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Reactive Alkyne Complexes of Tantalum and Their Metallacyclization Chemistry: Models for Alkyne Cyclotrimerization by the Early Transition Metals

Jamie R. Strickler, Pamela A. Wexler, and David E. Wigley*

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

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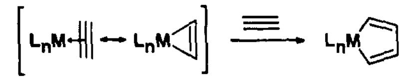
Summary: The reduction of $Ta(DIPP)_3Cl_2$ (DIPP = 2,6-diisopropylphenoxide) in the presence of bulky alkynes $RC{\equiv}CR'$ (R = R′ = Ph; R = Me_3Si, R′ = Me) provides the alkyne adducts $(DIPP)_3Ta(RC{\equiv}CR')$ in high yield. Unlike all previously known tantalum alkyne complexes, $(DIPP)_3Ta(PhC{\equiv}CPh)$ readily undergoes metallacyclization reactions with smaller alkynes $RC{\equiv}CR'$ (R = R′ = Me or Et) and terminal alkynes $RC{\equiv}CR'$ (R = CMe_3, $SiMe_3$, or Ph; R′ = H) to form the tantalacyclopentadienes $(DIPP)_3\overline{Ta(CPh{=}CPhCR'{=}C}R)$. The molecular structure of the related metallacyclic complex $(DIPP)_3\overline{Ta(CEt{=}CEtCEt{=}C}Et)$ has been determined. This compound crystallizes in the monoclinic space group $P2_1/n$ [No. 14] with a = 14.340 (15) Å, b = 16.322 (22) Å, c = 19.929 (11) Å, β = 94.05 (7)°, V = 4655.9 Å^3, and ρ(calcd) = 1.25 g cm^{-3} for mol wt 877.05 and Z = 4. Structure solution and refinement included 3191 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ of 9088 total (8245 unique) reflections measured for final discrepancy indices of R_F = 4.6% and R_{wF} = 4.5%. The molecular structure reveals a severely crowded coordination sphere, which is consistent with the fact that alkyne cyclotrimerization does not proceed beyond this point. By using the less crowded precursor $Ta(DIPP)_2Cl_3$ and decreasing the alkyne size from $Me_3SiC{\equiv}CSiMe_3$ to $PhC{\equiv}CPh$ to $MeC{\equiv}CMe$, successively higher coordinated alkyne cyclooligomers (C_2, C_4, and C_6 compounds, respectively) can be isolated.

A number of niobium and tantalum compounds catalytically cyclotrimerize[1] and polymerize[2] alkynes. Since metallacyclopentadienes (**3**) are most often implicated as cyclotrimerization intermediates,[3,4] one might expect these metallacycles to form by reacting isolable alkyne complexes (**1** or **2**) with more alkyne (Scheme I). However, known alkyne adducts of these metals, such as $(\eta^5\text{-}C_5Me_5)MCl_2(RC{\equiv}CR)$ (M = Nb,[5] Ta[6]) and $(\eta^5\text{-}C_5H_5)M(CO)_2(PhC{\equiv}CPh)$ (M = Nb,[7b] Ta[7c]), are unreactive toward other alkynes.[7-10] We have recently observed that alkoxide ligands can impart significantly different reactivity than that observed in cyclopentadienyl compounds[1c] and therefore sought to prepare tantalum alkyne complexes containing these ligands.

Scheme I



1 2 3

By reducing $Ta(DIPP)_3Cl_2$[11] (DIPP = 2,6-diisopropylphenoxide) with 2 equiv of Na/Hg in the presence of excess $PhC{\equiv}CPh$ (1.75 equiv in Et_2O, room temperature), an orange solution is obtained containing the complex $(DIPP)_3Ta(PhC{\equiv}CPh)$ (**4**) (eq 1). Pale yellow crystals

$$Ta(DIPP)_3Cl_2 + 2Na/Hg + RC{\equiv}CR' \rightarrow (DIPP)_3Ta(RC{\equiv}CR') \quad (1)$$

4, R = R′ = Ph
5, R = Me_3Si, R′ = Me

can be isolated in ca. 70% yield from pentane at −40 °C. Other bulky alkynes (viz. $Me_3SiC{\equiv}CMe$, eq 1) react similarly. The $^{13}C_{alkyne}$ resonance of **4** occurs at δ 216 ($CDCl_3$, 25 °C),[12] and hydrolysis of this compound (1:9 v/v in acetone) provides *cis*-PhCH=CHPh quantitatively (^1H NMR, internal standard). These data are consistent with a strongly bound, substantially reduced alkyne ligand[13] (structure **2**) analogous to that found in the cyclopentadienyl complexes $(\eta^5\text{-}C_5Me_5)MCl_2(RC{\equiv}CR)$.[5,6] However, unlike the cyclopentadienyl compounds, $(DIPP)_3Ta(PhC{\equiv}CPh)$ reacts readily at ambient temperature with other alkynes.

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(1) (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094. (b) Cotton, F. A.; Hall, W. T.; Cann, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233. (c) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525. (d) Lachmann, G.; Du Plessis, J. A. K.; Du Toit, C. J. *J. Mol. Catal.* **1987**, *42*, 151.

(2) See, for example: (a) Masuda, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473. (b) Masuda, T.; Niki, A.; Isobe, E.; Higashimura, T. *Macromolecules* **1985**, *18*, 2109.

(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 870–879.

(4) Other intermediates have been suggested, see: (a) Crocker, M.; Green, M.; Orpen, A. G.; Thomas, D. M. *J. Chem. Soc., Chem. Commun.* **1984**, 1141. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93.

(5) Belmonte, P. A.; Cloke, F. G. N.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 2365.

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

(7) (a) The compounds $(\eta^5\text{-}C_5H_5)M(CO)_2(PhC{\equiv}CPh)$ (M = Nb,[7b] Ta[7c]) react with $PhC{\equiv}CPh$ to give only $(\eta^5\text{-}C_5H_5)M(CO)(PhC{\equiv}CPh)_2$ and *not* metallacyclopentadienes. The free butadiene PhCH=CPhCPh=CHPh is formed only upon thermal degradation of the complexes.[7b,7c] (b) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, 100. (c) Aleksandrov, G. G.; Gusev, A. I.; Struchkov, Yu. T. *Zh. Strukt. Khim.* **1968**, *9*, 333.

(8) (a) We do not intend to slight the contributions made by workers who have observed the coupling of unsaturated moieties (including one alkyne) at tantalum or niobium centers; see, for example, ref 8b–d. (b) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4668. (c) Roskamp, E. J.; Pedersen, S. F. *Ibid.* **1987**, *109*, 6551. (d) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *Ibid.* **1987**, *109*, 6068.

(9) (a) No metallacyclic products are reported as byproducts from the syntheses of other tantalum alkyne adducts, e.g. ref 1a, 9b, and 9c. (b) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352. (c) Cotton, F. A.; Hall, W. T. *Ibid.* **1981**, *20*, 1285.

(10) (a) Reactions of this type are well established in the cobalt cyclization system; see, for example, ref 10b. (b) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907.

(11) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F. *Polyhedron* **1987**, *6*, 1765. See also ref 1c.

(12) Full spectroscopic and analytical details are available as supplementary material. Selected ^{13}C NMR data (C_6D_6, room temperature, unless otherwise noted): **4** ($CDCl_3$), δ 216.2 (C_{alkyne}); **5**, δ 226.0 (C_{alkyne}), 224.4 (C'_{alkyne}); **6**, δ 203.3 (C_α), 196.2 ($C_{\alpha'}$); **7** (toluene-d_8, 233 K), δ 204.4 (C_α), 199.9 ($C_{\alpha'}$); **9** (toluene-d_8), δ 210.7 (C_α), 203.8 ($C_{\alpha'}$); **10**, δ 203.6 (C_α), 200.4 ($C_{\alpha'}$); **13**, δ 224.9 (C_{alkyne}); **14**, δ 203.9 (C_α), 169.7 (C_β); **15**, δ 120.6 (C_6Me_6), 16.2 ($C_6\mathit{Me}_6$). Typical 2,6-diisopropylphenoxide resonances occur at δ 157 (C_{ipso}), 137 (C_o), 124 (C_p), 122 (C_m), 26 ($\mathit{C}HMe_2$), and 25 ($CH\mathit{Me}_2$). All carbon resonances of compounds **8–10** have not yet been located, due in part to more than one dynamic intramolecular process occurring over a wide temperature range, which effectively precluded undecoupled spectra in the regioselectivity assignments. Assignments are made as follows: **8**, C_α and $C_{\alpha'}$ are attached to *no* protons in attached proton test spectra and $^3J_{HH}$ = 15.8 Hz in $PhCH{=}CPhC\mathit{H}{=}C\mathit{H}(CMe_3)$; **9**, $^3J_{HH}$ = 18.7 Hz in $PhCH{=}CPhC\mathit{H}{=}C\mathit{H}(SiMe_3)$; **10**, $^3J_{HH}$ = 15.9 Hz in $PhCH{=}CPhC\mathit{H}{=}C\mathit{H}Ph$.

(13) (a) Alkyne ligands can be regarded not only as dianions but also as good π donors.[13b] (b) Theopold, K. H.; Holmes, S. J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1010.

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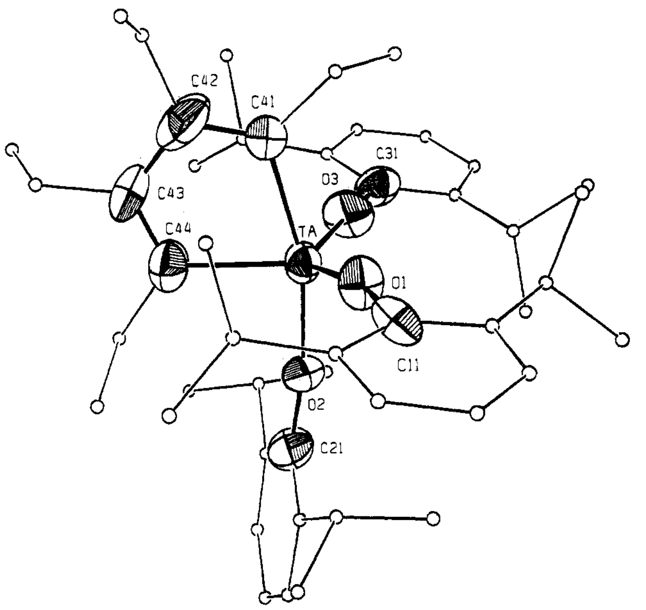
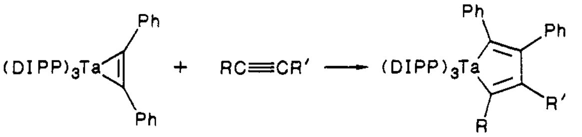


Figure 1. Molecular structure of $\mathrm{(DIPP)_3\overline{Ta\text{-}(CEt{=}CEtCEt{=}C}Et)}$ (DIPP = 2,6-diisopropylphenoxide) with the local coordination shown as 50% probability ellipsoids.

The addition of an excess of MeC≡CMe to a solution of $\mathrm{(DIPP)_3Ta(PhC{\equiv}CPh)}$ (≥2 equiv in $\mathrm{Et_2O}$, room temperature) results in an immediate color change from pale yellow to orange; orange crystals of $\mathrm{(DIPP)_3Ta(C_4Ph_2Me_2)}$ (**6**) form at −40 °C from pentane solution in 50% yield (eq 2). The ^{1}H NMR spectrum of **6** ($\mathrm{C_6D_6}$, 25 °C) includes



(2)

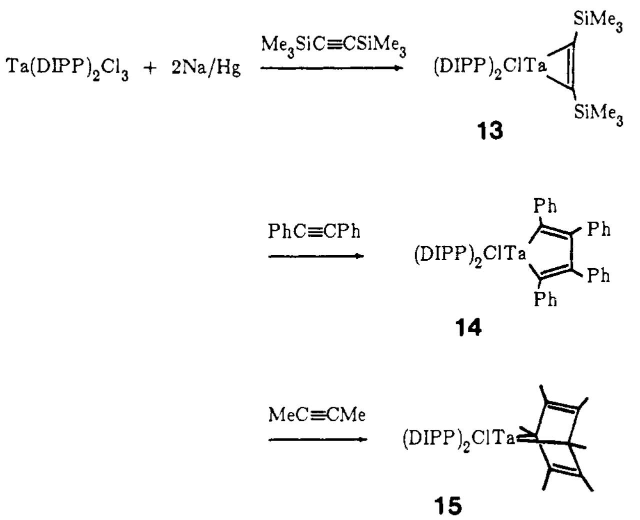
6, R = R′ = Me
7, R = R′ = Et
8, R = CMe$_3$, R′ = H
9, R = SiMe$_3$, R′ = H
10, R = Ph, R′ = H

two quartets at δ 2.38 and 1.80 (3 H each, α- and β-methyls, $^5J_{\mathrm{HH'}}$ (cis coupling) = 1.2 Hz) which do not equilibrate upon heating to 60 °C.[12] Additionally, the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR spectrum of **6** includes "$\mathrm{C_{alkyne}}$" resonances at δ 203 and 196 ($\mathrm{C_\alpha}$, $\mathrm{C_{\alpha'}}$) and δ 166 and 153 ($\mathrm{C_\beta}$, $\mathrm{C_{\beta'}}$).[12] Upon hydrolysis of **6**, PhCH=CPhCMe=CHMe is obtained in near quantitative yield (^{1}H NMR, internal standard). Compound **6** is clearly formulated as the metallacyclopentadiene complex $\mathrm{(DIPP)_3\overline{Ta(CPh{=}CPhCMe{=}C}Me)}$. Terminal alkynes RC≡CH (R = CMe$_3$, SiMe$_3$, and Ph) undergo metallacyclization with **4** with high regioselectivity (eq 2), as determined by NMR and by identification of the butadienes obtained upon protonolysis of **8** through **10**.[10,12] We have previously observed the formation of metallacycles $\mathrm{(DIPP)_3\overline{Ta(CR{=}CRCR{=}C}R)}$ (R = Me (**11**) or Et (**12**)) from the reduction of $\mathrm{Ta(DIPP)_3Cl_2}$ in the presence of 2-butyne or 3-hexyne, but in neither case was a discrete alkyne adduct isolated or observed.[1c,14]

The most suitable metallacyclopentadiene crystals for an X-ray study were obtained for compound **12**, $\mathrm{(DIPP)_3\overline{Ta(CEt{=}CEtCEt{=}C}Et)}$, the molecular structure of which is presented in Figure 1.[15,16] In the solid state, this compound assumes a trigonal-bipyramidal geometry with the small C41–Ta–C44 angle (75.7 (4)°) constraining the metallacyclic α-carbons to occupy one axial and one equatorial site. Bond length alternation in the carbon ring is evident,[17] and the metallacyclic ring is quite planar. Perhaps the most revealing structural feature is the severe crowding of the coordination sphere which is manifested in the linear Ta–O–$\mathrm{C_{ipso}}$ angles (from 165.2 (5)° to 174.6 (5)°).[17] Such crowding suggests that the "extent" of alkyne cyclotrimerization may be susceptible to steric effects in these early metal phenoxide compounds and is consistent with the fact that cyclotrimerization does not proceed further in this compound.[1c]

Scheme II

(DIPP = 2,6-Diisopropylphenoxide)



This steric control over cyclization is clear from the reactions presented in Scheme II. Using the less congested bis(phenoxide) complex $\mathrm{Ta(DIPP)_2Cl_3}$[18] and decreasing the alkyne size from Me$_3$SiC≡CSiMe$_3$ to PhC≡CPh to MeC≡CMe, successively higher coordinated cyclooligomers (alkyne adducts, tantalacyclopentadienes, and 7-tantalanorbornadienes,[1c] respectively) can be synthesized. Since this initial metallacyclization step has now been observed for tantalum and since 7-tantalanorbornadienes are active (though poor) cyclization catalysts,[1c] these alkoxide-supported d^2 compounds must be considered as relevant models for alkyne cyclization catalysts in the early transition metals. In addition, these alkoxides represent comparatively rare examples of reagents which can couple

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[14] (a) Wolczanski has reported the reaction of 2-butyne with (silox)$_3$Ta (silox = t-Bu$_3$SiO) which provides the adduct (silox)$_3$Ta(MeC≡CMe).[14b] (b) LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6382.

[15] Crystal data: monoclinic, space group $P2_1/n$; a = 14.340 (15) Å, b = 16.332 (22) Å, c = 19.929 (11) Å; β = 94.05 (7)°; V = 4655.9 Å^3; and ρ(calcd) = 1.25 g cm^{-3} for mol wt 877.05 and Z = 4. Structure solution and refinement included 3191 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ of 9088 total (8245 unique) reflections measured for final discrepancy indices are R_F = 4.6% and R_{wF} = 4.5%. Full structural details are available as supplementary material.

[16] (a) Two metallacyclopentadienes are known for niobium, one of which[16b] was synthesized from alkynes.[16b,c] These are the first reported tantalacyclopentadienes. (b) Sala-Pala, J.; Amaudrut, J.; Guerchais, J. E.; Mercier, R.; Douglade, J.; Theobald, J. G. *J. Organomet. Chem.* **1981**, *204*, 347. (c) Lemenovskii, D. A.; Baukova, T. V.; Zyzik, G.; Knizhnikov, V. A.; Fedin, V. P.; Perevalova, É. G. *Koord. Khim.* **1978**, *4*, 1033.

[17] Selected bond distances (Å): C41–C42 = 1.32 (1), C42–C43 = 1.49 (1), C43–C44 = 1.35 (1), Ta–C41 = 2.166 (9), Ta–C44 = 2.147 (8), Ta–O1 = 1.858 (4), Ta–O2 = 1.920 (5), Ta–O3 = 1.845 (5). Selected bond angles (deg): O1–Ta–O2 = 96.9 (2), O1–Ta–O3 = 124.3 (2), O1–Ta–C41 = 89.8 (3), O1–Ta–C44 = 118.5 (3), O2–Ta–O3 = 98.4 (2), O2–Ta–C41 = 164.9 (3), O2–Ta–C44 = 89.2 (3), O3–Ta–C41 = 88.9 (4), O3–Ta–C44 = 115.0 (3), C41–Ta–C44 = 75.7 (4), Ta–O1–C11 = 165.2 (5), Ta–O2–C21 = 170.8 (5), Ta–O3–C31 = 174.6 (5).

[18] Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 2575.

two different alkynes (including terminal alkynes) in a selective fashion.[19]

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also acknowledge support by a Flinn Foundation Grant of the Research Corp.

Supplementary Material Available: Analytical and spectroscopic data for compounds 4–10 and 13–15 and full details of the structure solution and tables of bond distances and angles, and atomic positional and thermal parameters for $(\mathrm{DIPP})_3\mathrm{Ta}(\mathrm{CEt{=}CEtCEt{=}CEt})$ (16 pages); listings of observed and calculated structure factor amplitudes (25 pages). Ordering information is given on any current masthead page.

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[19] (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987**, *109*, 2544.

Synthesis, Structure, and Reactivity of Complexes Containing the d^0 *cis*-ReO$_2$ Fragment

Shiang Cai, David M. Hoffman,* and Derk A. Wierda

Department of Chemistry, Harvard University
12 Oxford Street
Cambridge, Massachusetts 02138

Received May 5, 1988

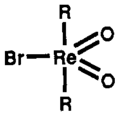
Summary: The Re(VII) *cis*-dioxo complexes $\mathrm{ReO_2(CH_2CMe_3)_2Br}$ and $\mathrm{ReO_2(CH_2CMe_3)_2X(py)}$ (X = Br, Cl, or F) have been prepared by oxidation of the Re(VI) dimer $[\mathrm{Re}(\mu\text{-O})\mathrm{O(CH_2CMe_3)_2}]_2$. Reaction of $\mathrm{ReO_2(CH_2CMe_3)_2Cl(py)}$ with an excess of $\mathrm{Zn(CH_2CMe_3)_2}$ gives $\mathrm{ReO_2(CH_2CMe_3)_3}$.

Complexes containing a d^0 *cis*-ReO$_2$ fragment are rare, and little is known concerning their structure and reactivity. In fact, the only well-characterized examples of these types of compounds are $\mathrm{ReO_2F_3}$ and $\mathrm{ReO_2R_3}$ (R = Me, $\mathrm{CH_2CMe_3}$, $\mathrm{CH_2SiMe_3}$).[1,2] The limited number of compounds available, together with the fact that the alkyl ligands in the organometallic $\mathrm{ReO_2R_3}$ compounds are not substitutionally labile, makes a comprehensive examination of the reaction chemistry difficult. We therefore set out to prepare complexes containing other types of ligands and report here the synthesis of the Re(VII) *cis*-dioxo alkyl halide complexes $\mathrm{ReO_2(CH_2CMe_3)_2Br}$ and $\mathrm{ReO_2(CH_2CMe_3)_2X(py)}$ (X = F, Cl, Br) by oxidation of the Re(VI) metal–metal singly bonded dimer $[\mathrm{Re}(\mu\text{-O})\mathrm{O(CH_2CMe_3)_2}]_2$ (**1**).[3,4]

The compound $\mathrm{ReO_2(CH_2CMe_3)_2Br}$ (**2**) is prepared by the formal oxidative addition of $\mathrm{Br_2}$ to the Re–Re bond in **1** (eq 1). Compound **2** is a volatile oil (mp −10 °C)

$$[\mathrm{Re}(\mu\text{-O})\mathrm{O(CH_2CMe_3)_2}]_2 + \mathrm{Br_2} \xrightarrow[15\ \mathrm{min}]{\mathrm{pentane}} \underset{72\%}{2\mathrm{ReO_2(CH_2CMe_3)_2Br}} \tag{1}$$

which can be vacuum distilled directly from the reaction mixture (23 °C, 10^{-4} Torr). The ^{1}H NMR spectra recorded for $\mathrm{CD_2Cl_2}$ solutions of **2** in the temperature range −90 to +23 °C consist of only two singlets, which suggests the neopentyl ligands lie in a mirror plane, and the IR spectrum has bands at 1001 and 961 cm^{-1} ($\mathrm{Re^{18}O_2}$, 951 and 916 cm^{-1}), the latter of greater intensity, which are charateristic of a *cis*-$\mathrm{M(=O)_2}$ moiety.[5] This spectroscopic data and the volatility of **2** are consistent with the monomeric trigonal-bipyramidal structure shown above, but the dimer formulation $\mathrm{R_2O_2Re}(\mu\text{-Br})_2\mathrm{ReO_2R_2}$, in which the rhenium centers are octahedrally coordinated, cannot be ruled out.[6]



R = $\mathrm{CH_2CMe_3}$

2

The inconvenience of handling and purifying oily $\mathrm{ReO_2(CH_2CMe_3)_2Br}$ prompted us to search for solid derivatives. Thus, we find compound **2** reacts rapidly with pyridine (eq 2) to give $\mathrm{ReO_2(CH_2CMe_3)_2Br(py)}$ (**3a**) which

$$\mathrm{ReO_2(CH_2CMe_3)_2Br} + \mathrm{py} \xrightarrow[10\ \mathrm{min}]{\mathrm{hexane/py}} \mathrm{ReO_2(CH_2CMe_3)_2Br(py)} \tag{2}$$

can be crystallized from concentrated hexane solutions (−50 °C). Complex **3a** is more conveniently prepared without isolating **2**, however, by sequentially carrying out reactions 1 and 2 in one flask and then extracting **3a** from the stripped reaction mixture with hexane. This procedure allows isolation of **3a** in 78% yield based on **1**. The chloride derivative $\mathrm{ReO_2(CH_2CMe_3)_2Cl(py)}$ (**3b**) is prepared in 43% yield by the reaction in pentane/pyridine (20:1) of **1** with an excess of $\mathrm{Cl_2}$ (eq 3). The yield of **3b**

$$[\mathrm{Re}(\mu\text{-O})\mathrm{O(CH_2CMe_3)_2}]_2 + \mathrm{Cl_2} + 2\mathrm{py} \xrightarrow[3\ \mathrm{min}]{\mathrm{pentane/py}} 2\mathrm{ReO_2(CH_2CMe_3)_2Cl(py)} \tag{3}$$

is lower (25%) if pyridine is added after the chlorination step. One possible explanation for the lower yield is that pyridine-free $\mathrm{ReO_2(CH_2CMe_3)_2Cl}$ is unstable to $\mathrm{Cl_2}$. $\mathrm{ReO_2(CH_2CMe_3)_2Cl(py)}$ can also be prepared by stirring **3a** in methylene chloride with an excess of AgCl (yield 90%).

The cation $[\mathrm{ReO_2(CH_2CMe_3)_2}]^+$, which is analogous to the known compound $\mathrm{MoO_2(mesityl)_2}$, is a logical Re(VII) *cis*-dioxo target molecule.[7] Our attempt to prepare $[\mathrm{ReO_2(CH_2CMe_3)_2}]^+$ by reacting **1** with an excess of $\mathrm{AgBF_4}$, however, did not give the cation as the final product; instead, $\mathrm{ReO_2(CH_2CMe_3)_2F(py)}$ (**3c**) is produced in 45% yield (eq 4). If $\mathrm{AgBPh_4}$ is substituted for $\mathrm{AgBF_4}$ in (4),

$$[\mathrm{Re}(\mu\text{-O})\mathrm{O(CH_2CMe_3)_2}]_2 + 2\mathrm{AgBF_4} + 4\mathrm{py} \xrightarrow[14\ \mathrm{days}]{\mathrm{pyridine}} 2\mathrm{ReO_2(CH_2CMe_3)_2F(py)} + 2\mathrm{Ag} + 2\mathrm{py{\cdot}BF_3} \tag{4}$$

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[1] (a) Beattie, I. R.; Crocombe, R. A.; Ogdden, K. S. *J. Chem. Soc., Dalton Trans.* **1977**, 1481. (b) Mertis, K.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1976**, 1488. (c) Cai, S.; Hoffman, D. M.; Wierda, D. A. *J. Chem. Soc., Chem. Commun.* **1988**, 313. (d) Cai, S.; Hoffman, D. M.; Lappas, D.; Woo, H.-G. *Organometallics* **1987**, *6*, 2273.

[2] Recent review articles on related oxo chemistry include: (a) Holm, R. H. *Chem. Rev.* **1987**, *87*, 1401. (b) Bottomley, F.; Sutin, L. *Adv. Organomet. Chem.* **1988**, *28*, 339. (c) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

[3] (a) Cai, S.; Hoffman, D. M.; Huffman, J. C.; Wierda, D. A.; Woo, H.-G. *Inorg. Chem.* **1987**, *26*, 3693. (b) Huggins, J. M.; Whitt, D. R.; Lebioda, L. *J. Organomet. Chem.* **1986**, *312*, C15.

[4] Full preparative details and characterization data, including ^{1}H and ^{13}C NMR, IR, and analytical data, are available for all new compounds as supplementary material.

[5] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley: New York, 1970; pp 114–115.

[6] Compound **2** decomposes in solution. Thus far, this has made it impossible to obtain consistent molecular weight data.

[7] Heyn, B.; Hoffmann, R. *Z. Chem.* **1976**, *16*, 195.

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