(0.0665 g) were dissolved in 1,2-dichloroethane (20 mL), and the solution was purged with argon for 45 min. The solution was transferred with use of a cannula into an argon-filled flask containing complex **2** (0.1618 g, 0.203 mmol) and $(CH_3CN)_2PdCl_2$ (0.1569 g, 0.665 mmol). The solution was stirred, and samples were removed periodically for GC analysis. The yield of *exo*-2,3-epoxynorbornane reached 74% after 10 min and then declined (23% after 6.5 h). A small amount of norcamphor (~10%) also formed. In addition, a product appeared concomitant with the decrease in epoxide. GC–MS showed this to have a molecular weight of 204, in agreement with the formula $C_{14}H_{20}O$ (norbornene + epoxynorbornane).

**B. Oxidation by 10.** A solution of norbornene (0.211 g, 2.24 mmol) in nitromethane (8 mL) was purged with argon for 30 min. Complex **10** (0.144 g, 0.296 mmol) was added and the flask sealed with a rubber septum. The flask was immersed in a hot oil bath (65 °C), the contents were stirred, and samples were removed periodically for GC analysis. A peak with a retention time corresponding to that of norcamphor rapidly grew in. After approximately 28 h, biphenyl (0.254 g) was added as an internal standard. Analysis showed a 23% yield of norcamphor, and GC–MS confirmed the identification of the ketone.

**C. Oxidation by 7 in the Presence of $(PhCN)_2PdCl_2$.** A solution of norbornene (0.073 g, 0.775 mmol) in acetonitrile (8 mL) was purged with argon for 30 min. $(PhCN)_2PdCl_2$ (0.1062 g, 0.277 mmol) and complex **7** (0.0603 g, 0.085 mmol) were added. The flask was sealed with a rubber septum and immersed in a hot oil bath (70 °C). After ~4.5 h, biphenyl (0.0069 g) was added. Periodic GC analysis showed the production of norcamphor with the yield reaching 20% after 1 day.

A solution of *exo*-2,3-epoxynorbornane (0.002 g) in $CH_3CN$ (2 mL) was added. GC analysis after 25 min showed that all the epoxide had reacted.

**Reaction of Complex 9 with Epoxides. A. exo-2,3-Epoxynorbornane.** A solution of *exo*-2,3-epoxynorbornane (0.0122 g, 0.11 mmol) in nitromethane (5 mL) was purged with argon for 45 min. Complex **9** (0.0869 g, 0.18 mmol) was added, and the flask was sealed with a rubber septum. The flask was immersed in a hot oil bath (65 °C), and samples were removed periodically for GC analysis. The reaction was complete in approximately 5 min. The peak corresponding to the epoxide had disappeared, and a small peak corresponding to a low yield of norcamphor had grown in.

**B. 1,2-Epoxyoctane.** Nitromethane (5 mL) was purged with argon for 45 min. 1,2-Epoxyoctane (15 μL) was added, followed by complex **8** (0.0733 g). The flask was sealed with a septum and immersed in a hot oil bath (60 °C). GC analysis after 5 min revealed the complete disappearance of the epoxide and the production of a low yield of 2-octanone.

**Registry No.** **1**, 69377-51-1; **2**, 75778-52-8; **3**, 77933-52-9; **4**, 37726-78-6; **5**, 84642-19-3; **6**, 82411-90-3; **7**, 84623-37-0; **8**, 53738-55-9; **9**, 62793-29-7; **10**, 84623-39-2; **11**, 84623-40-5; **12**, 40770-06-7; **13**, 84623-41-6; **14**, 40231-80-9; **15**, 77944-62-8; ethylene, 74-85-1; 1-octene, 111-66-0; norbornene, 498-66-8.

---

Contribution No. 2751 from the Central Research and Development Department,
E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

# Synthesis of Some $d^0$ Organoimido Complexes of the Early Transition Metals

WILLIAM A. NUGENT

*Received June 14, 1982*

A series of $d^0$ *tert*-alkylimido complexes has been prepared for the group 5–7 transition metals. The complexes have the general formula $M(NR)_nX_{4-n}$ where X is a monoanionic ligand and R is a tertiary alkyl group. Complexes where M = Nb, Ta, or W were prepared by in situ deprotonation of *tert*-alkylamido ligands. Complexes where M = V, Cr, Mo, or Re were prepared by treatment of the metal oxide or oxychloride with the corresponding *tert*-alkyl(trimethylsilyl)amine. Ligand exchange and insertion reactions gave access to a range of X ligands; examples include complexes with OR, $OSiR_3$, NHR, $NR_2$, $S_2CNR_2$, $CH_3$, Cl, and Br substituents.

## Introduction

Transition-metal imido (NH and NR) complexes are currently the focus of increasing research activity. Recently, the reactions of imido complexes have been studied as mechanistic models for important industrial processes including the Haber ammonia synthesis,[1] the reduction of nitriles,[2] and the ammoxidation of propylene.[3] Related species have been prepared as models for the intermediates in various enzymatic transformations.[4,5] Organoimido ligands have been increasingly utilized as ancillary ligands in organometallic chemistry,[6] and recent theoretical studies[7] suggest that imido ligands may prove uniquely effective in promoting catalytic olefin metathesis.

Recently we have reported several structural studies[8] on imido derivatives of the early transition metals. The novel imido complexes were generally obtained in high yield and have a number of potentially useful properties including re-

---

(1) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572–1574.

(2) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255–7259.

(3) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759–1760.

(4) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589–625.

(5) Mansuy, D.; Battioni, P.; Mahy, J. P. *J. Am. Chem. Soc.* **1982**, *104*, 4487–4489.

(6) (a) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077–3081. (b) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J. *J. Chem. Soc., Chem. Commun.* **1981**, 103–104. (c) Kress, J.; Wesolek, M.; Ny, J.-P. L.; Osborn, J. A. *Ibid.* **1981**, 1039–1040. (d) Chiu, K. W.; Jones, R. A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1981**, 2088–2097. (e) Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 31–36. (f) Thorn, D. L.; Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1981**, *103*, 357–363.

(7) Rappe, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 448–456.

(8) (a) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579–580. (b) Nugent, W. A.; Harlow, R. L. *Ibid.* **1979**, 342–343. (c) Nugent, W. A.; Harlow, R. L. *Ibid.* **1979**, 1105–1106. (d) Nugent, W. A.; Harlow, R. L. *Inorg. Chem.* **1979**, *18*, 2030–2032. (e) Nugent, W. A.; Harlow, R. L. *Ibid.* **1980**, *19*, 777–779. (f) Nugent, W. A.; Harlow, R. L.; McKinney, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 7265–7268.

0020-1669/83/1322-0965$01.50/0

markable thermal stability and solubility in hydrocarbons. Because of the current interest in this area, we now report synthetic details for these compounds.

The chemistry of transition-metal imido complexes was recently reviewed.[9] Considerable additional work in this area has appeared since that review.[10-12]

## Results and Discussion

**Group 5 Derivatives.** Treatment of freshly sublimed $TaCl_5$ with lithium dimethylamide and lithium *tert*-butylamide yielded, upon filtration, concentration, and cooling, ca. 40% of (*tert*-butylimido)tris(dimethylamido)tantalum as white hexagonal plates (eq 1). The analogous reaction with $NbCl_5$ afforded, after sublimation, ca. 20% of (*tert*-butylimido)tris(dimethylamido)niobium as a yellow crystalline solid. Compound **1a** (but not **1b**) could also be prepared by direct aminolysis of the dimethylamide according to reaction 2. An X-ray crystal structure showed **1a** is monomeric with three planar dimethylamido ligands and a linear *tert*-butylimido ligand.[8a]

$$MCl_5 + 4LiNMe_2 + LiNH\text{-}t\text{-}Bu \rightarrow (Me_2N)_3M(N\text{-}t\text{-}Bu) + 5LiCl + Me_2NH \quad (1)$$

**1a**, M = Ta
**1b**, M = Nb

$$Ta(NMe_2)_5 + t\text{-}BuNH_2 \rightarrow \mathbf{1a} + 2Me_2NH \quad (2)$$

The dimethylamido ligands of compounds **1** underwent the usual[13] insertion reactions with $CO_2$ and $CS_2$ to afford carbamate and dithiocarbamate derivatives, respectively. The synthetic utility of this reaction was demonstrated by the preparation and characterization of $(dtc)_3Ta(N\text{-}t\text{-}Bu)$ from **1a** and carbon disulfide (dtc = dimethyldithiocarbamate ligand).

We first attempted to prepare vanadium(V) imido complexes by the oxidation of $VCl_3(thf)_3$ with $Me_3SiN_3$ by analogy with the work of Chatt and co-workers on molybdenum imido complexes.[14] However, this led only to replacement of a chloride ligand by azide. The resultant soluble azidovanadium(III) species could be isolated by addition of pyridine or triphenylphosphine oxide or alternatively as the corresponding "ate" complex **2** according to eq 3. Therefore an alternative approach to vanadium(V) imido compounds was sought.

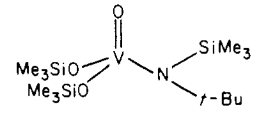
$$VCl_3(thf)_3 + Me_3SiN_3 \xrightarrow[(2)\ NBu_4Cl]{(1)\ -Me_3SiCl} \underset{\mathbf{2}}{NBu_4[(thf)_2VCl_3(N_3)]} \quad (3)$$

Compound **3** was prepared by reaction of chlorobis(trimethylsiloxo)oxovanadium[15] with *tert*-butyl(trimethylsilyl)amine[16] in hexane at −78 °C (eq 4). When the initially red-brown solution was warmed to room temperature, it became bright yellow. Filtration for the removal of $t\text{-}BuNH_2(SiMe_3)Cl$, distillation of the solvent, and recrystallization from hexamethyldisiloxane at −40 °C affords ca. 80% of **3a** as yellow sublimable needles. **3b** was prepared in a similar manner but in much lower yield with 1-adamantyl(trimethylsilyl)amine. The occurrence of linear alkylimido ligands in compounds **3** was indicated by their $^{51}V$ NMR spectra and by an X-ray crystal structure of **3b**.[8b]

$$(Me_3SiO)_3OVCl + 2RNH(SiMe_3) \rightarrow (Me_3SiO)_3V(NR) + RNH_2(SiMe_3)^+Cl^- \quad (4)$$

**3a**, R = *tert*-butyl
**3b**, R = 1-adamantyl

It is likely[17] that eq 4 proceeds via the intermediacy of the *tert*-butyl(trimethylsilyl)amide derivative **4**. The facile rearrangement of **4** can be rationalized in terms of the greater strength of the Si–O vs. that of the Si–N bond and the relief of steric repulsion in this congested amide intermediate.



4

**Group 6 Derivatives.** When the dioxydichlorides of chromium or molybdenum were treated with *tert*-butyl(trimethylsilyl)amine in refluxing hexane, the crystalline complexes **5a** and **5b** could be isolated in good yield. Although the insoluble products of this reaction were not characterized, the formation of products **5** can be rationalized by eq 5.

$$MCl_2O_2 + 4RNH(SiMe_3) \rightarrow (Me_3SiO)_2M(NR)_2 + 2RNH_2(SiMe_3)^+Cl^- \quad (5)$$

**5a**, M = Cr, R = *tert*-butyl
**5b**, M = Mo, R = *tert*-butyl
**5c**, M = Mo, R = 1-norbornyl

Excess $t\text{-}BuNH(SiMe_3)$ appears to be required for complete reaction in the case of **5a**. Preliminary X-ray crystallographic data show **5a** to be monomeric.[18] **5a** can also be prepared directly from $CrO_3$ and *tert*-butyl(trimethylsilyl)amine in refluxing hexane in 30% recrystallized yield.

The bridgehead norbornyl analogue **5c** was also prepared according to eq 5 with 1-norbornyl(trimethylsilyl)amine. However, the reaction of $MoO_2Cl_2$ with 1-adamantyl(trimethylsilyl)amine did not afford the corresponding adamantylimido compound. Instead, it gave the unusual octahedral alkylamido complex *trans*-$(AdNH)_2Mo(OSiMe_3)_4$, the X-ray crystal structure of which we have reported elsewhere.[8e]

Compound **5a** was cleanly converted to the corresponding monooxo derivative $(Me_3SiO)_2CrO(N\text{-}t\text{-}Bu)$ by treatment with

---

(9) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123–175.

(10) For Group 5 imido complexes: (a) Wiberg, N.; Haring, H.-W.; Schubert, U. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1980**, *35B*, 599–603. (b) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223–226. (c) Lemenovskii, D. A.; Konde, S. A.; Perevalova, E. G. *J. Organomet. Chem.* **1982**, *226*, 223–227. (d) Preuss, F.; Towae, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 1130–1135.

(11) For group 6 imido complexes: (a) Dehnicke, K.; Weiher, U.; Fenske, D. *Z. Anorg. Allg. Chem.* **1979**, *456*, 71–80. (b) *Ibid.* **1979**, *457*, 105–114. (c) Weller, F.; Muller, U.; Weiher, U.; Dehnicke, K. *Ibid.* **1980**, *460*, 191–199. (d) Korswagen, R.; Weidenhammer, K.; Ziegler, M. I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34B*, 1507–1511. (e) Korswagen, R.; Ziegler, M. I. *Ibid.* **1980**, *35B*, 1196–1200. (f) Henderson, R. A.; Davies, G.; Dilworth, J. R. *J. Chem. Soc., Dalton Trans.* **1981**, 40–50. (g) Chisholm, M. H.; Folting, K.; Huffmann, J. C.; Kirkpatrick, C. C.; Ratermann, A. L. *Inorg. Chem.* **1982**, *21*, 978–982. (h) Edelblut, A. W.; Wentworth, R. A. D. *Ibid.* **1980**, *19*, 2006–2010. (i) *Ibid.* **1980**, *19*, 1100–1117. (j) Maata, E. A.; Haymore, B. L.; Wentworth, R. A. D. *Ibid.* **1980**, *19*, 1055–1059. (k) Bevan, P. C.; Chatt, J.; Dilworth, J. R.; Henderson, R. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1982**, 821–824.

(12) For group 7 imido complexes: (a) Weiher, U.; Dehnicke, K.; Fenske, D. *Z. Anorg. Allg. Chem.* **1979**, *457*, 115–122. (b) La Monica, G.; Cenini, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1145–1149. (c) La Monica, G.; Cenini, S.; Porta, F. *Inorg. Chim. Acta* **1981**, *48*, 91–95. (d) Chiu, K. W.; Wong, W.-K.; Wilkinson, G.; Galas, A. M. R.; Hursthouse, M. B. *Polyhedron* **1982**, *1*, 37–44.

(13) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273–280.

(14) Chatt, J.; Choukroun, R.; Dilworth, J. R.; Hyde, J.; Vella, P.; Zubieta, J. *Transition Met. Chem.* (*Weinheim, Ger.*) **1979**, *4*, 59–63.

(15) Schmidt, M.; Schmidbauer, H. *Angew. Chem.* **1959**, *71*, 220.

(16) Pike, R. M. *J. Org. Chem.* **1961**, *26*, 232–236.

(17) (a) A rearrangement similar to that in eq 4 has been demonstrated for a phosphorus(V) (trimethylsilyl)amide: Neilson, R. H.; Jacobs, R. D.; Scheirman, R. W.; Wilburn, J. C. *Inorg. Chem.* **1978**, *17*, 1880–1882. (b) This synthetic approach is based on the work of Bürger and co-workers. They reported IR and NMR evidence that the reaction of $NaN(SiMe_3)_2$ with $VOCl_3$ afforded $[(Me_3Si)_2N]_2(Me_3SiO)V(NSiMe_3)$: Burger, H.; Smrekar, O.; Wannagat, U. *Monatsh. Chem.* **1964**, *95*, 292–302.

(18) A monomeric model for this structure gave an *R* index of approximately 0.06, but the complex appears disordered. Unit cell parameters at −47 °C are *a* = 12.840 (5) Å, *b* = 9.362 (3) Å, and *c* = 18.333 (6) Å, and the probable space group is orthorhombic, *Pbcn*.

1 equiv of benzaldehyde. The organic side product was the Schiff base benzylidene-*tert*-butylamine. This side product was conveniently removed by treatment with methyl triflate at room temperature to precipitate it as the iminium salt.

The tungsten analogues of compounds **5** could not be prepared via eq 5. (Neither $WO_2Cl_2$ nor $UO_2Cl_2$ reacted with *tert*-butyl-(trimethylsilyl)amine in refluxing hexane.) However, an alternative route to tungsten *tert*-butylimido complexes was developed. Tungsten hexachloride reacted violently with *tert*-butylamine in methylene chloride, and no discrete products could be isolated. However, in hexane, where $WCl_6$ has limited solubility, its reaction with excess *tert*-butylamine proceeds according to eq 6. Hexane-soluble **6** is readily separated from the insoluble *tert*-butylammonium chloride. Recrystallization from toluene at −40 °C affords white cubes of **6**, which was shown to be monomeric in a preliminary X-ray crystallographic study.[19] Protonolysis of **6** as in eq 7 affords additionally **7a** as a yellow distillable oil and **7b** as colorless crystals (eq 7).

$$WCl_6 + 10\ t\text{-}BuNH_2 \rightarrow \underset{\mathbf{6}}{(t\text{-}BuN)_2W(NH\text{-}t\text{-}Bu)_2} + 6\ t\text{-}BuNH_3Cl \quad (6)$$

$$\mathbf{6} + 2ROH \rightarrow \underset{\substack{\mathbf{7a},\ R = t\text{-}Bu \\ \mathbf{7b},\ R = Si(Ph)_3}}{(t\text{-}BuN)_2W(OR)_2} + 2\ t\text{-}BuNH_2 \quad (7)$$

The reaction of compound **7a** or **5b** with dimethylzinc in hexane, followed by cooling to −40 °C in the latter case, proceeds according to eq 8. Red-orange crystals of **8a** (60%) or violet **8b** (52% after recrystallization) precipitated from solution and were collected by filtration. The X-ray crystal structures of compounds **8** have been reported.[3,6f] An attempt to prepare **8a** directly from **6** and dimethylzinc led instead to a white crystalline solid believed to be the bimetallic derivative $(t\text{-}BuNH)_2(t\text{-}BuN)(CH_3)W[N(t\text{-}Bu)(ZnCH_3)]$. The NMR spectrum was consistent with a formulation wherein one methyl group was bonded to tungsten and one to zinc.

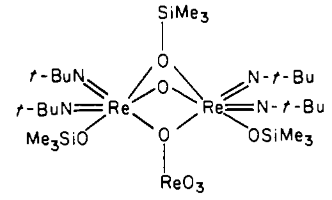
$$2(t\text{-}BuN)_2M(OR)_2 + 4Me_2Zn \rightarrow \underset{\substack{\mathbf{8a},\ M = W \\ \mathbf{8b},\ M = Mo}}{[(t\text{-}BuN)_2M(CH_3)_2]_2} + 4MeZnOR \quad (8)$$

The treatment of **8b** in hexane with elemental bromine (at room temperature) or chlorine (at −78 °C) resulted in each case in the formation of a yellow precipitate. Elemental analysis suggests that these reactions proceed according to eq 9 to afford the dihalides, **9**, but that the products are somewhat impure. To date, we have been unable to prepare complexes **9** completely free of impurities.

$$\mathbf{8b} + X_2 \rightarrow \underset{\substack{\mathbf{9a},\ X = Cl \\ \mathbf{9b},\ X = Br}}{2(t\text{-}BuN)_2MoX_2} \quad (9)$$

**Rhenium Derivatives.** Trimethylsilyl perrhenate[20] was treated with excess *tert*-butyl(trimethylsilyl)amine in hexane (48 h, 25 °C; eq 10). After distillation of the solvent, the resultant yellow oil was distilled in vacuo and then redissolved in hexamethyldisiloxane. Cooling to −40 °C afforded yellow needles of (trimethylsiloxo)tris(*tert*-butylimido)rhenium (**10**). In contrast, the reaction of trimethylsilyl perrhenate with an insufficiency of $t\text{-}BuNH(SiMe_3)$ affords a yellow low-melting solid, which was shown by means of an X-ray crystal structure[8c] to be **11**. Although the mechanism of its formation is not known, **11** may be rationalized as the product of silylation of the dimer $[(Me_3SiO)Re(N\text{-}t\text{-}Bu)_2O]_2$ by $Me_3SiOReO_3$.

$$Me_3SiOReO_3 + 3\ t\text{-}BuNH(SiMe_3) \rightarrow \underset{\mathbf{10}}{Me_3SiORe(N\text{-}t\text{-}Bu)_3} + 3Me_3SiOH \quad (10)$$



**11**

We have recently prepared trimethylsilyl pertechnetate, which corresponds to the $Me_3SiOReO_3$ starting material used for our preparation of Re imido complexes. Since this compound has apparently not been previously reported, and since there is current interest in technetium coordination chemistry, synthetic details are also given below.

## Experimental Section

Elemental analyses were done by the Physical and Analytical Division of the Du Pont Central Research and Development Department. All reactions and subsequent manipulations were carried out under dry nitrogen. The $^{13}C$ NMR spectra of the new complexes are discussed elsewhere.[22]

In several of the preparations described below, hexamethyldisiloxane was used as a recrystallization solvent. Its use appears to be advantageous for the crystallization of waxy low-melting solids in general; in several cases X-ray quality crystals were obtained when other hydrophobic solvents gave poor crystals or none at all. We are grateful to Dr. W. H. Knoth of this department for suggesting its use in this regard.

**Materials.** The following were sparged with dry nitrogen and stored over 4A molecular sieves: *tert*-butylamine, hexane, ether, toluene, hexamethyldisiloxane, methylene chloride, and carbon disulfide. Reagent grade $NbCl_5$ and $TaCl_5$ were sublimed in vacuo prior to use.

Silver perrhenate was prepared by oxidation of recovered rhenium oxides with nitric acid followed by precipitation with silver nitrate.[20] 1-Norbornylamine was prepared from the 1-norbornanecarboxylic acid by the method of Kauer;[21] the acid was kindly provided by Dr. J. C. Kauer of this department. Tantalum pentakis(dimethylamide) was prepared from $TaCl_5$ and lithium dimethylamide by following the general procedure of Bradley.[13]

Trimethylsilyl perrhenate was prepared by a literature procedure from silver perrhenate and chlorotrimethylsilane.[20] *tert*-Butyl(trimethylsilyl)amine, 1-adamantyl(trimethylsilyl)amine, and 1-norbornyl(trimethylsilyl)amine were prepared, by following the general procedure of Pike, from the corresponding amines and chlorotrimethylsilane in ether[16] and were purified by fractional distillation. Trimethylsilyl vanadate was prepared by the literature procedure[15] from sodium trimethylsilanolate and vanadium oxide trichloride in hexane. Lithium *tert*-butylamide was prepared by the reaction of *n*-butyllithium with *tert*-butylamine in hexane followed by distillation of the solvent.

Other starting materials were reagent grade chemicals used as received.

**(*tert*-Butylimido)tris(dimethylamido)tantalum (1a).** A mixture of tantalum pentachloride (14.67 g, 41 mmol), lithium dimethylamide (8.36 g, 164 mmol), and lithium *tert*-butylamide (3.24 g, 41 mmol) in 150 mL of hexane was stirred for 48 h. The mixture was filtered to remove 8.43 g of white solid (vs. 8.7 g of LiCl theoretical). The resultant red-brown solution was evaporated, and the residue was sublimed in vacuo at 43 °C to afford the crude compound, which was

---

[19] The compound is unfortunately disordered, and a model of the predicted structure would refine only to an *R* index of approximately 0.12. The determination was further complicated by an apparent second phase, which was present independent of the method used to grow the crystals. Weissenberg photographs gave a second set of diffuse spots that could not be indexed on the basis of the standard unit cell. At −98 °C the parameters found are as follows: $a = 21.000$ (4) Å, $b = 7.602$ (2) Å, $c = 14.852$ (3) Å, $\beta = 106.89$ (1)°, monoclinic, space group *C*2.

[20] Schmidt, M.; Schmidbauer, H. *Inorg. Synth.* **1967**, *9*, 149–151.

[21] Kauer, J. C. U.S. Patent 3 546 290.

[22] Nugent, W. A.; McKinney, R. J.; Kasowski, R. V.; Van-Catledge, F. A. *Inorg. Chim. Acta Lett.* **1982**, *65*, L91–L93.

pale yellow and showed a small amount of impurity by NMR thought to be ca. 6% of $(Me_2N)_4TaCl$. The product was twice recrystallized by dissolving it in a minimum amount of hexane and cooling the solution to −35 °C. The final yield was 5.75 g (37%) of colorless hexagonal plates, mp 68–69 °C. NMR (toluene-$d_8$): $\delta$ 1.43 (s, 9 H, *t*-Bu), 3.20 (s, 18 H, NMe). Anal. Calcd for $C_{10}H_{27}N_4Ta$: C, 31.25; H, 7.08; N, 14.57. Found: C, 30.98; H, 6.74; N, 14.31. Mol wt (cryoscopic, benzene): calcd, 384; found, 388.

**1a. Alternative Procedure.** A solution of freshly prepared $Ta(NMe_2)_5$ (4.97 g, 12.4 mmol) in 50 mL of hexane was treated with 1.3 mL (12.4 mmol) of *tert*-butylamine. After the solution was stirred for 60 h, the solvent was evaporated and two sublimations afforded 3.1 g of a gummy solid. NMR (toluene-$d_8$): $\delta$ 1.38 (s, 9 H, *t*-Bu), 3.19 (s, 18 H, NMe), 3.23 (small s, impurity). Recrystallization of this material (hexane, −35 °C) afforded material with properties essentially identical with those reported above.

**(*tert*-Butylimido)tris(dimethylamido)niobium (1b).** A mixture of niobium pentachloride (11.08 g, 41 mmol), lithium dimethylamide (8.36 g, 164 mmol), and lithium *tert*-butylamide (3.24 g, 41 mmol) in 150 mL of hexane was stirred for 48 h. The mixture was filtered to remove 8.4 g of a white solid (vs. 8.7 g of LiCl in theoretical). After the solvent was evaporated, the brown residue was sublimed in vacuo three times at 130, 100, and 80 °C, respectively. The final product consisted of 2.2 g (18%) of a clear yellow solid, mp 58–60 °C. NMR (toluene-$d_8$): $\delta$ 1.39 (s, 9 H, *t*-Bu), 3.16 (s, 18 H, NMe). Anal. Calcd for $C_{10}H_{27}N_4Nb$: C, 40.54; H, 9.19; N, 18.91. Found: C, 39.50; H, 8.67; N, 18.16. Mol wt (cryoscopic, xylene): calcd, 296; found, 281.

**(*tert*-Butylimido)tris(dimethyldithiocarbamato)tantalum.** To a solution of 1.0 g of **1a** in 5.0 mL of thf was added cautiously 470 $\mu$L of $CS_2$ over the course of 1 min. The resultant yellow solution was cooled to −20 °C overnight. The product was collected by filtration and dried at 50 °C on the vacuum line overnight. NMR ($CD_2Cl_2$): $\delta$ 1.19 (s, 9 H, *t*-Bu), 3.30 (s, 18 H, NMe). Anal. Calcd for $C_{13}H_{27}N_4S_6Ta$: C, 25.48; H, 4.44; N, 9.14. Found: C, 25.16; H, 4.46; N, 8.38.

**Tetrabutylammonium Azidobis(tetrahydrofuran)trichlorovanadate(III) (2).** $VCl_3$ (1.58 g, 10 mmol) was dissolved by refluxing it in 100 mL of dry thf. To the cooled dark violet solution was added 1.15 g (10 mmol) of azidotrimethylsilane dissolved in 5 mL of thf. The solution was light brown after 1.5 h of stirring. To 45 mL of the resultant solution was added excess (2.0 g) $NBu_4Cl$ as the solid, and the mixture was stirred for 48 h. The violet precipitate was then collected by filtration and washed with pentane. Anal. Calcd for $C_{24}H_{52}Cl_3N_4O_2V$: C, 49.19; H, 8.94; N, 9.56; V, 8.69. Found: C, 49.01; H, 9.31; N, 10.00; V, 8.94.

**(*tert*-Butylimido)tris(trimethylsiloxo)vanadium (3a).** A solution of 4.25 g of oxotris(trimethylsiloxo)vanadium and 1.10 g of vanadium oxide trichloride in 25 mL of hexane was cooled to −78 °C. To this was added dropwise 5.5 g of *tert*-butyl(trimethylsilyl)amine in 25 mL of hexane. The solution was allowed to warm slowly to room temperature over 3 h. The solution was filtered, and the solvent was distilled off. Recrystallization of the residue from hexamethyldisiloxane at −40 °C afforded 5.86 g (79%) of **3a** as yellow sublimable (70 °C) needles, mp 55–56 °C. The $^{51}V$ NMR spectrum of **3a** is a broad 1:1:1 triplet due to coupling to $^{14}N$ ($J = 95$ Hz). $^{1}H$ NMR (toluene-$d_8$): $\delta$ 0.25 (s, 27 H, SiMe), 1.22 (s, 9 H, *t*-Bu). Anal. Calcd for $C_{13}H_{36}O_3NSi_3V$: C, 40.07; H, 9.31; N, 3.59. Found: C, 39.17; H, 8.96; N, 3.72. Mol ion *m*/*e*: calcd, 389.1441; found, 389.1434. Mol wt (cryoscopic, *p*-xylene): calcd, 390; found, 403.

**(1-Adamantylimido)tris(trimethylsiloxo)vanadium (3b)** was prepared in an analogous manner with 1-adamantyl(trimethylsilyl)amine. Volatile impurities were removed from the initially formed yellow oil by distillation in vacuo. The residue was sublimed under high vacuum at 150 °C and then recrystallized from hexane at −40 °C to afford **3b** in 5% overall yield. Anal. Calcd for $C_{19}H_{42}NO_3Si_3V$: C, 48.79; H, 9.05; N, 2.99. Found: C, 48.82; H, 9.01; N, 3.30.

Synthetic details for compounds **5a**, **5b**, **6**, **7a**, and **7b** have been given elsewhere.[8e]

**Bis(*tert*-butylimido)bis(trimethylsiloxo)chromium (5a). Alternative Preparation from $CrO_3$ Rather than $CrO_2Cl_2$.** A mixture of 1.9 g of $CrO_3$, 16 g of *tert*-butyl(trimethylsilyl)amine, and 50 mL of hexane was refluxed for 0.5 h. The solvent was distilled off on the vacuum line, and the residue was redissolved in hexamethyldisiloxane. Cooling to −40 °C afforded 2.96 g (42%) of material shown by NMR to consist of >90% of **5a**. However, the impurities proved difficult to remove, and several further recrystallizations from hexamethyldisiloxane were required to obtain **5a** with properties identical with those reported previously. Thus, despite the much lower cost of $CrO_3$ vs. that of $CrO_2Cl_2$, the earlier procedure[8e] is preferred for its simplicity and high yield.

**Bis(1-norbornylimido)bis(trimethylsiloxo)molybdenum (5c)** was prepared by refluxing 0.594 g of molybdenum dichloride dioxide with 2.21 g of 1-norbornyl(trimethylsilyl)amine in 25 mL of hexane. After filtration and distillation of the solvent, the residue was redissolved in 5 mL of hexane and cooled to −40 °C. The resultant 0.90 g (61%) of yellow powder could be recrystallized from toluene at −40 °C to afford **5c** as yellow cubes, mp 112–115 °C. Anal. Calcd for $C_{20}H_{40}MoN_2O_2Si_2$: C, 48.76; H, 8.18; N, 5.69. Found: C, 48.97; H, 8.16; N, 5.56.

**(*tert*-Butylimido)oxobis(trimethylsiloxo)chromium** was prepared by the reaction of **5a** (3.7 g, 10 mmol) with benzaldehyde (1.1 g, 10 mmol) in 50 mL of toluene. The solution was heated at 70 °C overnight and then cooled to room temperature whereupon methyl trifluoromethanesulfonate (2.4 g, 14.6 mmol) was added. The mixture was allowed to stand overnight, after which 2.9 g of precipitated benzylidene-*tert*-butylmethylammonium triflate was removed by filtration. Removal of the solvent afforded the product (2.5 g, 79%) as a red oil. The NMR spectrum appeared clean although the elemental analysis suggests a small amount of nitrogen-containing impurity may be present. Quite possibly such an impurity could be removed by vacuum distillation, but this was not attempted because of the explosive nature[23] of the corresponding dioxo complex, $(Me_3SiO)_2CrO_2$. NMR (benzene-$d_6$): $\delta$ 0.24 (s, 18 H, SiMe), 1.41 (s, 9 H, *t*-Bu). Anal. Calcd for $C_{10}H_{27}CrNO_3Si_2$: C, 37.83; H, 8.59; N, 4.41. Found: C, 36.79; H, 8.19; N, 5.19.

**Bis($\mu$-*tert*-butylimido)bis(*tert*-butylimido)tetramethylditungsten (8a)** was prepared by treating 3.48 g of **7a** in 9 mL of hexane with 1.83 g of dimethylzinc. The mixture was allowed to stand at room temperature overnight whereupon 1.6 g (61%) of red-orange crystals was collected by filtration; mp 131 °C dec. (Cooling the remaining solution afforded additional **8a**, but it was contaminated with white needles of $(Me_3SiO)ZnMe$). NMR (toluene-$d_8$): 0.98 (s, 12 H, Me), 1.40 (s, 36 H, *t*-Bu). The methyl resonance showed characteristic satellites resulting from 14.4% $^{183}W$ ($s = {}^1/_2$), with $J = 7$ Hz. Anal. Calcd for $C_{20}H_{48}N_4W_2$: C, 33.72; H, 6.79; N, 7.86. Found: C, 33.89; H, 6.78; N, 7.83.

**Bis($\mu$-*tert*-butylimido)bis(*tert*-butylimido)tetramethyldimolybdenum (8b)** was prepared by reaction of 5.0 g of **5b** in 25 mL of toluene with 3.0 g of dimethylzinc. Cooling the resultant violet solution to −40 °C afforded 3.22 g (64%) of **8b**, which was recrystallized from toluene to afford X-ray-quality violet crystals: 52% overall yield, mp 102 °C dec. NMR (toluene-$d_8$): $\delta$ 1.02 (s, 12 H, Me), 1.39 (s, 36 H, *t*-Bu). Anal. Calcd for $C_{20}H_{48}N_4Mo_2$: C, 44.78; H, 9.02; N, 10.44. Found: C, 45.16; H, 8.81; N, 10.93.

**Reaction of 6 with Dimethylzinc.** The reaction of 0.847 g of **6** and 0.424 g of dimethylzinc in 3 mL of hexane initially afforded a white amorphous precipitate, which was removed by filtration. The remaining solution was cooled to −40 °C to afford a small quantity of white crystals believed to be $(t\text{-BuNH})_2(t\text{-BuN})(CH_3)W[N(t\text{-Bu})(ZnCH_3)]$. NMR (toluene-$d_8$): $\delta$ −0.22 (s, 3 H, ZnMe), 0.65 (s, 3 H, WMe, $J(^{183}W{-}^{1}H) = 10$ Hz), 0.97 (s, 9 H, ZnN-*t*-Bu), 1.44 (s, 18 H, NH-*t*-Bu), 1.46 (s, 9 H, N-*t*-Bu), 1.83 (br s, 2 H, N H ). Anal. Calcd for $C_{18}H_{44}N_4WZn$: C, 38.21; H, 7.84; N, 9.90. Found: C, 38.33; H, 7.89; N, 9.94.

**Reaction of 8b with Chlorine.** A slow stream of $Cl_2$ was bubbled through a solution of 0.5 g of **8b** in 10 mL of hexane at −78 °C. After 0.5 min $N_2$ was bubbled through to remove excess chlorine. After the solution was warmed to room temperature, 0.40 g of a yellow solid was collected by filtration, which appears to be crude **9a**. We were unable to purify **9a** by sublimation or recrystallization. Anal. Calcd for $C_8H_{18}Cl_2N_2Mo$: C, 31.09; H, 5.87; N, 9.06. Found: C, 29.53; H, 6.15; N, 7.96.

**Reaction of 8b with Bromine.** To 1.0 g of **8b** in 70 mL of hexane was added 1.0 g of $Br_2$. A yellow-orange precipitate formed immediately and was collected by filtration. The product was broad melting (mp 132–135 °C) and showed in addition to the NMR singlet at $\delta$ 1.60 expected for **9b** a number of smaller resonances. Anal. Calcd

---

(23) Schmidt, M.; Schmidbauer, H. *Angew. Chem.* **1958**, *70*, 704. Abel, E. W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem., Biochem., Biophys., Biol.* **1960**, *15B*, 57.

for $C_8H_{18}Br_2MoN_2$: C, 24.14; H, 4.57; N, 7.04. Found: C, 26.35; H, 5.13; N, 7.11.

**Tris(*tert*-butylimido)(trimethylsiloxo)rhenium (10)** was prepared by stirring a mixture of 2.38 g of trimethylsilyl perrhenate, 12 mL of *tert*-butyl(trimethylsilyl)amine, and 24 mL of hexamethyldisiloxane for 48 h. The solvent was removed, and the residue was distilled through an air-cooled condenser under high vacuum. To the resultant yellow oil was added 3 mL of hexamethyldisiloxane. Cooling to −40 °C afforded 2.3 g (64%) of **10** as bright yellow crystals, mp 36–38 °C. NMR (benzene-$d_6$): $\delta$ 0.23 (s, 9 H, SiMe), 1.36 (s, 27 H, *t*-Bu). Anal. Calcd for $C_{15}H_{36}N_3OReSi$: C, 36.87; H, 7.42; N, 8.59. Found: C, 36.46; H, 7.34; N, 8.90.

**($\mu$-Oxo)($\mu$-trimethylsiloxo)($\mu$-perrhenato)bis[bis(*tert*-butylimido)(trimethylsiloxo)rhenium] (11)** was prepared as in the above procedure but with a reduced amount (6 mL) of *tert*-butyl(trimethylsilyl)amine. After 24 h, the solution was filtered, concentrated, and cooled to −40 °C to afford yellow crystals of **11** suitable for X-ray diffraction. Anal. Calcd for $C_{25}H_{63}N_4O_8Re_3Si_3$: C, 25.22; H, 5.33; N, 4.71. Found: C, 25.44; H, 5.48; N, 4.56.

**Trimethylsilyl pertechnetate** was prepared as follows. To a solution of 1.1 g of ammonium pertechnetate in 20 mL of $H_2O$ (New England Nuclear) was added 1.5 g of silver nitrate. The resultant yellow precipitate of silver pertechnetate was collected by filtration and dried in vacuo (1.50 g, 91%). This material was suspended in 10 mL of hexamethylsiloxane, and 0.6 g of chlorotrimethylsilane was added. After 2 h, 0.745 g of white solid (94% of theoretical for AgCl) was removed by filtration. The solvent was removed in vacuo to afford 1.23 g of white solid, which melted to a colorless oil at room temperature. The NMR spectrum (toluene-$d_8$) consisted of a singlet at $\delta$ −0.07.

**Acknowledgment.** The author thanks Dr. G. W. Parshall for suggesting this area of research and his colleagues at Du Pont's Central Research Department for many stimulating discussions during the course of these studies. Thanks are also due to Dr. J. C. Kauer for a sample of 1-norbornanecarboxylic acid and to Dr. R. L. Harlow for preliminary x-ray crystallographic studies on compounds **5a** and **6**. I am grateful to W. M. Gray and J. W. Lockhart for skilled technical assistance.

**Registry No.** **1a**, 69039-11-8; **1b**, 69039-12-9; **2**, 84416-72-8; **3a**, 70024-35-0; **3b**, 71852-01-2; **5a**, 71851-94-0; **5b**, 71851-95-1; **5c**, 84416-73-9; **6**, 72207-45-5; **7a**, 72207-46-6; **8a**, 73448-07-4; **8b**, 73448-06-3; **9a**, 84416-75-1; **9b**, 84416-76-2; **10**, 73321-57-0; **11**, 73460-33-0; $(dtc)_3Ta(NBu\text{-}t)$, 84416-70-6; $(Me_3SiO)_2CrO(NBu\text{-}t)$, 83619-58-3; $(t\text{-}BuNH)_2(t\text{-}BuN)(CH_3)W[N(t\text{-}Bu)(ZnCH_3)]$, 84416-74-0; $Me_3SiOReO_3$, 16687-12-0; $TaCl_5$, 7721-01-9; $LiNMe_2$, 3585-33-9; LiNHBu-*t*, 37828-54-9; $Ta(NMe_2)_5$, 19824-59-0; *t*-$BuNH_2$, 75-64-9; $NbCl_5$, 10026-12-7; $Cs_2$, 75-15-0; $VCl_3$, 7718-98-1; $Me_3SiN_3$, 4648-54-8; $(Me_3SiO)_3OVCl$, 5590-56-7; *t*-$BuNH(SiMe_3)$, 5577-67-3; $RNH(SiMe_3)$ (R = 1-adamantyl), 36960-58-4; $CrO_3$, 1333-82-0; $MoCl_2O_2$, 13637-68-8; $RNH(SiMe_3)$ (R = 1-norbornyl), 84416-77-3; $Me_2Zn$, 544-97-8; $Me_3SiOReO_3$, 16687-12-0; vanadium oxide trichloride, 7727-18-6; benzaldehyde, 100-52-7; hexamethyldisiloxane, 107-46-0; ammonium pertechnetate, 13598-66-8; chlorotrimethylsilane, 75-77-4.

---

Contribution from the Department of Chemistry,
University of Idaho, Moscow, Idaho 83843

# New Routes to Bis(*F*-alkyl) Sulfones

TAKESHI IMAGAWA,[1a] GARY L. GARD,[1b] THOMAS W. MIX,[1c] and JEAN'NE M. SHREEVE*

*Received September 8, 1982*

Bis(*F*-alkyl) sulfones result from the interaction of $CF_3SO_2F$ with $C_2F_4$ at 90–100 °C and surprisingly from $SOF_4$ with $C_2F_4$ at 25 °C, both in the presence of CsF in diglyme. Hydrolysis of bis(*F*-alkyl) sulfoxydifluorides also gives sulfones.

## Introduction

Bis(polyfluoroalkyl) sulfones and other less fluorinated sulfones continue to be the subjects of considerable study, particularly in cases where the $R_fSO_2^-$ group is utilized either as a nucleophile or as a nucleophilic leaving group.[2-6] Some examples of the known synthetic pathways for sulfone preparation include the following:

(I) alkyl organometallic reagents with $CF_3SO_2F$[7,8]

$$CF_3SO_2F + CH_3MgCl \xrightarrow{(C_2H_5)_2O} \underset{70\%}{CF_3SO_2CH_3} + \underset{7\%}{(CF_3SO_2)_2CH_2}$$

$$CF_3SO_2F + 2NaCH(CO_2C_2H_5)_2 \xrightarrow[50\ ^\circ C]{THF} \underset{40\%}{CF_3SO_2CH(CO_2C_2H_5)_2} + CH_2(CO_2C_2H_5)_2$$

(II) alkyl bromides and potassium *F*-methanesulfonate[9]

$$RCH_2Br + KSO_2CF_3 \xrightarrow[CH_3CN]{I^-} RCH_2SO_2CF_3 + KBr$$

$$R = C_6H_5\ (95\%);\ C_6H_5CO\ (80\%);\ n\text{-}C_3H_7\ (70\%)$$

(III) oxidation of sulfides and sulfoxides[10-12]

$$C_2H_5SC_2F_3ClH + KMnO_4 \xrightarrow[5\ ^\circ C]{gl\ HOAc} \underset{86\%}{C_2H_5SO_2C_2F_3ClH}$$

$$CF_3SCH_2CH_2SCF_3 + CrO_3 \xrightarrow[95\ ^\circ C]{gl\ HOAc} CF_3SO_2CH_2CH_2SO_2CF_3$$

While all of the preceding methods are effective in preparing partially fluorinated sulfones, their utility in producing poly-

---

(1) (a) Research Associate on leave from Kyoto University, Kyoto, Japan, 1981–1982. (b) Visiting Professor on leave from Portland State University, Portland, OR, 1982. (c) Merix Corp., Babson Park, Wellesley, MA 02181.

(2) Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306.

(3) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 1.

(4) Hanack, M.; Laping, K. *Tetrahedron Lett.* **1977**, 4493.

(5) Laping, K.; Hanack, M. *Tetrahedron Lett.* **1979**, 1309.

(6) Massa, F.; Hanack, M.; Subramanian, L. R. *J. Fluorine Chem.* **1982**, *19*, 601.

(7) Koshar, R. J.; Mitsch, R. A. *J. Org. Chem.* **1973**, *38*, 3358.

(8) Yagupol'ski, L. M.; Ogoika, P. I.; Aleksandrou, A. M. *Zh. Org. Khim.* **1974**, *10*, 1991; *J. Org. Chem. USSR* (*Engl. Transl.*) **1974**, *10*, 2003.

(9) Hendrickson, J. B.; Giga, A.; Wareing, J. *J. Am. Chem. Soc.* **1974**, *96*, 2275.

(10) Rapp, K. E.; Pruett, R. L.; Barr, J. T.; Bahner, C. T.; Gibson, J. D.; Lafferty, R. H., Jr. *J. Am. Chem. Soc.* **1950**, *72*, 3642.

(11) Harris, J. F., Jr. *J. Org. Chem.* **1967**, *32*, 2063.

(12) Truce, W. E.; Birum, G. H.; McBee, E. T. *J. Am. Chem. Soc.* **1952**, *74*, 3594.

0020-1669/83/1322-0969$01.50/0