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 $(DIPP)_3Ta(CEt{=}CEtCEt{=}CEt)$ (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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Synthesis, Structure, and Reactivity of Complexes Containing the d^0 *cis*-ReO$_2$ Fragment

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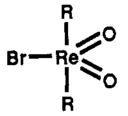
Summary: The Re(VII) *cis*-dioxo complexes $ReO_2(CH_2CMe_3)_2Br$ and $ReO_2(CH_2CMe_3)_2X(py)$ (X = Br, Cl, or F) have been prepared by oxidation of the Re(VI) dimer $[Re(\mu\text{-}O)O(CH_2CMe_3)_2]_2$. Reaction of $ReO_2(CH_2CMe_3)_2Cl(py)$ with an excess of $Zn(CH_2CMe_3)_2$ gives $ReO_2(CH_2CMe_3)_3$.

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 ReO_2F_3 and ReO_2R_3 (R = Me, CH_2CMe_3, CH_2SiMe_3).[1,2] The limited number of compounds available, together with the fact that the alkyl ligands in the organometallic 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 $ReO_2(CH_2CMe_3)_2Br$ and $ReO_2(CH_2CMe_3)_2X(py)$ (X = F, Cl, Br) by oxidation of the Re(VI) metal–metal singly bonded dimer $[Re(\mu\text{-}O)O(CH_2CMe_3)_2]_2$ (**1**).[3,4]

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

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

which can be vacuum distilled directly from the reaction mixture (23 °C, 10^{-4} Torr). The ^1H NMR spectra recorded for 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} ($Re^{18}O_2$, 951 and 916 cm^{-1}), the latter of greater intensity, which are charateristic of a *cis*-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 $R_2O_2Re(\mu\text{-}Br)_2ReO_2R_2$, in which the rhenium centers are octahedrally coordinated, cannot be ruled out.[6]



R = CH$_2$CMe$_3$

2

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

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

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 $ReO_2(CH_2CMe_3)_2Cl(py)$ (**3b**) is prepared in 43% yield by the reaction in pentane/pyridine (20:1) of **1** with an excess of Cl_2 (eq 3). The yield of **3b**

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

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

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

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

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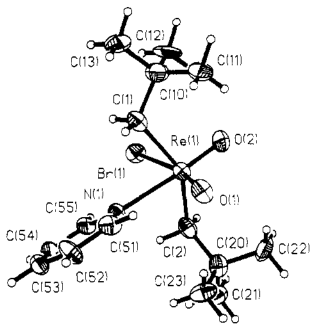

Figure 1. ORTEP plot of $ReO_2(CH_2CMe_3)_2Br(py)$ (**3a**) showing the atom-numbering scheme (50% probability level). Selected distances (Å) and angles (deg): Re(1)–Br(1), 2.680 (1); Re(1)–O(1), 1.696 (7); Re (1)–O(2), 1.680 (7); Re(1)–N(1), 2.396 (7); Br(1)–Re(1)–O(1), 165.6 (2); O(1)–Re(1)–O(2), 107.4 (3); O(1)–Re(1)–C(1), 95.6 (3); O(2)–Re(1)–C(1), 103.4 (4); O(1)–Re(1)–C(2), 100.0 (4); O(2)–Re(1)–C(2), 99.3 (4); Br(1)–Re(1)–N(1), 83.7 (2); O(2)–Re(1)–N(1), 170.7 (3); C(1)–Re(1)–N(1), 75.0 (3); C(2)–Re(1)–N(1), 78.8 (3).

a mixture of products is obtained which we have not yet been able to separate.

The structure of **3a** has been determined by an X-ray crystallography study; an ORTEP drawing of one of the two similar independent molecules in the unit cell is given in Figure 1.[8] One noteworthy strucural feature in **3a** is the bending of the neopentyl methylene groups away from the Re═O multiple bonds (C(1)–Re–C(2) = 147.1 (4)°). An analogous structural feature was also observed in the octahedral *cis*-dioxo *trans*-dialkyl compounds $MoO_2R_2(bpy)$ (R = Me, CH_2CMe_3, CH_2Ph).[9] In all of these complexes it is likely that the closed $RH_2C{-}M{-}CH_2R$ angles are due to electronic effects because the bending facilitates metal p_x–d_{xz} mixing (*xz* plane bisecting the O–M–O angle), which in turn enhances Re–O π bonding.[10]

The pyridine ligands in **3a–c** rapidly dissociate on the ^1H NMR time scale at 23 °C, but spectra recorded for the compounds at low temperatures (<−35 °C) are consistent with expectations based upon the solid-state structure of **3a**; e.g., **3c** reveals an AB quartet with coupling to ^{19}F ($^2J_{HH}$ = 12.1 Hz, $^3J_{H_aF}$ = 9.2 Hz, $^3J_{H_bF}$ = 13.8 Hz, $CH_aH_bCMe_3$) and a singlet (CH_2CMe_3) as well as five separate resonances assigned to the protons of coordinated pyridine.

In order to determine if substitution reactions can be carried out on the Re(VII) complexes without reduction of the metal center, we attempted the preparation of $ReO_2(CH_2CMe_3)_3$ (**4**)[1c] from **3a** and **3b**. Compound **3b** reacts with an excess of $Zn(CH_2CMe_3)_2$ (eq 5) to give **4** in

$$ReO_2(CH_2CMe_3)_2Cl(py) + Zn(CH_2CMe_3)_2 \xrightarrow[-5\ ^\circ C,\ 30\ min]{toluene} ReO_2(CH_2CMe_3)_3 + ZnCl(CH_2CMe_3) \quad (5)$$

79% yield and a small amount of **1**,[3] a product of reduction. Under similar conditions, reaction of **3a** with an excess of $Zn(CH_2CMe_3)_2$ generates **4** and **1** in 53% and 26% isolated yields, respectively, indicating, as expected, that the bromide complex is more easily reduced than the chloride.

We have shown that oxidation reactions can be used to prepare Re(VII) *cis*-ReO_2 complexes from Re(VI) $[Re(\mu\text{-}O)O(CH_2CMe_3)_2]_2$ in moderate to good yields. Similar oxidation reactions involving the Re(VI) dimers $[Re(\mu\text{-}O)O(R)_2]_2$ (R = Me,[11] CH_2SiMe_3,[1d] CH_2CMe_2Ph[3b]) should yield Re(VII) compounds analogous to **3a–c**. Additionally, reaction 5 shows that substitution of halide by alkyl can be accomplished with only a small amount of undesirable Re(VII) reduction. Substitutions of the halides with other types of ligands (e.g., alkoxides via trimethylalkoxysilane reagents) are therefore feasible. Further studies concerning the reactivity of **2** and **3a–c** are in progress.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research.

Supplementary Material Available: Experimental procedures and spectroscopic data for all new compounds, procedure for the X-ray structure determination, complete tables of bond distances and angles, atomic coordinates, non-hydrogen atom anisotropic displacement parameters, a packing diagram, and an ORTEP plot of the other independent molecule in the unit cell (19 pages); a listing of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

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(8) Crystal data for $C_{15}H_{27}NO_2BrRe$ at −80 (1) °C: triclinic, space group $P\bar{1}$, a = 10.304 (3) Å, b = 12.360 (4) Å, c = 14.553 (4) Å, α = 90.72 (2)°, β = 93.77 (2)°, γ = 91.59 (2)°, Z = 4. A total of 5909 reflections were collected in the range 4° < 2θ < 45° (0,−k,−l to h,k,l). Of these, 4852 were unique reflections and 3897 with $F_0 > 4\sigma(F_o)$ were used in the structure solution. $R(F) = 0.0364$; $R_w(F) = 0.0409$.

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(10) See Figure 15.4 on p 292 and its accompanying discussion in the following reference: Albright, T. A. Burdett, J. K.; Whangbo, M. H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985.

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Selective Formation of Alkenylcyclopentadienyl Substituents by Means of Olefin/Butadiene Coupling at Zirconium

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Summary: Coupling of a Cp-bonded (Cp = cyclopentadienyl) substituent with a C_4H_6 unit at zirconium is observed by reacting $(\eta^5\text{-}C_5H_4CH_2CH{=}CH_2)_2ZrCl_2$ (**5**) with the (butadiene)magnesium reagent **6**. Treatment of the resulting metallacyclic π-allyl-type coupling product **8** with stoichiometric gaseous HCl yields the mixed Cp-substituted metallocene dihalide (Cp-allyl) $[\eta^5\text{-}C_5H_4(CH_2)_4CH{=}CHCH_3]ZrCl_2$ (**9**). Repetition of this reaction sequence cleany converts **9** into $[\eta^5\text{-}C_5H_4(CH_2)_4CH{=}CHCH_3]_2ZrCl_2$ (**11**). The *trans*-5-heptenylcyclopentadienyl substituent is prepared regio- and stereoselectively by the CC coupling/HCl addition reaction at the early-transition-metal center.

Substituted η-cyclopentadienyl ligands are gaining ever increasing importance in organometallic chemistry; e.g., using various new Cp-substituted metal complexes has led to very interesting developments of novel catalyst systems recently.[1] An increasing number of synthetic entries to

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