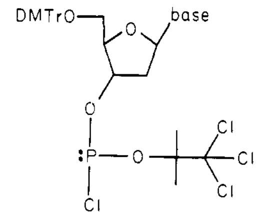
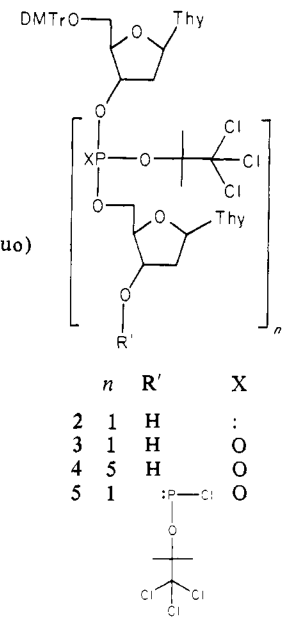
Chart I



1, (base = Thy, bzCyt, bzAde, ibGuo)



which was hydrolyzed completely to d-T and d-pT by snake venom phosphodiesterase.

For routine synthesis of oligonucleotides with phosphodiester backbones it is desirable to cleave the P–O protecting groups before removing the oligomers from the insoluble support. Heretofore this has not been possible with trichloroethyl phosphotriesters since neither zinc[11] nor radical anions[12] are effective on substrates bound to silica supports. A search for a new reagent for deprotection revealed that tributylphosphine[13] in DMF–Et_3N at 80 °C converts nucleoside trichloroethyl and trichlorodimethylethyl phosphotriesters efficiently to the corresponding nucleoside phosphotriesters for reactions conducted both in solution and on insoluble supports.

Use of the phosphorochloridite reagents (**1**) in conjunction with deprotection by Bu_3P is illustrated by the synthesis of d-T_{16} and d-GCAAATATCATTTT. Reactions were carried out on silica (80 mg, 3 μmol of d-(DMTr)T in a column similar to that previously described.[4a] Preliminary experiments showed the following sequence to be effective: treatment with (1) 3% Cl_3CCOOH in CH_3NO_2,[4e] 2.5 min, (2) pyridine, 2 min, (3) reagent **1** in 3:1 CH_2Cl_2–*N*-methylimidazole,[14] 15 min, (4) pyridine, 2 min, (5) I_2 in 40:20:1 THF-pyridine-H_2O or 0.2 M *m*-chloroperbenzoic acid in CH_2Cl_2–pyridine, 2 min, (6) pyridine, 2 min, (7) CH_3NO_2, 2 min. With this procedure yields averaged above 95% per cycle for addition of a nucleotide unit (trityl cation test). On completion, the loaded silica was heated with 2:1:4 Bu_3P–Et_3N–DMF (80 °C, 3 h) and NH_4OH (50 °C, 12 h). The ammoniacal solutions were evaporated and the products analyzed by HPLC. The chromatographic profiles (Figure 1) show that the efficiency through the synthetic cycles and deprotection steps is good. Samples purified by HPLC and chromatography on silica gel[4c] were characterized by hydrolysis to the component nucleotides and nucleosides (d-T or d-G) by snake venom phosphodiesterase and, after labeling with ^{32}P (polynucleotide kinase), by sizing by electrophoresis on a polyacrylamide gel (single spots were obtained corresponding to a hexadecamer for the thymidine derivative and to a tetradecamer for the mixed oligomer).

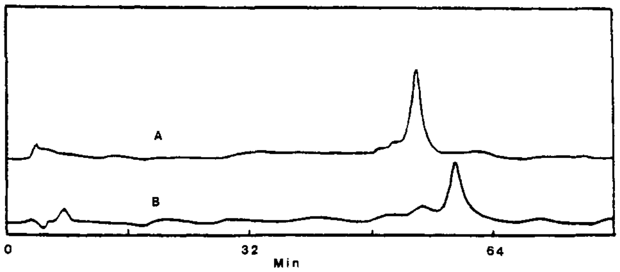


Figure 1. HPLC analysis of reaction mixtures from preparation of (A) d-T_{16} and (B) d-GCAAATATCATTTT; Whatman Partisil PXS ODS-3 column, starting with 11% CH_3CN, 89% 0.1 M aqueous $Et_3NH^+OAc^-$ and increasing CH_3CN at rate of 0.1%/min.

The ease of preparing the active reagents, high selectivity in reactions,[15] stability of the intermediate triesters, and efficiency in deprotection make this approach promising for routine synthesis of oligonucleotides for studies in molecular biology. In addition, in combination with procedures utilizing methyl protecting groups for P–O, this chemistry provides flexibility in synthesizing and subsequently modifying oligonucleotides possessing enzyme-resistant sites (i.e., stable triester links) at specified points in phosphodiester chains.

Acknowledgment. This research was supported by the National Institute of General Medical Sciences of the National Institutes of Health (GM10265). Gel electrophoresis was carried out by David D. Miller.

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[11] Eckstein, F.; Rizk, I. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 695.

[12] Letsinger, R. L.; Finnan, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 7197.

[13] Other phosphine derivatives, e.g., $[(CH_3)_2N]_3P$, are also active.

[14] *N*-Methylimidazole accelerates the condensation reaction.

[15] For another means of achieving selectivity see: Beaucage, S. L.; Caruthers, M. H. *Tetrahedron Lett.* **1981**, *22*, 1859.

Rhenium(VII) Neopentylidene and Neopentylidyne Complexes[1]

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In the past several years a variety of d^0 alkylidene[2] and alkylidyne[3] complexes of Nb, Ta, Mo, and W have been prepared, most of them by a variation of the α-hydrogen abstraction reaction.[4] An interesting question is whether as yet unknown Re(VII) alkylidene and alkylidyne complexes can be prepared by using related methods. We report here that they can be, but so far at least one other π-bonding ligand (dianion or trianion) must be present in order for the metal to sustain its relatively high oxidation state.

The starting point in this chemistry is $Re(N\text{-}t\text{-}Bu)_3(OSiMe_3)$, a compound that can be prepared in high yield from Re_2O_7 and $NH(SiMe_3)\text{-}t\text{-}Bu$.[5] Addition of 4 equiv of gaseous HCl to $Re(N\text{-}t\text{-}Bu)_3(OSiMe_3)$ in dichloromethane produces 1 equiv of $t\text{-}BuNH_3Cl$ and orange $Re(N\text{-}t\text{-}Bu)_2Cl_3$ in >85% yield.[6] Since $Re(N\text{-}t\text{-}Bu)_2Cl_3$ is a monomer in dichloromethane and the *tert*-butyl groups are equivalent by ^1H and ^{13}C NMR, we propose that it is a trigonal bipyramidal species with equatorial imido ligands (cf. other five-coordinate d^0 complexes containing two π-bonding ligands isoelectronic with imido ligands such as $Ta(CHCMe_3)_2(mesityl)(PMe_3)_2$[7] and $W(O)(CHCMe_3)(PEt_3)Cl_2$[8]).

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[1] Multiple Metal-Carbon Bonds. 30. For part 29 see ref 15.

[2] Schrock, R. R. In "Reactions of Coordinated Ligands"; Braterman, P. S., Ed.; Plenum Press: New York, in press.

[3] (a) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774. (b) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *Ibid.* **1981**, *103*, 3932.

[4] Wood, C. D.; McLain, S. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 3210.

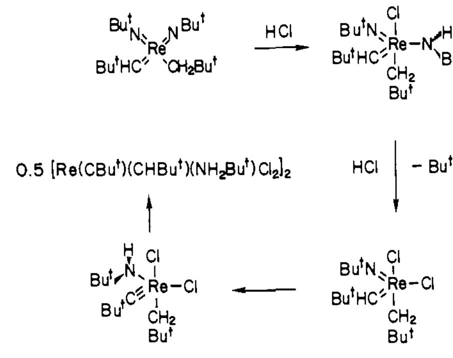
[5] (a) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1979**, *1105*. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123.

[6] Anal. Calcd for $ReC_8H_{18}N_2Cl_3$: C, 22.09; H, 4.17. Found: C, 22.15; H, 4.11.

[7] Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1930.

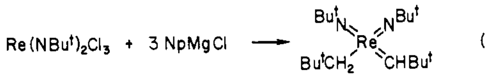
0002-7863/82/1504-6806$01.25/0

Scheme I



Trialkyl complexes, $Re(N\text{-}t\text{-}Bu)_2R_3$ ($R = Me, CH_2Ph, CH_2SiMe_3$) can be made in high yield from $Re(N\text{-}t\text{-}Bu)_2Cl_3$ by using the appropriate alkylating reagent.[9a] All indications are[9b] that they are also trigonal bipyramidal species that do not readily exchange axial and equatorial R groups at a rate on the order of the NMR time scale. This proposal differs from that concerning the structure of ReO_2Me_3, where axial and equatorial oxo ligands were postulated.[10]

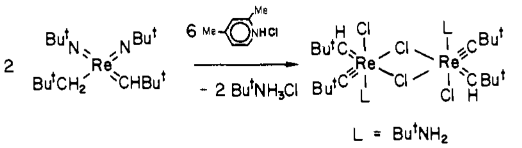
All attempts to prepare $Re(N\text{-}t\text{-}Bu)_2Np_3$ ($Np = CH_2CMe_3$) have failed. Instead, a monomeric neopentylidene complex is obtained as a distillable yellow-orange oil in >70% yield (doubly distilled; eq 1).[11] One might presume $Re(N\text{-}t\text{-}Bu)_2Np_3$ is an



$$Re(NBu^t)_2Cl_3 + 3\ NpMgCl \longrightarrow Re(NBu^t)_2(CH_2Bu^t)(CHBu^t) \qquad (1)$$

intermediate since yellow crystalline $Re(N\text{-}t\text{-}Bu)_2(CHSiMe_3)(CH_2SiMe_3)$[12] can be obtained quantitatively by photolyzing $Re(N\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_3$ in pentane through Pyrex with a medium-pressure mercury lamp. (The connection between thermal α-hydrogen atom abstraction reactions and photochemical ones has been noted in tantalum chemistry.[4]) Of course we cannot exclude the possibility that formation of $Re(N\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ is a more complex reaction (cf. the preparation of $Ta(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)_3$[13a]). Photolysis of $Re(N\text{-}t\text{-}Bu)_2(CH_2Ph)_3$ produces a complex mixture of products which by ^1H NMR contains $Re(N\text{-}t\text{-}Bu)_2(CHPh)(CH_2Ph)$ (C*H*Ph at δ 12.4); unlike $Re(N\text{-}t\text{-}Bu)_2(CHSiMe_3)(CH_2SiMe_3)$, $Re(N\text{-}t\text{-}Bu)_2(CHPh)(CH_2Ph)$ is not stable under the reaction conditions. Photolysis of $Re(N\text{-}t\text{-}Bu)_2Me_3$ is even more complex; there is no obvious indication (other than evolution of methane) that $Re(N\text{-}t\text{-}Bu)_2(CH_2)Me$ forms. These results are analogous to those obtained in other systems,[2,13b] i.e., the ease of α-hydrogen abstraction again appears to vary in the order $R = CH_2CMe_3 > CH_2SiMe_3 > CH_2Ph \gg CH_3$.

$Re(N\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ reacts with 3 equiv of 2,4-lutidine hydrochloride in dichloromethane to give a species whose proposed structure is shown in eq 2. Two isomers are

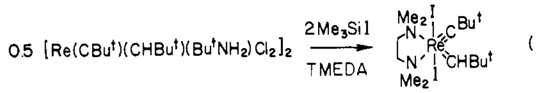


$$2\ Re(NBu^t)_2(CH_2Bu^t)(CHBu^t) \xrightarrow[-2\ Bu^tNH_3Cl]{6\ \text{Me}_2C_5H_3N\cdot HCl} [Re(CBu^t)(CHBu^t)L(\mu\text{-}Cl)Cl]_2 \qquad (2)$$

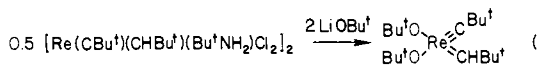
$L = Bu^tNH_2$

observed, probably the result of either different orientations of the neopentylidene ligand in the $C_\alpha{=}Re{\equiv}C_\alpha$ plane or a cisoid arrangement of $t\text{-}BuNH_2$ ligands instead of the transoid arrangement shown. An interesting feature of the ^{13}C NMR spectrum of this species is that the signal for the alkylidyne α-carbon atom is found *upfield* from that for the alkylidene α-carbon atom in each isomer.[14] A plausible sequence of reactions leading to $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(NH_2\text{-}t\text{-}Bu)Cl_2]_2$ (Scheme I) is based in part on the fact that if pyridine hydrochloride is used instead of 2,4-lutidine hydrochloride, the product is an unstable pyridine adduct of $Re(C\text{-}t\text{-}Bu)(NH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)Cl_2$ (two isomers), which decomposes to $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(NH_2\text{-}t\text{-}Bu)Cl_2]_2$. The most striking feature of the reaction to give $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(NH_2\text{-}t\text{-}Bu)Cl_2]_2$ is that protons move from carbon *to* nitrogen, the reverse of what was found recently in a tunsten system where $W(NHPh)(CCMe_3)L_2Cl_2$ is converted into $W(NPh)(CHCMe_3)L_2Cl_2$ (L = e.g., PMe_3).[15]

Two other neopentylidyne neopentylidene complexes can be prepared as shown in eq 3 and 4. The signal for the neo-



$$0.5\ [Re(CBu^t)(CHBu^t)(Bu^tNH_2)Cl_2]_2 \xrightarrow[\text{TMEDA}]{2Me_3SiI} Re(CBu^t)(CHBu^t)(TMEDA)I_2 \qquad (3)^{16}$$



$$0.5\ [Re(CBu^t)(CHBu^t)(Bu^tNH_2)Cl_2]_2 \xrightarrow{2\,LiOBu^t} Re(CBu^t)(CHBu^t)(OBu^t)_2 \qquad (4)^{17}$$

pentylidyne α-carbon atom in $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(TMEDA)I_2$ also is found above that for the neopentylidene α-carbon atom in the ^{13}C NMR spectrum,[16] but in $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ the normal order is found.[17]

On the basis of recent results concerning the metathesis of olefins by d^0 tungsten alkylidene complexes[18] and the metathesis of acetylenes by d^0 tungsten alkylidyne complexes,[19] we might expect that the Re(VII) complexes prepared here would react with olefins or acetylenes. $Re(N\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$ does not react readily with *cis*-2-pentene while $[Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(NH_2\text{-}t\text{-}Bu)Cl_2]_2$ and $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(O\text{-}t\text{-}Bu)_2$ do not react readily with diphenylacetylene, 4-octyne, *cis*-2-pentene, or 1-pentene. However, $Re(C\text{-}t\text{-}Bu)(CH\text{-}t\text{-}Bu)(TMEDA)I_2$ will convert several eqivalents of 3-heptyne into 3-hexyne and 4-octyne before metathesis ceases. The details of this acetylene metathesis reaction are not yet known.

Acknowledgment. We thank the National Science Foundation for supporting this research (Grants CHE79 05307, CHE82 21282).

Registry No. $Re(N\text{-}t\text{-}Bu)_3(OSiMe_3)$, 73321-57-0; Re_2O_7, 1314-68-7; $NH(SiMe_3)\text{-}t\text{-}Bu$, 5577-67-3; $Re(N\text{-}t\text{-}Bu)_2(CH\text{-}t\text{-}Bu)(CH_2\text{-}t\text{-}Bu)$,

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[8] Churchill, M. R.; Missert, J. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 3388.

[9] (a) $Re(N\text{-}t\text{-}Bu)_2Me_3$, a colorless liquid (mp ≈10 °C), was prepared by using excess $AlMe_3$ in toluene. Orange crystalline $Re(N\text{-}t\text{-}Bu)_2(CH_2Ph)_3$ was prepared by using 3 equiv of $PhCH_2MgCl$ in ether (Anal. Calcd for $ReC_{29}H_{39}N_2$: C, 57.86; H, 6.53. Found: C, 58.35; H, 6.59). Yellow, light-sensitive $Re(N\text{-}t\text{-}Bu)_2(CH_2SiMe_3)_3$ was prepared by using 1.5 equiv of $Zn(CH_2SiMe_3)_2$ and 1.5 equiv of NEt_4Cl in dichloromethane (Anal. Calcd for $ReC_{20}H_{51}N_2Si_3$: C, 40.70; H, 7.83. Found: C, 40.94; H, 7.99). (b) The alternative square-pyramidal geometry with basal imido ligands can be ruled out since in such a species where $R = CH_2Ph$ or CH_2SiMe_3 the methylene protons would be diastereotopic.

[10] Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488.

[11] Anal. Calcd for $ReC_{18}H_{39}N_2$: , 46.03; H, 8.39. Found: C, 46.12; H, 8.31. Parent ions (^{185}Re, 37%; ^{187}Re, 63%) observed in mass spectrum; *C*HCMe$_3$ found at 262.2 ppm (J_{CH} = 134 Hz) in ^{13}C NMR spectrum.

[12] Anal. Calcd for $ReC_{16}H_{39}N_2Si_2$: C, 38.28; H, 7.83. Found: C, 38.65; H, 7.99. Parent ions observed in mass spectrum; *C*HSiMe$_3$ found at 237.5 ppm (J_{CH} = 128 Hz).

[13] (a) Schrock, R. R.; Fellmann, J. D. *J. Am. Chem. Soc.* **1978**, *100*, 3359. (b) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *Ibid.* **1980**, *102*, 6236.

[14] Pale orange cubes from dichloromethane. Major isomer: *C*CMe$_3$ at 294.3, *C*HCMe$_3$ at 298.4 (J_{CH} = 128 Hz). Minor isomer: *C*CMe$_3$ at 293.7, *C*HCMe$_3$ at 299.2 (J_{CH} = 125 Hz). Molecular weight in dichloromethane (differential vapor pressure) 939 (995 calcd).

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

[16] Orange-red plates from toluene; *C*HCMe$_3$ is found at 299.6 (J_{CH} = 119 Hz), *C*CMe$_3$ at 292.1 ppm. Anal. Calcd for $ReC_{16}H_{35}N_2I_2$: C, 27.63; H, 5.07. Found: C, 27.92; H, 5.08. $Re(CCMe_3)(CHCMe_3)py_2I_2$ also has been prepared. Anal. Calcd for $ReC_{20}H_{29}N_2I_2$: C, 32.57; H, 3.96. Found: C, 33.01; H, 4.16.

[17] Extremely air- and moisture-sensitive sublimable yellow microcrystals (mp ~30 °C); *C*HCMe$_3$ is found at 229.9 (J_{CH} = 126 Hz), *C*CMe$_3$ at 287.4 ppm. Parent ions were observed in the mass spectrum.

[18] (a) Schrock, R.; Rocklage, S.; Wengrovius, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73. (b) Wengrovius, J.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (c) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514.

[19] (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75.

J. Am. Chem. Soc. **1982**, *104*, 6808–6809

83487-27-8; Re(N-*t*-Bu)$_2$Me$_3$, 83487-28-9; Re(N-*t*-Bu)$_2$(CH$_2$Ph)$_3$, 83487-29-0; Re(N-*t*-Bu)$_2$(CH$_2$SiMe$_3$)$_3$, 83487-30-3; Re(N-*t*-Bu)$_2$Cl$_3$, 83487-31-4; Re(N-*t*-Bu)$_2$Np$_3$, 83487-32-5; Re(N-*t*-Bu)$_2$(CHSiMe$_3$)(CH$_2$SiMe$_3$), 83487-33-6; Re(N-*t*-Bu)$_2$(CHPh)(CH$_2$Ph), 83487-34-7; [Re(C-*t*-Bu)(CH-*t*-Bu)(NH$_2$-*t*-Bu)Cl$_2$]$_2$, 83510-97-8; Re(C-*t*-Bu)(NH-*t*-Bu)(CH$_2$-*t*-Bu)Cl$_2$(Py), 83510-98-9; Re(C-*t*-Bu)(CH-*t*-Bu)(TMEDA)I$_2$, 83510-99-0; Re(C-*t*-Bu)(CH-*t*-Bu)(O-*t*-Bu)$_2$, 83487-35-8; Re(CCMe$_3$(CHCMe$_3$)Py$_2$I$_2$, 83511-00-6.

Reaction of Tungsten(VI) Alkylidyne Complexes with Acetylenes To Give Tungstenacyclobutadiene and Tungsten Cyclopentadienyl Complexes

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Received July 29, 1982

We have reported that W(C-*t*-Bu)(O-*t*-Bu)$_3$ will catalytically metathesize dialkylacetylenes at a high rate, presumably by forming unstable tungstenacyclobutadiene intermediates.[2] On the other hand, while complexes such as W(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$,[3] W(C-*t*-Bu)(dme)Cl$_3$,[4] and [NEt$_4$][W(C-*t*-Bu)Cl$_4$][2] will react with acetylenes, they do not metathesize them catalytically. We report here that W(C-*t*-Bu)(dme)Cl$_3$ reacts with dialkylacetylenes to give a stable tungstenacyclobutadiene complex, that tungstenacyclobutadiene complexes containing certain alkoxide ligands (but not three *tert*-butoxide ligands) are also stable, and that cyclopentadienyl complexes are formed in the presence of excess dialkylacetylene, even (slowly) in the active alkyne metathesis system.

Excess 3-hexyne reacts with [NEt$_4$][W(C-*t*-Bu)Cl$_4$] in dichloromethane to give a pentane-soluble paramagnetic red complex with the empirical formula W(C-*t*-Bu)(CH$_3$CH$_2$C$\equiv$CCH$_2$CH$_3$)$_3$Cl$_2$ in ~50% yield. 2-Butyne reacts more rapidly with [NEt$_4$][W(C-*t*-Bu)Cl$_4$] to give an analogous ether-soluble species. Both can be obtained more straightforwardly by reacting an excess of the alkyne with W(C-*t*-Bu)(dme)Cl$_3$.[4] In this reaction a less soluble, paramagnetic, orange complex with the empirical formula W(C-*t*-Bu)(alkyne)$_2$Cl$_4$[5] also forms in ~50% yield by weight. A molecular weight study of "W(C-*t*-Bu)(EtC$\equiv$CEt)$_2$Cl$_4$" in dichloromethane at 0 °C (by differential vapor pressure measurement) showed it to be a dimer.

An X-ray structural study[6] of "W(C-*t*-Bu)(MeC$\equiv$CMe)$_3$Cl$_2$" shows it to be W(η^5-C$_5$Me$_4$-*t*-Bu)(MeC$\equiv$CMe)Cl$_2$, a species that is closely related to the diamagnetic Ta(III) derivatives, Ta(η^5-C$_5$Me$_5$)(alkyne)Cl$_2$.[7] As in Ta(η^5-C$_5$Me$_5$)(PhC$\equiv$CPh)Cl$_2$,[7] the axis of the acetylene ligand in W(η^5-C$_5$Me$_4$-*t*-Bu)(MeC$\equiv$CMe)Cl$_2$ lies parallel to the plane of the cyclopentadienyl ligand, and the acetylene carbon–carbon bond length is lengthened considerably as a result of its strong bond to the metal. Therefore, we propose that the "[W(C-*t*-Bu)(alkyne)$_2$Cl$_4$]$_2$" species are also substituted cyclopentadienyl complexes, [W(η^5-C$_5$R$_4$-*t*-Bu)Cl$_4$]$_2$. Most likely W(η^5-C$_5$R$_4$-*t*-Bu)(RC$\equiv$CR)Cl$_2$ and [W(η^5-C$_5$R$_4$-*t*-Bu)Cl$_4$]$_2$ form via disproportionation of some intermediate tungsten(IV) complex, possibly "W(η^5-C$_5$R$_4$-*t*-Bu)Cl$_3$" as shown in eq 1 and 2.

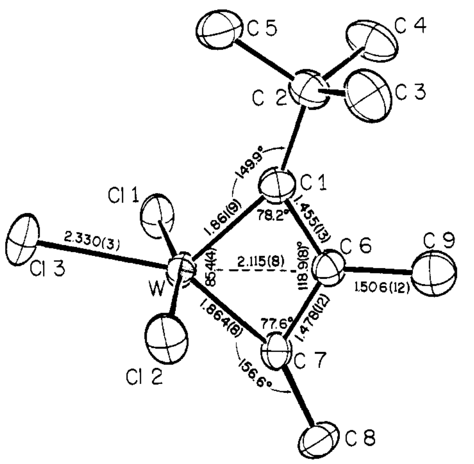
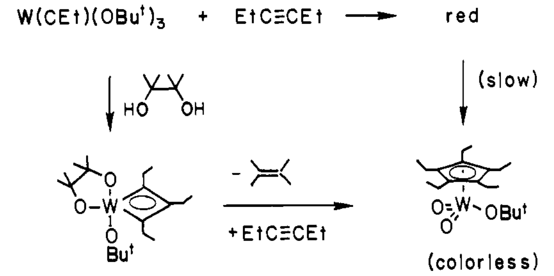


Figure 1. ORTEP-II diagram (30% ellipsoids) of W[C-*t*-BuCMeCMe]Cl$_3$ with hydrogen atoms omitted.

Scheme I



$$\mathrm{W(C\text{-}\mathit{t}\text{-}Bu)(dme)Cl_3} + 2\mathrm{RC{\equiv}CR} \rightarrow \text{“}\mathrm{W(\eta^5\text{-}C_5R_4\text{-}\mathit{t}\text{-}Bu)Cl_3}\text{”} \tag{1}$$

$$\text{“}\mathrm{W(\eta^5\text{-}C_5R_4\text{-}\mathit{t}\text{-}Bu)Cl_3}\text{”} \xrightarrow{0.5\mathrm{RC{\equiv}CR}} 0.5\mathrm{W(\eta^5\text{-}C_5R_4\text{-}\mathit{t}\text{-}Bu)(RC{\equiv}CR)Cl_2} + 0.25[\mathrm{W(\eta^5\text{-}C_5R_4\text{-}\mathit{t}\text{-}Bu)Cl_4}]_2 \tag{2}$$

Addition of only 1 equiv of 3-hexyne or 2-butyne to W(C-*t*-Bu)(dme)Cl$_3$ yields violet diamagnetic complexes with the formula W(C-*t*-Bu)(RC$\equiv$CR)Cl$_3$.[8] ^{13}C NMR studies suggested that these species are tungstenacyclobutadiene complexes.[9] An X-ray structural study[10] of W(C-*t*-Bu)(MeC$\equiv$CMe)Cl$_3$ confirmed this proposal (Figure 1). The molecule is nearly a trigonal bipyramid with axial chloride ligands ($\angle$Cl(1)–W–Cl(2) = 166.12 (9)°) and

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(1) (a) Massachusetts Institute of Technology; (b) State University of New York at Buffalo.

(2) (a) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (b) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75.

(3) Clark, D. N.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 6774.

(4) Purple W(C-*t*-Bu)(dme)Cl$_3$ is prepared by treating W(C-*t*-Bu)(CH$_2$-*t*-Bu)$_3$ in a mixture of pentane, ether, and 1 equiv of 1,2-dimethoxyethane (dme) with 3 equiv of HCl: Schrock, R. R.; Clark, D. N.; Sancho, J.; Wengrovius, J. H.; Rocklage, S. M.; Pedersen, S. F. *Organometallics* **1982**, in press.

(5) W(C-*t*-Bu)(CH$_3$CH$_2$C$\equiv$CCH$_2$CH$_3$)$_2$Cl$_4$. Anal. Calcd for WC$_{17}$H$_{29}$Cl$_4$: C, 36.52; H, 5.23; Cl, 25.37. Found: C, 36.66; H, 5.28; Cl, 26.17. MW (differential vapor pressure, CH$_2$Cl$_2$, 0 °C); Calcd: 1118. Found: 1141 at 3×10^{-2} M.

(6) W(η^5-C$_5$Me$_4$-*t*-Bu)(MeC$\equiv$CMe)Cl$_2$ crystallizes in the monoclinic space group $P2_1/c$ with a = 8.411 (1) Å, b = 26.639 (5) Å, c = 8.971 (1) Å, β = 114.320 (1)°, and ρ(calcd) = 1.89 g cm^{-3} for Z = 4 and M_r 522.2. The final R_F = 3.2% for 181 variables refined against all 2244 absorption corrected data. This structure will be reported in its entirety by M.R.C. and H.J.W.

(7) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1981**, *20*, 387.

(8) W(C-*t*-Bu)(CH$_3$CH$_2$C$\equiv$CCH$_2$CH$_3$)Cl$_3$. Anal. Calcd for WC$_{11}$H$_{19}$Cl$_3$: C, 29.93; H, 4.34; Cl, 24.09. Found: C, 30.23; H, 4.50; Cl, 24.39.

(9) ^{13}C{^{1}H} NMR spectrum of W(C-*t*-Bu)(CH$_3$C$\equiv$CCH$_3$)Cl$_3$ (CD$_2$Cl$_2$) δ 267.5 and 263.4 (C$_\alpha$), 150.7 (C$_\beta$), 44.3 (C*C*Me$_3$), 29.5 (CC*Me*$_3$), 25.6 and 17.2 (C*Me*). ^{13}C{^{1}H} NMR spectrum of W(C-*t*-Bu)(CH$_3$CH$_2$C$\equiv$CCH$_2$CH$_3$)Cl$_3$ (C$_6$D$_6$): δ 267.6 and 266.7 (C$_\alpha$), 150.3 (C$_\beta$) 43.8 (C*C*Me$_3$), 32.0 and 24.5 (C*C*H$_2$CH$_3$), 29.8 (CC*Me*$_3$), 14.3 and 11.9 (CCH$_2$*C*H$_3$).

(10) W[C-*t*-BuCMeCMe]Cl$_3$ crystallizes in the centrosymmetric monoclinic space group $P2_1/c$ with a = 10.271 (2) Å, b = 10.113 (2) Å, c = 12.721 (3) Å, β = 96.10 (2)°, V = 1313.8 (5) Å^3, and ρ(calcd) = 2.09 g cm^{-3} for Z = 4 and M_r 413.4. Diffraction data were collected via a coupled 2θ–θ scan technique[11] using a Syntex P2$_1$ diffractometer and were corrected for absorption. All non-hydrogen atoms were located and refined, the final discrepancy factors being R_F = 4.6% and R_{wF} = 4.4% for all 2327 independent reflections (none rejected) with 4° ≤ 2θ ≤ 50.0°.

(11) Churchill, M. R.; Lashewycz, R. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 265.

0002-7863/82/1504-6808$01.25/0