon atoms of coordinated 2-butyne. As the temperature is raised the resonances assigned to coordinated 2-butyne coalesce. (No exchange with added 2-butyne is observed by NMR.) A crystal structure that could not be refined completely showed that the alkoxide had added to C_α of a rhenacyclobutadiene ring as shown. The IR spectra of **11** contains a weak to medium strength absorption at 1723 cm^{-1}, and a strong absorption at 1625 cm^{-1}, consistent with C≡C and C=C stretching modes. We speculate that when ReC_α in a rhenacyclobutadiene complex is sterically accessible, then addition of OR to it is a viable alternative to removal of a β proton in an α substitutent on the rhenacyclobutadiene ring. This is another way in which rhenium can be reduced in the presence of acetylenes over the long term and be rendered inactive.

Metathesis of Unsymmetrical Internal Acetylenes by 5d. 3-Heptyne, 4-nonyne, and 5-undecyne (20 equiv each) initially are metathesized rapidly by **5d**. However, activity stops within 5 min (Figure 4). Metathesis of 40, 60, 80, and 100 equiv of 5-undecyne at approximately equal concentrations of **5d** becomes less and less efficient as shown in Figure 5. In all cases the expected primary metathesis products are observed in a ratio of ~1:1 and type 1 rhenacyclobutadiene complexes were the only identifiable organometallic species present. No new rhenacyclobutadiene complexes were observed.

All data now suggest that rhenacyclobutadiene complexes of type 1 are formed under metathesis conditions, but we can now say that contrary to what was proposed initially,[8] metathesis activity *ceases* when all of the rhenium is in the form of a rhenacycle of type 1. Rhenacyclobutadiene complexes of type 1 cannot be the active intermediates in rapid acetylene metathesis. It also should be noted that rhenacyclobutadiene complexes of type 1 also form from **5e**, but they form so rapidly that little if any catalytic activity is observed.

Since we have found that rhenacycles of type 1 do not form when OR = $OC(CF_3)_2Me$ and the substituent on the alkyne is isopropyl, metathesis of alkynes with substituents as large or larger than isopropyl should be possible (unless the substituent becomes entirely too large, e.g., *tert*-butyl). Indeed **5d** will catalyze the cometathesis shown in eq 24 in 2 h starting with 100 equiv of each

$$i\text{-PrC}{\equiv}\text{C-}i\text{-Pr} + sec\text{-BuC}{\equiv}\text{C-}sec\text{-Bu} \rightleftarrows 2\,i\text{-PrC}{\equiv}\text{C-}sec\text{-Bu} \quad (24)$$

of the symmetric alkynes.[15] This result contrasts strongly with the fact that 100 equiv of 5-undecyne is only partially metathesized after 1 h (with no change thereafter). The reaction mixture shown in eq 24 is inactive after 12 h, presumably because of reductive deactivation processes analogous to those mentioned above, or possibly because the catalyst is destroyed eventually by small amounts of impurities. In a reaction between **5d** and 3 equiv of *sec*-BuC≡C-*sec*-Bu in C_6D_6 the expected Re≡C-*sec*-Bu complex is observed, although the reaction is markedly slower than that between **5d** and *i*-PrC≡C-*i*-Pr for steric reasons. We conclude that a type 2 metallacycle is active for metathesis, and that even in circumstances where that type is not observable, it is responsible for any observed metathetical activity.

Discussion

A characteristic of rhenium(VII) organometallic chemistry that is beginning to stand out is the apparent ease with which rhenium–carbon triple bonds can form at the expense of rhenium–nitrogen multiple bonds. This is opposite to what has been observed in high oxidation state tungsten and molybdenum chemistry

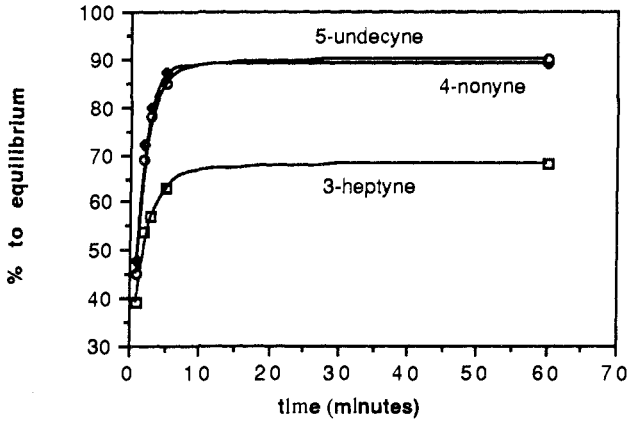


Figure 4. Metathesis of three alkynes by 10.1 mM solutions of **5d** in pentane at 25 °C.

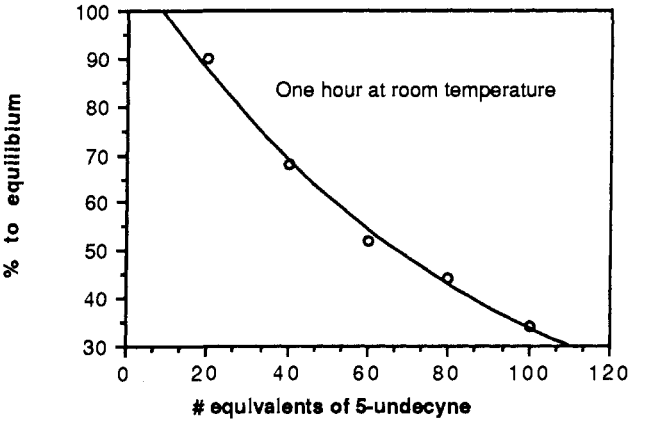


Figure 5. Metathesis of 5-undecyne by 10.1 mM solutions of **5d** in pentane at 25 °C after 1 h.

where imido alkylidene complexes are formed upon migration of a proton from nitrogen (in an amido ligand) to carbon (in an alkylidyne ligand).[3,4] One plausible explanation of the apparent preference for Re–carbon triple bonds is that as the oxidation state of the metal increases, the metal is best stabilized by a less electronegative carbon atom (versus nitrogen) that is bound through a covalent triple bond (versus a pseudo triple bond between an imido nitrogen atom and the metal at best). Another example of migration of protons from carbon to nitrogen in Re(VII) chemistry is formation of rhenium neopentylidene/neopentylidyne complexes by protonation of $Re(NAr)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$.[16]

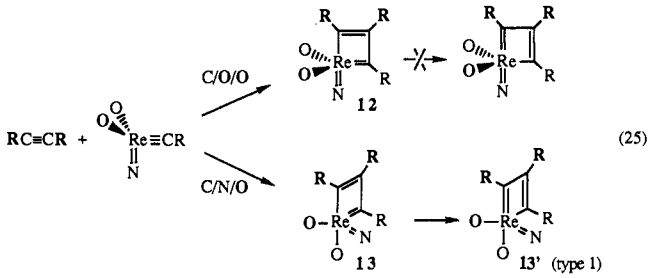
The mechanism of metathesis of acetylenes observed here (alkylidyne → rhenacyclobutadiene → alkylidyne') is analogous to the most common mechanism of acetylene metathesis by tungsten alkylidyne complexes[1] and firmly establishes Re(VII) as a viable oxidation state in metathetical reactions. (Another mechanism has been observed that consists of addition of an acetylene to a metallacyclobutadiene complex to give (e.g.) a "metallabenzene" from which acetylene is lost to give the metallacyclobutadiene complex back again.[13]) The observations of what can be called reductive processes (Re(VII) → Re(V)) in the long run is not surprising, since high oxidation state rhenium should be at least as susceptible to reduction as tungsten or molybdenum complexes in analogous oxidation states. Even Mo and W complexes undergo a variety of reactions that could be considered reductive processes (e.g., loss of ROH to form "deprotiometallacylces" and formation of cyclopropenyl or cyclopentadienyl complexes).[1] Finding the appropriate "ancillary" ligands that will sustain the high oxidation state and also promote acetylene metathesis has been the challenge for all three metals. Fortunately alkoxides have the appropriate electronic and steric characteristics, and since a wide variety of alkoxides is available,

(15) We thank Dr. W. E. Crowe for this suggestion.

(16) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448.

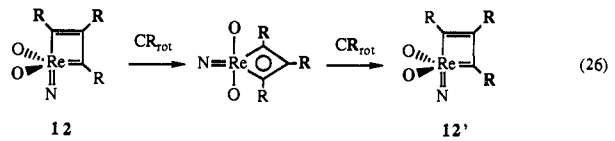
each system can be finely tuned.

The main subject on which we want to focus is the details of forming and rearranging rhenacyclobutadiene intermediates, in particular rhenacycles of types 1 and 2. Let us propose that an acetylene approaches the metal in the sterically most sensible way, i.e., on a face of pseudo-tetrahedral Re(C-*t*-Bu)(NAr)$(OR)_2$, and that the rhenacycle that forms first is approximately a trigonal bipyramid in which one of the entering carbon atoms is in an axial position. Addition of an acetylene to the N/O/**O** face would not lead to a rhenacycle, so only addition to one of the two C/N/O faces or addition to the C/O/**O** face need to be considered (eq 25; alkoxide and imido substituents are omitted for simplicity).



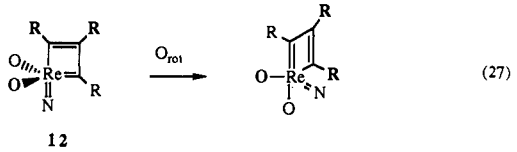
(25)

In rhenacycle **12**, formed by addition of the acetylene to a C/O/**O** face, the equatorial Re=C π bond is virtually independent of the axial Re=N bond. It also should be noted that **12** is likely to remain in this particular localized form, since otherwise the $Re{=}C_{axial}$ bond would compete with the Re=N bond, as shown in the extreme alternative localized form in eq 25. But **RC≡CR** cannot be lost directly from **12**, since that would be a higher energy pathway than that by which it was formed. Therefore **12** must rearrange to an analogous TBP molecule that contains CR in the axial position. That can be accomplished by a pseudorotation about equatorial CR first, followed by pseudorotation about C**R** in the new TBP species (eq 26). RC≡C**R** then can be lost from **12'** and Re(C**R**)(NAr)$(OR)_2$ formed. Note that pseudorotation about equatorial N in the TBP intermediate shown in eq 26 is not possible since C_α and C_α' cannot both be in axial positions



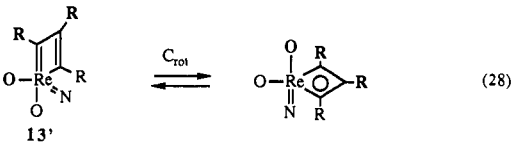
(26)

in a TBP species. Note also that this intermediate is analogous to that implicated for **6d** and other type 2 metallacycles that are active for metathesis. The only possible result of pseudorotation about CR in **12** is formation of **12'**. The only other pseudorotation that is possible in **12** (about O) would lead to a type 1 rhenacycle (eq 27).



(27)

Acetylene attack on the C/N/**O** face of the catalyst yields **13** (eq 25), a species that should tautomerize to give a type 1 rhemacycle (**13'**). Pseudorotation about N in **13'** is degenerate; it is the process proposed for equilibration of C_α and C_α' in type 1 rhenacycles (eq 12). Pseudorotation about equatorial C in **13'** leads to another possible TBP rhenacycle having the ring bound in equatorial positions (eq 28). The only possible fate of this TBP rhenacycle is to revert to **13'**. Therefore attack on the C/N/O face should lead irreversibly to type 1 rhenacycles.



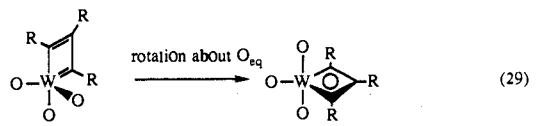
(28)

There are two logical explanations of the metathesis results that we have observed here. One is that the lowest energy pathway is acetylene attack on the C/N/O face (or C/N/**O** face) of the catalyst to form a type 1 rhenacycle. When the coordination sphere is especially crowded (large OR or a large substituent in the acetylene or adlkylidyne ligand) the acetylene is forced to add to what must be a less sterically crowded C/O/**O** face and be metathesized as a consequence of the pseudorotations shown in eq 26. In the most extreme cases (involving diisopropylacetylene or di-*sec*-butylacetylene) the initial and all subsequent rhenacycles can only form by attack of an acetylene on the C/O/**O** face. A type 1 rhenacycle must not form under these circumstances for steric reasons and metathesis therefore is relatively long-lived. In other circumstances (smaller acetylene substituents) metathesis is not long-lived because of competing attack by the acetylene on the C/N/O face. Only stoichiometric metathesis is observed in the case of $OC(CF_3)_2H$ complexes for steric reasons; the relatively small alkoxide in combination with a relatively small alkylidyne ligand (compared to neopentylidyne) makes attack on the C/N/O face greatly favored. One could argue that the C/O/O face is less crowded than the C/N/O face since the diisopropylphenylimido ligand sweeps out a greater volume than in alkoxide ligand and the Re=N bond is significantly shorter than the Re–O bond.

The second possible explanation is that attack on the C/O/**O** face is preferred, but the usual next step is pseudorotation about O in **12** to give the inactive rhenacycle (eq 27). However, if this "competitive pseudorotation" explanation is correct, it is not clear why pseudorotation about C (eq 26) becomes the exclusive course of the reaction in the most crowded circumstances. Therefore we prefer the "competitive face attack" proposal presented immediately above to the "competitive pseudorotation" proposal.

Another reason for favoring the "competitive face attack" proposal is that it makes the most sense from an orbital perspective. A derivation of the frontier orbitals in a bent (ArN)Re(CR) fragment is analogous to that for a bent metallocene if one assumes that the imido ligand forms 2π bonds and a 1σ bond,[17,15] i.e., "bent" (ArN)Re(CR) is isoelectronic and isolobal with bent CpZrCp. Therefore the LUMO in Re(CR)(NAr)$(OR')_2$ complexes is likely to be an a-type orbital that lies in the ReO_2 plane, i.e., perpendicular to the C–Re–N plane and pointing approximately toward each C/N/O face in the tetrahedron. A more qualitative explanation is that the acetylene attacks the face opposite the ligand with the weakest trans effect; oxygen is the most electronegative atom bound to the metal (a weaker σ donor) and an alkoxide is the poorest π-bonding ligand.

Let us come back briefly to acetylene metathesis reactions involving complexes of the type M(CR')$(OR)_3$ (M = Mo or W)[1] in order to point out that there is only one way to form a tungstacyclobutadiene ring (by acetylene attack on one of the three C/O/O faces) and that the TBP species shown in eq 29 (alkoxide



(29)

substituents omitted) is the tungstacycle that is observed and that loses an acetylene to reform an alkylidyne complex. This tungsten system contrasts strongly with that reported here where the electronically and sterically preferred face for acetylene attack leads to a rhenacycle that does not lose an acetylene readily. The importance of symmetric coordination spheres (as in the Mo and W systems) as a means of limiting metallacyclobutadiene intermediates to one type only now can be fully appreciated.

The results found here should be compared with those concerning metathesis of olefins by complexes of the type Mo(CHR')(NAr)$(OR)_2$ (M = Mo, W). Olefin attack on the C/N/O face in M(CHR')(NAr)$(OR)_2$ complexes is also believed to be

(17) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley: New York, 1985.

the most likely,[3b,4b] and adducts containing a phosphine or amine ligand have been shown to have TBP structures that result from attack by the donor on the C/N/O face (axial base).[18] There is also much evidence that the unobservable initial TBP metallacyclobutane complex containing an axial/equatorial ring system must rearrange in order to lose an olefin.[3b,4b,19] But an obvious and important difference is that metallacyclobutane rings probably cannot distort to the extent that metallacyclobutadiene rings can without actually breaking up to give olefin plus alkylidene. Therefore metallacyclobutane complexes cannot be stabilized toward loss of olefin by asymmetry in the metallacyclobutane ring. Relatively stable metallacyclobutane complexes *have* been observed, but the MC_3 ring in these square-pyramidal species is symmetric. The current theory is that the square-pyramidal species are relatively stable because they are further from the TBP transition state necessary for loss of olefin from the metal than are the TBP metallacycles having the ring bound in equatorial positions.[19]

Experimental Section

General Procedures. All experiments were performed in a nitrogen-filled drybox or by using standard Schlenk techniques. Reagent grade diethyl ether, tetrahydrofuran, and toluene were distilled from sodium benzophenone kety under nitrogen. Pentane was washed with 5% nitric acid in sulfuric acid, stored over calcium chloride, and then distilled from sodium benzophenone ketyl under nitrogen. Dichloromethane was distilled from calcium hydride under nitrogen. All deuterated NMR solvents were passed through a column of activated alumina or stored over molecular sieves.

$Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$ was prepared as reported in the literature.[7] 2,5-Dimethyl-3-hexyne and 3,6-dimethyl-4-octyne were prepared by the method reported by Nicholas.[20] 2,7-Dimethyl-4-octyne was prepared by reaction of 4-methyl-1-pentynyllithium with 1-trifluoromethanesulfonato-2-methylpropane as adapted from Brandsma.[21] (CAUTION! Neat trifluoromethanesulfonato-2-methylpropane (isobutyl triflate) should be diluted with diethyl ether immediately and stored cold.) All other reagents were purchased from commercial sources and purified by standard techniques.

NMR data are listed in parts per million downfield from TMS for proton and carbon. Coupling constants are quoted in hertz. Spectra were obtained in benzene-d_6 at 25 °C unless otherwise noted. Complete NMR data can be found in the supplementary material.

Preparation of Compounds. **$[ArNH_3][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (1a).** HCl gas (210 mL, 0.4 mmol) was added via syringe to a stirred diethyl ether (250 mL) solution of $Re(NAr)_2(CH\text{-}t\text{-}Bu)Cl$ (2.0 g, 3.12 mmol) at −78 °C. A fine orange precipitate formed after 5 min and the mixture was then warmed to 25 °C over 1 h. The precipitate was collected by filtration and washed with diethyl ether (250 mL); yield 2.24 g (96%). IR (Nujol) cm^{-1} 3210 (br, ArNH), 3065 (v br, $ArNH_3$).

$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (1b). $[ArNH_3][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (10.62 g, 14.1 mmol) was partially dissolved in dichoromethane. Over an hour, tetraethylammonium chloride (3.69 g, 21.2 mmol, 1.50 equiv) was added as the mixture was stirred vigorously. The dark red slightly cloudy solution was filtered and concentrated slowly until red crystals began to form. Diethyl ether was added carefully until most of the product precipitated. The flask was cooled and left overnight at −40 °C to give red microcrystals in two crops (9.60 and 0.23 g, 99%). IR (Nujol) cm^{-1} 3190 (NH). Anal. Calcd for $ReC_{25}H_{47}Cl_4N_2$: C, 42.67; H, 6.73. Found: C, 42.96; H, 6.81.

$[Re(C\text{-}t\text{-}Bu)(NHAr)Cl_2(\mu\text{-}Cl)]_2$ (2a). $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (2.00 g, 2.84 mmol) was dissolved in 10 mL of dichloromethane. Powdered zinc dichloride (0.388 g, 2.84 mmol) was added, and the mixture was stirred at ambient temperature for 1.5 h, during which time $[NEt_4][ZnCl_3]$ precipitated from solution. Pentane was added and the mixture filtered and concentrated to dryness. The residue was extracted with a 1:1 mixture of pentane–dichloromethane and the extract was concentrated slowly under vacuum to give 1.12 g (73%) of bright red-orange solid that was purified by recrystallization from dichloromethane by adding pentane and cooling. IR (KBr/Nujol) 3110 cm^{-1} (s, br, NH). Anal. Calcd for $ReC_{17}H_{27}NC_{13}$: C, 37.95; H, 5.06; N, 2.60; Cl, 19.77. Found: C, 38.07; H, 5.21; N, 2.52; Cl 19.96.

$Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(py)$ (3a). Powdered zinc dichloride (0.200 g, 1.47 mmol) was added to a dichloromethane solution of $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (1.00 g, 1.42 mmol). The mixture was stirred for 0.5 h at ambient temperature, during which time the zinc dichloride was consumed. Pyridine (0.118 g, 1.49 mmol) was then added and white $[NEt_4][ZnCl_3]$ precipitated rapidly. A small amount of pentane was added and the mixture was cooled to −40 °C for 1 h. Filtration through Celite followed by evaporation of the filtrate gave 0.75 g (86%) of crude product. Recrystallization from dichloromethane/pentane gave orange needles of pure $Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(py)$. IR (KBr/Nujol) 3110 cm^{-1} (br, NH). Anal. Calcd for $ReC_{22}H_{32}N_2Cl_3$: C, 42.82; H, 5.23; N, 4.54; Cl, 17.24. Found: C, 42.41; H, 5.31; N, 4.48; Cl, 17.48.

$Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(THF)$ (3b). $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (0.75 g, 1.06 mmol) was dissolved in 2 mL of dichloromethane. Powdered $ZnCl_2$ (0.145 g, 1.06 mmol) and THF (173 μL, 2.13 mmol) were added and the mixture was stirred for 0.5 h. Pentane (0.5 mL) was added and the mixture was cooled in order to precipitate out the bulk of $[NEt_4][ZnCl_3]$. Filtration, concentration to half volume, addition of pentane, and cooling to −40 °C yielded 0.45 g (69%) of red crystalline product. IR (KBr/Nujol) 3171 cm^{-1} (s, sharp, NH). Anal. Calcd for $ReC_{21}H_{35}NOCl_3$: C, 41.34; H, 5.78; N, 2.30; Cl, 17.43. Found: C, 41.32; H, 5.87; N, 2.23; Cl, 17.45.

$Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(py)_2$ (4a). An orange solution of $Re(C\text{-}t\text{-}Bu)(NHAr)Cl_3(py)$ (0.750 g, 1.21 mmol) in dichloromethane was cooled to −40 °C. A solution of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 0.185 g, 1.22 mmol) in several milliliters of a 1:1 mixture of dichloromethane and pyridine was prepared, cooled to −40 °C, and added dropwise with stirring. The solution turned blue-violet as DBU·HCl precipitated. Pentane was added to precipitate most of the hydrochloride salt, and the solution was then filtered and the filtrate concentrated to give a blue solid which was recrystallized from a mixture of dichloromethane and pentane to yield 0.60 g (75%) of dark blue crystals.

Alternatively, 1 mL of pyridine and 1.05 equiv (203 mg, 1.49 mmol) of powdered $ZnCl_2$ were added to 1.00 g (1.42 mmol) of $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ in 2 mL of dichloromethane. After 1 h the mixture was cooled (without filtering) to −40 °C, and a solution of DBU (0.218 g, 1.44 mmol) dissolved in 1 mL of cold pyridine was added dropwise with stirring. After several minutes a small amount of pentane was added and the mixture was cooled to −40 °C for 1 h. The reaction mixture was filtered and concentrated to dryness. The residue was extracted with toluene. Slow evaporation of the toluene solution gave 0.70 g (75%) of dark blue microcrystalline solid which could be recrystallized from a mixture of toluene and pentane. Anal. Calcd for $ReC_{27}H_{36}N_3Cl_2$: C, 49.16; H, 5.50; N, 6.37; Cl, 10.75. Found: C, 49.01; H, 5.45; N, 6.36; Cl, 10.53.

$Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(DME)$ (4b). Powdered $ZnCl_2$ (0.29 g, 2.13 mmol) was added to a solution of $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (1.50 g, 2.13 mmol) partially dissolved in 15 mL of freshly distilled 1,2-dimethoxyethane and the mixture was stirred at room temperature for 1 h. The mixture was cooled to −40 °C and a cold solution containing triethylamine (0.216 g, 2.13 mmol) in 1 mL of dimethoxyethane was added dropwise with stirring. The solution rapidly turned purple and white triethylamine hydrochloride precipitated. Several milliliters of pentane were added and the mixture was cooled to −40 °C for 1 h and filtered. The filtrate was evaporated to give 1.20 g (95%) of purple $Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(DME)$ which was left under vacuum for 1.5 h in order to remove excess DME. The residue was extracted with pentane and the extract was concentrated to a small volume and cooled to −40 °C to give 0.90 g (71%) of purple plates. Anal. Calcd for $ReC_{21}H_{36}NO_2Cl_2$: C, 42.63; H, 6.13; N, 2.37; Cl, 11.98. Found: C, 42.35; H, 6.23; N, 2.38; Cl, 11.94.

$Re(C\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ (5a). LiO-*t*-Bu (0.068 g, 0.85 mmol) was added to a suspension of $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (0.20 g, 0.28 mmol) in diethyl ether (15 mL) at −40 °C. The mixture was allowed to warm to 25 °C over a period of 1 h to give a pale yellow solution containing suspended lithium chloride. The mixture was filtered through Celite and the solvent was removed from the filtrate in vacuo. The residue was extracted with pentane and the extract was reduced in volume to yield 0.14 g (85%) of yellow product that could be recrystallized from cold pentane.

In an alternative synthesis $Re(C\text{-}t\text{-}Bu)(NAr)Cl_2(py)_2$ (0.200 g, 0.303 mmol) was dissolved in minimal dichloromethane and at −40 °C 2.2 equiv of lithium *tert*-butoxide (0.063 g, 0.667 mmol) were added with vigorous stirring. After 1 h at room temperature the reaction was worked up as above to yield 0.165 g (94%) of yellow crystals. Anal. Calcd for $ReC_{25}H_{44}NO_2$: C, 52.06; H, 7.69; N, 2.43. Found: C, 52.38; H, 7.86; N, 2.66.

$Re(C\text{-}t\text{-}Bu)(NAr)[OC(CF_3)Me_2]_2$ (5b). The synthesis was analogous to that for **5a** employing $LiOCMe_2(CF_3)$ (0.914 g, 6.82 mmol) and

(18) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. Submitted for publication.

(19) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535.

(20) Nicholas, K. M.; Siegel, J. *J. Am. Chem. Soc.* **1985**, *107*, 4999.

(21) Brandsma, L. *Preparative Acetylenic Chemistry*; Elsevier Publishing Co.: New York, 1971; p 30.

$[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (1.50 g, 2.13 mmol) in 40 mL of dichloromethane at −40 °C; yield 1.17 g of orange-red product (80%). Anal. Calcd for $ReC_{25}H_{38}NO_2F_6$: C, 43.85; H, 5.59; N, 2.05. Found: C, 43.79; H, 5.69; N, 2.02.

Re(C-*t*-Bu)(NAr)(DIPP)$_2$ (5c). The synthesis was analogous to that for **5a** employing LiDIPP(diethyl ether) (0.495 g, 1.90 mmol) and $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (0.45 g, 0.64 mmol) in 20 mL of diethyl ether at −40 °C; yield 0.43 g (86%). The product slowly lost solvent of crystallization. Anal. Calcd for $ReC_{41}H_{60}NO_2$: C, 62.72; H, 7.70; N, 1.78. Found: C, 62.61; H, 7.81; N, 1.82.

Re(C-*t*-Bu)(NAr)[OC(CF$_3$)$_2$Me]$_2$ (5d). $LiOC(CF_3)_2Me$ (1.71 g, 9.09 mmol) was added to $[NEt_4][Re(C\text{-}t\text{-}Bu)(NHAr)Cl_4]$ (2.00 g, 2.84 mmol) in 110 mL of dichloromethane at −30 °C. The red crystalline product was isolated by a procedure analogous to those noted for **5a–c** above; yield 1.70 g (75%). Anal. Calcd for $ReC_{25}H_{32}NO_2F_{12}$: C, 37.88; H, 4.07; N, 1.77. Found: C, 38.09; H, 4.25; N, 1.70.

[Li·DME][Re(C-*t*-Bu)(NAr)[OC(CF$_3$)$_2$H]$_3$]. Re(C-*t*-Bu)(NAr)Cl_2-(DME) (6.23 g, 10.5 mmol) was dissolved in 10 mL of diethyl ether, $LiOC(CF_3)_2H$ (5.53 g, 31.8 mmol) was added, and the solution was stirred overnight at room temperature. Pentane (10 mL) was then added and the reaction mixture was cooled to −40 °C and filtered through Celite. The filtrate was evaporated to dryness to give an orange-brown solid that was extracted twice with a 1:1 mixture of diethyl ether and pentane. The filtrate was concentrated slowly in vacuo to give 10.4 g (96%) of an orange-brown crystalline solid. Anal. Calcd for $ReC_{30}H_{39}LiNO_5F_{18}$: C, 35.03; H, 3.82; N, 1.36; Li, 0.67. Found: C, 34.70; H, 3.88; N, 1.42; Li, 0.69.

Re(C-*t*-Bu)(NAr)[OC(CF$_3$)$_2$H]$_2$(THF) (5e). [Li·DME]{Re(NAr)(C-*t*-Bu)[OC(CF$_3$)$_2$H]$_3$} (10.35 g, 10.1 mmol) was dissolved in THF and $ZnCl_2$ (2.06 g, 15.1 mmol) was added slowly as the mixture was stirred. The mixture was stirred at room temperature for several hours and concentrated in vacuo to one-half the volume. Pentane (10 mL) was added, the mixture was cooled to −40 °C, and the solution was decanted, leaving behind a purple oil containing [Li·DME]{$ZnCl_2$[OC(CF$_3$)$_2$H]}. The solution was evaporated to dryness and the residue was extracted three times with pentane. The extract was concentrated to give 8.2 g (97%) of a dark orange solid that was recrystallized from a mixture of dichloromethane and pentane to give, in two crops, 5.7 g (68%) pure and 2.15 g (25%) crude product. Anal. Calcd for $ReC_{27}H_{36}NO_3F_{12}$: C, 38.76; H, 4.34; N, 1.67. Found: C, 38.60; H, 4.32; N, 1.73.

Re(NAr)(C$_3$Et$_3$)[OC(CF$_3$)$_2$Me]$_2$ (6a). 3-Hexyne (714 μL, 6.36 mmol) was added to a solution of Re(C-*t*-Bu)(NAr)[OC(CF$_3$)$_2$Me]$_2$ (2.40 g, 3.03 mmol) in cold (−40 °C) pentane. After 5 min the solution was filtered and carefully evaporated to yield 2.30 g (90%) of dark red crystals. Anal. Calcd for $ReC_{29}H_{38}NO_2F_{12}$: C, 41.13; H, 4.52; N, 1.65. Found: C, 40.86; H, 4.31; N, 1.89.

Re(NAr)(C$_3$-*n*-Pr$_3$)[OC(CF$_3$)$_2$Me]$_2$ (6b). **6b** was prepared in a manner analogous to that described for **6a** from **5d** (0.50 g, 0.63 mmol) and 278 μL (1.89 mmol) of alkyne in pentane. The crude product was dissolved in a minimum of pentane and 4-octyne (18.5 μL, 0.126 mmol) was added before cooling the solution overnight at −40 °C to give dark red rectangular crystals (0.21 g, 37%). The yield is limited by the high solubility of the product. Anal. Calcd for $ReC_{32}H_{44}NO_2F_{12}$: C, 43.24; H, 4.99; N, 1.58. Found: C, 43.51; H, 5.14; N, 1.77.

Re(NAr)(C$_3$-*i*-Bu$_3$)[OC(CF$_3$)$_2$Me]$_2$ (6c). **5d** (1.50 g, 1.89 mmol) was dissolved in 15 mL of pentane and the solution was cooled to −40 °C. 2,7-Dimethyl-4-octyne (2.62 g, 18.9 mmol) was added with stirring. The solution gradually darkened and after 2.5 h the mixture was filtered and the pentane was removed in vacuo. The resulting solution of products in neat alkynes was cooled overnight at −40 °C to give 0.27 g of dark microcrystalline Re(NAr)(C$_3$-*i*-Bu$_3$)[OC(CF$_3$)$_2$CH$_3$]$_2$. Subsequent removal of alkynes in high vacuum and recrystallization from pentane at −40 °C yielded 0.73 g of dark green crystalline [H(CF$_3$)$_2$CO](ArN)-Re[C(*i*-Bu)C(*i*-Bu)C=C(H)(*i*-Pr)](*i*-BuC≡C-*i*-Bu) (**10**) described later. Anal. Calcd for $ReC_{35}H_{50}NO_2F_{12}$: C, 45.16; H, 5.41; N, 1.50. Found: C, 45.51; H, 5.46; N, 1.38.

Re(NAr)(C-*i*-Pr)[OC(CF$_3$)$_2$Me]$_2$. 2,5-Dimethyl-3-hexyne (7.9 μL, 0.516 mmol) was added to a solution of **5d** (20 mg, 0.025 mmol) in 0.5 mL of C_6D_6 at ambient temperature. An equilibrium mixture of **5d**, 2,5-dimethyl-3-hexyne, Re(NAr)(C-*i*-Pr)[OC(CF$_3$)$_2$Me]$_2$, and 2,2,5-trimethyl-3-hexyne was observed (K_{eq}(198) = 4.0 ± 0.5). 2,5-Dimethyl-3-hexyne (0.35 g, 3.18 mmol) was added to a toluene solution of **5d** (0.50 g, 0.63 mmol). After 1 h, all volatile components were removed under high vacuum. The resultant red solid was dissolved in a mixture of toluene and pentane. After several days at −80 °C several large red crystals (~20 mg) were collected and washed twice with cold pentane. Anal. Calcd for $ReC_{24}H_{30}NO_2F_{12}$: C, 37.02; H, 3.88; N, 1.80. Found: C, 37.41; H, 4.00; N, 1.79.

Re(NAr)(C$_3$-*i*-Pr$_3$)[OC(CF$_3$)$_2$Me]$_2$ (6d). **5d** (0.075 g, 0.095 mmol) was dissolved in a minimum of pentane (~0.30 mL) and 2,5-dimethyl-3-hexyne (72.0 μL, 0.473 mmol) was added. After 1 h at room temperature, the solution was cooled overnight at −40 °C. Removal of solvent by pipet left red crystals of **6d** (60 mg; 70%) which were immediately cooled to −40 °C to prevent loss of 2,5-dimethyl-3-hexyne. When dissolved in tol-d_8, an approximately 1:1 mixture of **5d** and 2,5-dimethyl-3-hexyne was observed by ^{1}H NMR at room temperature. ^{1}H and ^{13}C NMR spectra of **6d** were obtained at low temperatures. **6d** was too unstable for elemental analysis.

Re(NAr)(C$_3$Et$_3$)[OC(CF$_3$)$_2$H]$_2$ (7a). Re(C-*t*-Bu)(NAr)[OC-(CF$_3$)$_2$H]$_2$(THF) (**5e**) (0.75 g, 0.90 mmol) was dissolved in 10 mL of pentane and the solution was cooled to −40 °C. 3-Hexyne (252 μL, 2.24 mmol) was added and the solution changed from orange to deep red. Removal of the volatile components left 0.70 g (~90%) of crude product. The product (in pentane) was treated with an additional 0.5 equiv of 3-hexyne to consume a small amount (<10%) of unreacted **5e**. Solvent and volatile byproducts were removed in vacuo. Recrystallization from cold pentane gave dark red crystals. Anal. Calcd for $ReC_{27}H_{34}NO_2F_{12}$: C, 39.61; H, 4.19; N, 1.71. Found: C, 39.87; H, 4.15; N, 1.78.

Observation of Re(NAr)(C$_3$-*n*-Pr$_3$)[OC(CF$_3$)$_2$H]$_2$ (7b). 4-Octyne (10.5 μL, 0.072 mmol) was added to **5e** (0.020 g, 0.024 mmol) in pentane at −40 °C. The solution turned red and darkened. The volatile components were removed in vacuo and the major product, Re(NAr)(C$_3$-*n*-Pr$_3$)[OC(CF$_3$)$_2$H]$_2$, was observed by ^{1}H NMR [δ 4.2 (m, 2, $C_\alpha CH_AH_BCH_2CH_3$), 3.8 (m, 2, $C_\alpha CH_AH_BCH_2CH_3$), 2.2 (m, 2, $C_\beta CH_2CH_2CH_3$)].

Re(NAr)(C$_3$-*i*-Bu$_3$)[OC(CF$_3$)$_2$H]$_2$ (7c). 2,7-Dimethyl-4-octyne (0.62 g, 4.48 mmol) was added to **5e** (1.50 g, 1.79 mmol) at −40 °C in pentane. Solvent and 2,2,7-trimethyl-3-heptyne was removed in vacuo, leaving an oily, highly pentane soluble residue. Recrystallization from a minimum of cold (−40 °C) pentane gave large purple crystals (0.60 g, 37%). Anal. Calcd for $ReC_{33}H_{46}NOF_{12}$: C, 43.90; H, 5.13; N, 1.55. Found: C, 43.69; H, 5.10; N, 1.61.

Re(NAr)(C$_3$-*i*-Pr$_3$)[OC(CF$_3$)$_2$H]$_2$ (7d). Diisopropylacetylene (0.527 g, 4.78 mmol) was added to a pentane solution of **5e** (1.00 g, 1.20 mmol) at room temperature. After 90 min, solvent and volatiles were removed in vacuo to give a dark-red solid. Recrystallization from a mixture of diethyl ether and pentane cooled to −40 °C gave purple crystals (0.45 g, 44%). Anal. Calcd for $ReC_{30}H_{40}NO_2F_{12}$: C, 41.86; H, 4.68; N, 1.63. Found: C, 41.95; H, 4.68; N, 1.48.

Re(NAr)[C(*t*-Bu)CHC(*i*-Bu)][OC(CF$_3$)$_2$H]$_2$ (7e). 4-Methyl-1-pentyne (17 μL, 0.16 mmol) was added to a solution of **5e** (0.10 g, 0.12 mmol) at −40 °C in 1 mL of diethyl ether. The solution was stripped to dryness and the residue was recrystallized at −40 °C in 1 mL of diethyl ether. The solution was stripped to dryness and the residue was recrystallized at −40 °C from a minimum of pentane to give red crystals (0.05 g, 51%). The red crystals were contaminated with ~15% unreacted **5e**. Although more **5e** was consumed when an excess of 4-methyl-1-pentyne was used, decomposition reactions decreased the purity of the isolated product. Attempts to scale up the reaction were not successful.

Re(CEtCEtC=CHMe)(NAr)[OC(CF$_3$)$_2$H](py) (8a). Pyridine (91.0 μL, 1.13 mmol) was added to a pentane solution of **7a** (0.62 g, 0.75 mmol). The solution turned amber-green. The solution was filtered and evaporated to dryness in vacuo. Large crystals (0.20 g, 36%) were obtained by crystallizing the residue from cold pentane. IR 3078 cm^{-1} (vinylic C–H). Anal. Calcd for $ReC_{29}H_{37}N_2OF_6$: C, 47.73; H, 5.11; N, 3.84. Found: C, 47.91; H, 5.14; N, 3.77.

Re[C(*i*-Bu)C(*i*-Bu)C=C(H)(*i*-Pr)](NAr)[OC(CF$_3$)$_2$H](py) (8b). Pyridine (30.0 μL, 0.374 mmol) was added to **7c** (0.225 g, 0.249 mmol) in pentane. The color changed from deep red to amber-green. The solution was warmed to room temperature, filtered, and evaporated to dryness. The residue was recrystallized from a minimum of pentane at −40 °C. A crust of yellow-green product (0.15 g, 74%) was collected and washed with cold pentane. Anal. Calcd for $ReC_{35}H_{49}N_2OF_6$: C, 51.65; H, 6.07; N, 3.44; Found: C, 51.63; H, 6.11; N, 3.31.

Re[C(*i*-Bu)C(*i*-Bu)C=C(H)(*i*-Pr)](*i*-BuC≡C-*i*-Bu)[OC-(CF$_3$)$_2$Me](NAr) (10). (See synthesis of Re(NAr)(C$_3$-*i*-Bu$_3$)[OC-(CF$_3$)$_2$Me]$_2$ (**6c**).) The crude product was recrystallized from pentane at −40 °C to yield 0.73 g (43%) of dark green crystals. IR (KBr/Nujol) 3080 cm^{-1} (vinylic C–H) 1730 cm^{-1} (weak, C=C, metallacyclopropene). Anal. Calcd for $ReC_{41}H_{64}NOF_6$: C, 55.51; H, 7.27; N, 1.58. Found: C, 55.69; H, 7.34; N, 1.38.

Re[C(Me)C(Me)=C(Me){OC(CF$_3$)$_2$Me}](2-butyne)(NAr)[OC-(CF$_3$)$_2$Me] (11). 2-Butyne (200 μL, 2.52 mmol) was added to **5d** (0.50 g, 0.63 mmol) dissolved in 5 mL of pentane at −40 °C and the solution was allowed to warm to room temperature. The solution was filtered and the filtrate was concentrated and cooled to −40 °C for 12 h to give 0.39 g (72%) of analytically pure, yellow-orange crystals. Anal. Calcd for $ReC_{30}H_{38}NO_2F_{12}$: C, 41.96; H, 4.46; N, 1.63. Found: C, 41.75; H, 4.55; N, 1.65.

X-ray Study of 2a. An orange prismatic crystal was mounted on a glass fiber. Data were collected at −72 °C on a Rigaku AFC6R diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ = 0.71069) and a 12 KW rotating anode generator. A total of 3590 reflections were collected of which 3367 were unique. Equivalent reflections were merged. The intensities of three representative reflections which were measured after every 197 reflections remained constant throughout data collection indicating crystal and electronic stability. No decay correction was applied. The structure was solved by a combination of the Patterson method and direct methods. The refinement was by full matrix least squares with TEXSAN. The *tert*-butyl group of the alkylidyne ligand failed to refine adequately as a full occupancy moiety. The disorder was modeled as a 2/1 orientation disorder with group isotropic temperature factors. The occupancy of the solvent was set at 0.50 because of the reasonable values of the refined temperature factors. The carbon of the solvent was refined isotropically. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions (d_{C-H} = 0.95 Å) (space group $P2_1/c$, a = 9.953 (4) Å, b = 12.398 (9) Å, c = 19.720 (6) Å, β = 93.08 (3)°, V = 2430 (2) Å^3, Z = 4, ρ = 1.473 g/cm^3, R = 0.050, R_w = 0.084). A full description of the structural study can be found in the supplementary material.

X-ray Study of 6a. Details of the structural study of **6a** can be found in Supplementary Material elsewhere.[8]

Acknowledgment. We thank the National Science Foundation for supporting this research (Grant CHE 88-22508) and for a predoctoral fellowship (to I.W.). We also thank the U.S. Department of Energy, Division of University and Industry Programs, for funds to purchase the X-ray diffractometer (Grant DE-FG05-86ER75292) and Dr. W. E. Crowe for useful discussions.

Supplementary Material Available: Complete NMR data for all compounds, description of the structural study of **2a** with an ORTEP drawing and a fully labeled drawing, and a listing of final positional and thermal parameters (18 pages); listing of final observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Singly Bridged Arrangements on Group 14 X_2H_4 Potential Surfaces

Georges Trinquier

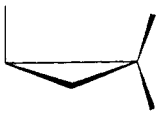
Contribution from the Laboratoire de Physique Quantique, C.N.R.S. U.R.A. 505, Université Paul-Sabatier, 31062 Toulouse Cedex, France. *Received May 14, 1990*

Abstract: Theoretical exploration of the Sn_2H_4 and Pb_2H_4 singlet potential energy surfaces led to a local minimum corresponding to an isomer with an unsymmetrical structure presenting a single X–H–X bridge and a short X–X distance. For tin and lead, this isomer lies at 8 and 15 kcal/mol, respectively, above the preferred doubly bridged structure and at 25 and 13 kcal/mol, respectively, below the dissociation products $2XH_2(^1A_1)$. The molecule can be seen as two singlet XH_2 moieties bound by a three-center two-electron bridge and a $n_\sigma \rightarrow p_\pi$ dative bond $HX \leftarrow H \cdots XH_2$. Electronic correlation, analyzed through a CASCF+OVB procedure, strengthens the X–X bond and makes it more covalent, suggesting another limiting form $H\ddot{X}–XH_3$ with an internal H bridge. Several indexes support a direct Sn–Sn link stronger than that of Pb–Pb. These singly bridged forms occupy a key position on the group 14 X_2H_4 potential energy hypersurfaces since they can be topologically related to the doubly bridged forms (both trans C_{2h} and cis C_{2v}), the methylmethylene-like forms $H\ddot{X}—XH_3$ and the doubly bonded forms $H_2X{=}XH_2$. With germanium and silicon the singly bridged arrangement is caught in the well of $H\ddot{X}–XH_3$, but it should remain a crossing point between the four isomers. This provides a new global view of the X_2H_4 potential surfaces for which the largest number of true minima—five—is observed only for Sn_2H_4.

In a previous work, the existence of doubly bridged structures was established for group 14 X_2H_4 potential energy surfaces.[1] These geometries, which can be C_{2h} trans, **1**, or C_{2v} cis, **2**, have

1 **2**

proven to be true minima except for C_2H_4, where **1** was found to be a saddle point and **2** a critical point of index 2. The trans-bridged form **1** is even found to be the absolute minimum on the Sn_2H_4 and Pb_2H_4 surfaces. We report here the existence of another type of minimum corresponding to the singly bridged structure **3**. This unsymmetrical arrangement was found to be



3

a true minimum on the Sn_2H_4 and Pb_2H_4 potential surfaces. Attempts to reach such a local minimum failed for the lighter analogues Ge_2H_4 and Si_2H_4, where the singly bridged arrangement is caught in the low hollow of the methylmethylene-type form $H_3X–XH$.

After a methodological section, we will comment on the structures of the singly bridged forms, trying to figure out a bonding scheme and to gauge correlation effects by use of orthogonal valence-bond (OVB) analyses. Then we will reconsider the shapes of the X_2H_4 potential hypersurfaces in relation to this new connecting point.

Computational Procedures

SCF calculations were performed with the PSHONDOG algorithm,[2a] which uses effective core potentials taking into account relativistic effects through mass correction and Darwin terms.[2b] The valence basis sets used are of double-ζ plus polarization (DZP) quality with polarization function exponents taken at $\eta_p(H)$ = 0.80, $\eta_d(Sn)$ = 0.20, and $\eta_n(Pb)$ = 0.15. Geometries were optimized with a gradient technique. The optimization is ended when the gradient components are lower than 10^{-4}. Harmonic force fields are calculated through a numerical derivation of the analytical first derivatives, using a single-point differencing formula. Correlation effects were not included in the optimization process since these were shown to have no dramatic influence on the geometries of the Sn_2H_4

(1) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130.

(2) (a) Pélissier, M.; Komiha, N.; Daudey, J. P. *J. Comput. Chem.* **1988**, *9*, 298. (b) Barthelat, J. C.; Pélissier, M.; Durand, Ph. *Phys. Rev. A* **1981**, *21*, 1773.

0002-7863/91/1513-144$02.50/0