Tantalum μ-Alkylidyne Compounds Containing *o*-Phenyl- and *o*-(1-Naphthyl)phenoxides: Probing Molecular Structure and Dynamics

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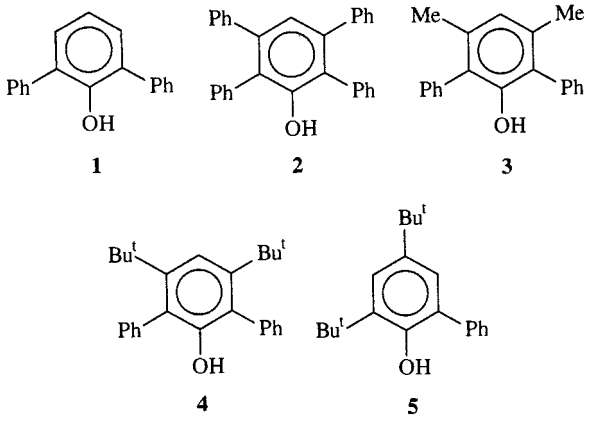
Received January 13, 1999

The new *o*-(1-naphthyl)phenols 2-(1-naphthyl)-4,6-di-*tert*-butylphenol, 2,6-bis(1-naphthyl)-phenol, 2,6-bis(1-naphthyl)-3,5-dialkylphenol (alkyl = Ph, Me, Bu^t), and 2-(1-naphthyl)-3,5,6-triphenylphenol have been synthesized. The reaction of these phenols and their *o*-phenyl counterparts with the compound $[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$ has been investigated. This reaction produces the monosubstitution products $[(ArO)(Me_3SiCH_2)Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$ at rates which are strongly dependent on the nature of the phenol substituents. The NMR spectroscopic properties of the resulting derivatives can be used to probe the phenoxide structure. Nonchiral phenoxides yield singlets for the CH_2SiMe_3 methylene protons and one set of μ-$CSiMe_3$ resonances, whereas the presence of a chiral phenoxide generates diastereotopic CH_2SiMe_3 protons and nonequivalent μ-$CSiMe_3$ groups. The solid-state structure of the 2-(1-naphthyl)-3,5,6-triphenylphenoxide and 2,6-bis(1-naphthyl)phenoxide derivatives shows that the 1,3-dimetallacyclobutadiene core remains intact with Ta−Ta distances of 2.8943(6) and 2.8886(7) Å, respectively. The rate expression for substitution of the first alkyl group in $[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$ (**11**) by 2-phenyl-4,6-di-*tert*-butylphenol (**5**) in C_6D_6 solvent is first order in both [**11**] and [**5**] with a second-order rate constant of $[1.40(7)] \times 10^{-4}$ mol^{-1} L^{-1} s^{-1} at 30(1) °C. Use of the deuterated phenol ArOD gave a rate constant of $[0.25(3)] \times 10^{-4}$ mol^{-1} L^{-1} s^{-1}, hence demonstrating the primary kinetic isotope effect $k_H/k_D = 5.6(5)$. Competition reactions have yielded the relative rates of substitution of **11** by various phenols.

Introduction

The aryloxide ligand derived from 2,6-diphenylphenol (**1**) has been extensively utilized in both inorganic and organometallic chemistry. With the metal titanium, the



compound $[Ti(OC_6H_3Ph_2)_2Cl_2]$ represents an important starting material for the generation of metallacyclic species which carry out both stoichiometric and catalytic carbon−carbon bond forming reactions.[1] When this ligand attached to the group 5 metals niobium and tantalum, both intramolecular metalation and hydrogenation of the *o*-phenyl rings has been observed.[2] To retard unwanted cyclometalation processes, ligands derived from *meta*-substituted 2,6-diphenylphenols, e.g. **2**−**4**, have been utilized.[3]The π (η^6) binding of substituent phenyl rings of *o*-phenylphenoxides to low-valent tungsten metal centers has led to the isolation of reactive 16-electron species which can carry out the 4-electron reduction of substrates.[4] In the chemistry of the lanthanide metals the 2,6-diphenylphenoxide ligand has been found to support interesting structural motifs, some of which involve the η^n binding of the *o*-Ph group to the electrophilic metal center.[5] In the case of the p-block metals an important new class of Lewis acidic aluminum phenoxides have been developed by Yama-

(1) (a) Thorn, M. G.; Etheridge, Z. C.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1998**, *17*, 3636. (b) Thorn, M. G.; Hill, J. E.; Waratuke, S. A.; Johnson, E. S.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 8630. (c) Johnson, E. S.; Balaich, G. J.; Rothwell, I. P. *J. Am. Chem. Soc.* **1997**, *119*, 7685. (d) Waratuke, S. A.; Johnson, E. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1996**, 2617. (e) Balaich, G. J.; Rothwell, I. P. *Tetrahedron* **1995**, *51*, 4463. (f) Balaich, G. J.; Hill, J. E.; Waratuke, S. A.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1995**, *14*, 656. (g) Hill, J. E.; Balaich, G. J.; Fanwick, P. E. and Rothwell, I. P. *Organometallics* **1993**, *12*, 2911.

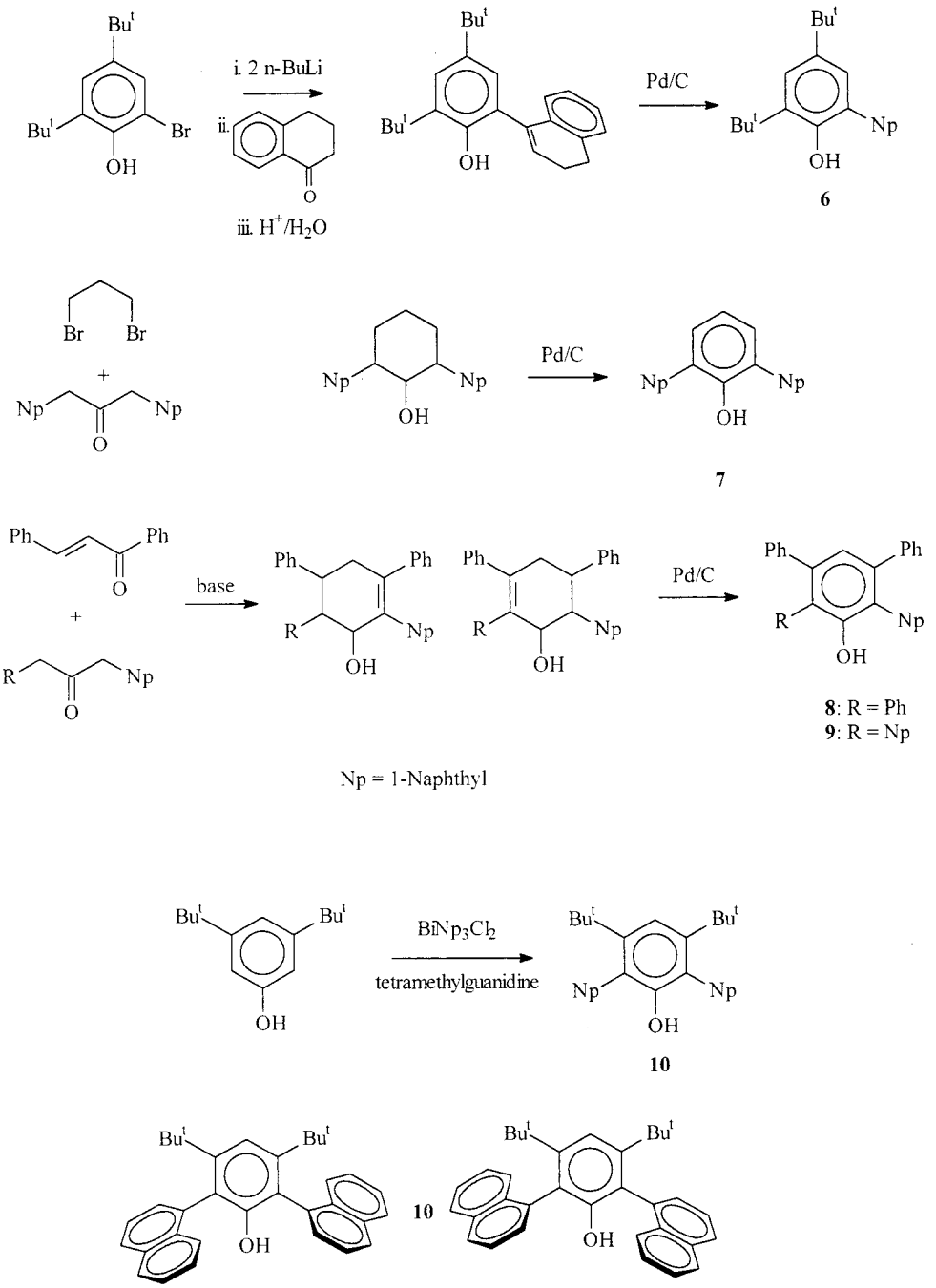
(2) (a) Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* (*Feature Article*) **1997**, 1331. (b) Rothwell, I. P. *Acc. Chem. Res.* **1988**, *21*, 153.

(3) Vilardo, J. S.; Lockwood, M. A.; Hanson, L. G.; Clark, J. R.; Parkin, B. C.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1997**, 3353.

(4) (a) Lockwood, M. A.; Fanwick, P. E.; Eisenstein, O.; Rothwell, I. P. *J. Am. Chem. Soc.* **1996**, *118*, 2762. (b) Lockwood, M. A.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **1995**, *14*, 3363.

10.1021/om990015+ CCC: $18.00
Publication on Web 07/08/1999

Scheme 1



moto and co-workers, including the compound [Al(OC$_6$H$_3$Ph$_2$)$_3$].[6]

This importance of *o*-phenylphenoxides has prompted us to begin an investigation of the chemistry associated with related *o*-(1-naphthyl)phenols.[7] This study is stimulated by the potential chirality of such ligands. In this paper we report the synthesis of a number of new *o*-(1-naphthyl)phenols as well as a series of μ-alkylidyne derivatives of tantalum. The spectroscopy and dynamic properties of these ligands have been probed and compared to those of related *o*-phenyl compounds.

(5) Deacon, G. B.; Feng, T. C.; Junk, P. C.; Skelton, B. W.; White, A. H. *Chem. Ber.-Recl.* **1997**, *130*, 851 and references therein.
(6) Saito, S.; Yamamoto, H. *J. Chem. Soc., Chem. Commun.* (*Feature Article*) **1997**, 1585.
(7) Vilardo, J. S.; Thorn, M. G.; Fanwick, P. E.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1998**, 2425.

Results and Discussion

Synthesis of *o*-(1-Naphthyl)phenols. On the basis of the existing literature dealing with *o*-phenylphenols, there appear to be many strategies that can be applied to the synthesis of *o*-(1-naphthyl)phenols. Previously we have shown that the ligand 2-phenylphenol reacts with isobutylene to provide 2-phenyl-4,6-di-*tert*-butylphenol (**5**), some of whose metal chemistry has been explored.[8] In the case of the ligand 2-(1-naphthyl)-4,6-di-*tert*-butylphenol, we have utilized the corresponding 2-bromo species as our starting point (Scheme 1). The sequence outlined leads to gram quantities of the phenol **6**. An alternative approach involves construction of the phenol

(8) Visciglio, V. M.; Fanwick, P. E.; Rothwell, I. P. *Inorg. Chim. Acta* **1993**, *211*, 203.

nucleus by a sequence of condensation/dehydrogenation steps.[9] The key starting point in this synthesis is the correctly substituted 1,3-diarylpropanones. This method has been used to generate not only 2,6-bis(1-naphthyl)-phenol (**7**), but also the *m*-phenyl-substituted derivative **8**. Solution spectroscopic studies show that this procedure leads to a 50/50 mixture of the two isomeric forms (*meso* and *erythro* or *dl*) of the phenol (vide infra). Use of the nonsymmetrical diarylpropanone allows isolation of 2-(1-naphthyl)-3,5,6-tetraphenylphenol (**9**) in very low yield. A third approach builds upon the bismuth-promoted phenylation of phenols developed by Barton and co-workers.[10] This method has previously been used to produce the metalation-immune 2,6-diphenyl-3,5-di-*tert*-butylphenol (**4**). The corresponding arylation with tris(1-naphthyl)bismuth produces 2,6-bis(1-naphthyl)-3,5-di-*tert*-butylphenol (**10**) in low yield along with a significant amount of the mono(naphthyl) compound. In this case only one isomeric form of **10** can be detected, and the subsequent chemistry shows this to be the chiral form.

The ^{1}H and ^{13}C NMR spectra of **7** and **8** show the presence of two isomeric forms in equimolar amounts. This is most readily observed by the presence of two sharp OH resonances in the ^{1}H NMR spectrum. It therefore appears that the synthesis generates both the nonchiral *meso* along with the *dl* pair of chiral phenols. In the case of simple 2,6-bis(1-naphthyl)phenol, variable-temperature NMR studies show that exchange of the two forms can occur on the NMR time scale. Crystallographic studies of 2,6-diphenylphenols as well as some of the 2,6-bis(1-naphthyl)phenols in this study (see below) show that these molecules are monomeric in the solid state. Previous work on the spectroscopy of *o*-phenylphenols has shown that they remain monomeric in solution with strong evidence for π hydrogen bonding between the OH proton and an *o*-phenyl ring.[11] The coalescence of OH signals in **7** may occur via intermolecular proton exchange. However, we also observe coalescence of signals arising from 1-naphthyl groups. We therefore conclude that both spectroscopic changes arise via restricted rotation about the naphthyl−phenoxide bond. From the coalescence temperature for exchange of OH and naphthyl signals, the barrier to naphthyl rotation in this molecule can be estimated as 18.0(5) kcal mol^{-1} at 67 °C. Analysis of crystals of the 2,6-bis(1-naphthyl)phenol by X-ray diffraction methods showed the presence of the *dl* pair in the solid state (Figure 1).

In the case of the phenol **8** the *m*-phenyl groups would be expected to severely hinder naphthyl rotation. Recrystallization of the initial reaction mixture from CH_2Cl_2/heptane was found to lead to purification of the *meso* form, identified by X-ray diffraction (Figure 1).[12] Solutions of *meso*-**8** were observed (NMR) to only slowly convert into the *dl* form over days at 100 °C.

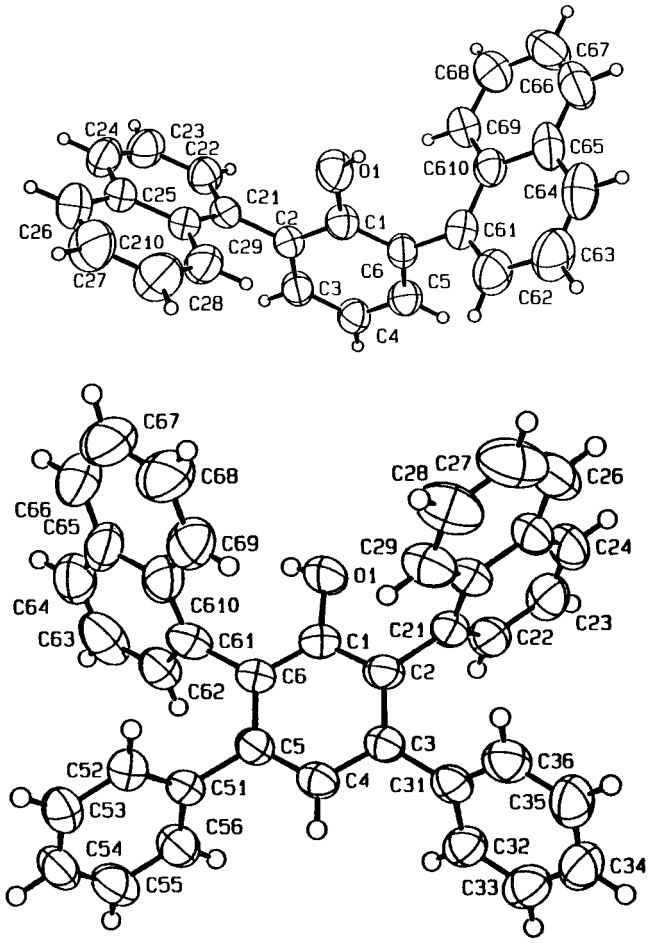


Figure 1. ORTEP views of (top) [$HOC_6H_3Np_2$-2,6] (**7**) and (bottom) [HOC_6HNp_2-2,6-Ph_2-3,5] (**8**; *meso* form).

The treatment of 3,5-di-*tert*-butylphenol with [$BiCl_2$-(1-naphthyl)$_3$] in the presence of a base was found to produce a reaction mixture containing two phenolic species. Separation by chromatography allowed purification of **10**, which was found to exhibit only one set of NMR signals. Subsequent reactivity studies confirmed this species to be the chiral form. The preferential formation of this isomeric form may be a consequence of the stepwise arylation process that occurs with the bismuth reagents. It seems reasonable to conclude that the first naphthyl group introduced directs the stereochemistry of the second group to form the erythro isomer. The second (majority) phenolic product was identified (NMR, mass spectrometry) as the intermediate 2-(1-naphthyl)-3,5-di-*tert*-butylphenol.

Reaction of *o*-Arylphenols with [$Ta_2(\mu$-$CSiMe_3)_2(CH_2SiMe_3)_4$]. The compound [$Ta_2(\mu$-$CSiMe_3)_2(CH_2SiMe_3)_4$] (**11**), first isolated by Wilkinson and coworkers,[13] represents a thermally very stable organometallic derivative of tantalum that has been shown to contain a 1,3-dimetallacyclobutadiene core. The termi-

(9) (a) Yang, H.; Hay, A. S. *Synthesis* **1992**, 467. (b) Yates, P.; Hyre, J. R. *J. Org. Chem.* **1962**, *27*, 4101. (c) Hay, A. S.; Clark, R. F. *Macromolecules* **1970**, *3*, 533. (d) Dana, D. E.; Hay, A. S. *Synthesis* **1982**, 164.

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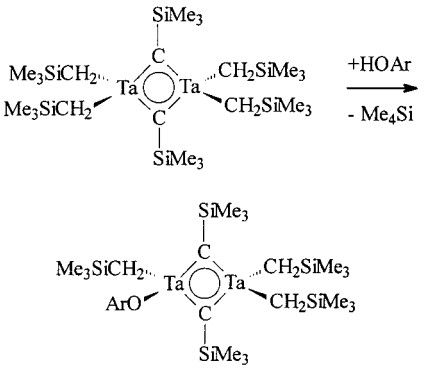
(12) Saito, S.; Kano, T.; Hatanaka, K.; Yamamoto, H. *J. Org. Chem.* **1997**, *62*, 5651.

(13) (a) Huq, F.; Mowat, W.; Skapski, A. C.; Wilkinson, G. *J. Chem. Soc., Chem. Commun.* **1971**, 1477. (b) Mowat, W.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1120.

(14) Riley, P. N.; Profilet, R. D.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1996**, *15*, 5502.

Scheme 2



nal alkyl groups have been shown to be able to undergo stepwise substitution with protic reagents.[14] Previous work by our group has shown that 2,6-diphenylphenol will initially substitute one terminal alkyl group. We decided to use this reaction to explore various aspects of the chemistry of these new and existing *o*-arylphenols. All of the phenols employed in this study (Scheme 2) react (1 equiv in benzene solution) with **11** to cleanly produce the corresponding species $[Ta_2(\mu\text{-}CSiMe_3)_2(OAr)(CH_2SiMe_3)_3]$ along with 1 equiv of Me_4Si. A number of the reactions were carried out in a preparative manner, whereas some were simply carried out in C_6D_6 solvent and the products subjected to spectroscopic characterization.

The ^1H and ^{13}C NMR spectra of these derivatives (Table 1) are highly informative. In the case of the nonchiral ligands four distinct Me_3Si resonances are observed in the ^1H NMR spectra in the ratio of 2:1:1:1 due to the two equivalent μ-CSiMe_3 alkylidyne bridges and three nonequivalent CH_2SiMe_3 alkyl groups. Three singlets for the alkyl methylene protons CH_2SiMe_3 can also be resolved. The most upfield-shifted of these methylene groups is very sensitive to the nature of the aryloxide ligand and can be assigned to the alkyl group attached to the same metal center as the aryloxide. Previous work has shown that *o*-phenylphenoxides have the effect of upfield-shifting the protons of adjacent alkyl groups attached to the same metal center. This arises due to the diamagnetic anisotropy associated with the *o*-phenyl rings, which, due to the molecular architecture, adopt conformations in solution which shield adjacent protons. We have also previously shown in a study of tantalum alkyl alkylidene compounds $[(ArO)_2Ta(=CHSiMe_3)(CH_2SiMe_3)]$ that as the bulk of the *meta* substituents is increased, the upfield shifting becomes more dramatic. We ascribe this effect to a decrease in conformational flexibility with increasing bulk in the *meta* position which leads to a "locking out" of the *o*-phenyl rings perpendicular to the central phenoxide nucleus. This conformation would be expected to lead to the most dramatic diamagnetic shielding. This postulate was supported by structural studies on parent 2,6-diphenylphenols as well as some metal derivatives. It was also noticed that the chemistry of the 2,6-diphenyl-3,5-di-*tert*-butylphenoxide ligand was significantly different from that of the other ligands, consistent with this ligand being sterically more demanding. This was also ascribed to a decrease in conformational flexibility for the *o*-phenyl rings, leading to a more rigid and bulkier ligand. Identical spectroscopic effects can be seen for the series of 2,6-diphenylphenoxides obtained in this study (Table 1). It can be seen that the methylene protons on the adjacent alkyl group move progressively upfield as the bulk of the *meta* substituent increases: R = H, δ +0.03 ppm; R = Ph, −0.24 ppm; R = Me, −0.33 ppm; R = *t*-Bu, −0.5 ppm.

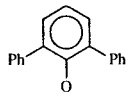
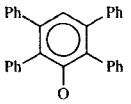
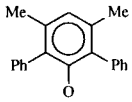
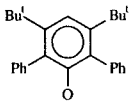
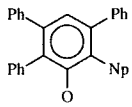
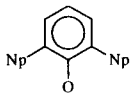
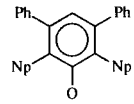
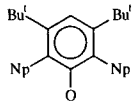
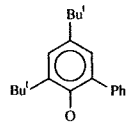
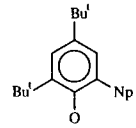
The presence of one *o*-(1-naphthyl) substituent in the ligand 2-(1-naphthyl)-3,5,6-triphenylphenol generates a chiral environment. This leads to nonequivalent μ-C$SiMe_3$ groups (^1H and ^{13}C NMR) as well as diastereotopic methylene protons for the three CH_2SiMe_3 alkyl groups in **16**. In this case the methylene protons of the alkyl adjacent to the aryloxide are shifted upfield to δ −1.14 and −1.34 ppm, consistent with greater diamagnetic shielding associated with 1-naphthyl groups compared to phenyl groups. Similar spectroscopic properties are present for the 2-(1-naphthyl)-4,6-di-*tert*-butylphenoxide derivative **21**. In this case we have examined the variable-temperature NMR spectrum of **21** to try and estimate the barrier to naphthyl rotation *within* the metal complex. At 85 °C in toluene-d_8, the diastereotopic methylene protons of the alkyl groups remain as sharp AB patterns. Furthermore, the nonequivalent μ-$CSiMe_3$ protons remain as two sharp singlets separated by 13 Hz (300 MHz) at this temperature. We can therefore estimate that the barrier to 1-naphthyl rotation in **21** is higher than the value of 18.0(5) kcal mol^{-1} at 67 °C measured for 2,6-bis(1-naphthyl)phenol.

In the case of the 2,6-bis(1-naphthyl)phenols **7** and **8**, reaction with **11** generated products **17** and **18** containing both the *meso* and chiral forms of the ligands. The nonchiral form leads to singlets for the alkyl methylene protons, whereas the chiral form generates doublets for these protons. In the ^{13}C NMR spectrum of these mixtures, three μ-*C*$SiMe_3$ resonances are present, one for the nonchiral form and two for the chiral derivative. Integration shows that these isomers are present in solution in an approximately 50/50 ratio. Analysis of crystals of the 2,6-bis(1-naphthyl)phenoxide derivative **7** by X-ray diffraction showed the presence of the chiral form (both enantiomers) in the unit cell. Reaction of the isolated *meso* form of **8** with **11** generated the *meso* form of **18**. In the case of the 3,5-di-*tert*-butyl-substituted phenol **10** the reaction with the alkylidyne dimer yielded the product **19**, whose spectroscopic properties confirm the chiral nature of the aryloxide. In this case the methylene protons on the adjacent alkyl group appear as doublets at δ −1.64 and −1.90 ppm.

Kinetic Studies. It was noticed during the syntheses that the rate of formation of the monosubstituted derivatives was highly dependent on the nature of the phenolic reagent. A kinetic study of the reaction of **11** with bulky 2-phenyl-4,6-di-*tert*-butylphenol (**5**) shows the reaction to be first order in both [**11**] and [**5**] (Figure 2). These data yield a second-order rate constant of $[1.40(7)] \times 10^{-4}$ mol^{-1} L^{-1} s^{-1} at 30(1) °C. A kinetic run using the deuterated phenol $DOC_6H_2Ph\text{-}2\text{-}Bu^t_2\text{-}4,6$ (Figure 2) showed the primary kinetic isotope effect k_H/k_D = 5.6(5) at 30(1) °C.

We have been able to measure the relative rates of substitution of the terminal alkyl groups using competition experiments. A large excess of an equimolar mixture (C_6D_6 solution) of two phenols was added to a solution of **11**, and ^1H NMR spectra were recorded to

Table 1. Selected NMR Spectroscopic Data (C_6D_6)

Compound		CH_2[a]	CH_2	μ-CSi*Me*$_3$	CH_2Si*Me*$_3$	μ-*C*SiMe$_3$	*C*H_2SiMe$_3$	μ-CSi*Me*$_3$	CH_2Si*Me*$_3$
	**12**	0.03	1.23 0.90	-0.10	0.41 0.34 0.16	399.3	79.8 78.3 64.7	4.70	3.80 3.40 3.35
	**13**	-0.24	1.25 1.02	-0.04	0.52 0.32 0.16	398.3	79.9 78.9 64.5	5.01	3.91 3.71 3.51
	**14**	-0.33	1.25 1.01	0.05	0.56 0.34 0.18	397.6	79.3 78.1 63.4	5.05	3.95 3.77 3.58
	**15**	-0.50	1.34 1.06	-0.02	0.62 0.33 0.19	397.6	79.7 78.4 63.9	5.36	4.09 3.69
	**16**	-1.14 -1.34	1.18	-0.11	0.49 0.24 0.16	398.6 397.9	79.4 78.9 64.4	5.12 4.79	3.73 3.48 3.42
	**17**	(d,l) -1.15 -1.24 (meso) -1.25	(meso) 1.17 0.95	(d,l) -0.11 -0.43 (meso) -0.31	0.41 0.38 0.22 0.21 0.19 0.13	(d,l) 399.8 396.2 (meso) 398.1	79.6 79.3 78.0 77.1 64.2 63.8	3.4 3.3 3.2	5.1 4.5 4.5 4.1 3.6 3.6
	**18**	(d,l) -1.37 -1.56 (meso) -1.50	(d,l) 1.37 1.22 (meso) 1.18 0.92	(d,l) -0.10 -0.45 (meso) -0.34	0.41 0.36 0.16 0.13 0.12 0.07	(d,l) 399.8 396.0 (meso) 398.0	79.6 79.2 77.9 77.1 64.2 64.0	3.2 3.0 -0.3	5.1 4.4 4.0 3.4 3.3 3.2
	**19**	-1.64 -1.90	1.61 0.80	-0.04	0.46 -0.14 -0.46	399.5 396.0	79.9 79.0 64.0	5.57 4.73	3.69 3.67 3.65
	**20**	-0.14	1.44 0.97	0.00	0.54 0.40 0.20	397.9	79.8 77.5 66.9	5.0	3.9 3.7 3.4
	**21**	-1.38 -1.64	1.97 0.97 1.82 0.62	-0.01 -0.04	0.61 0.30 0.28	399.6 396.4	79.2 78.4 67.0	5.3 4.9	3.64 3.57 3.46

[a] Alkyl adjacent to aryloxide.

determine the ratio of the two possible substitution products. These data are given in Table 2. The fastest rate of substitution occurred with 2,6-diphenylphenol, and all other rates are given relative to this standard. It can be seen that as the bulk of the *meta* substituent is increased the rate of substitution decreases, with the 3,5-di-*tert*-butyl ligand reacting 25 times slower than 2,6-diphenylphenol. Replacement of an *o*-phenyl ring with a *tert*-butyl substituent leads to a bulkier ligand which substitutes much more slowly. Although we believe that steric effects dominate the trends in Table 2, electronic effects cannot be totally ignored, although they are more difficult to interpret. For example, electron-donating substituents will lead to an increase in electron density at the phenolic oxygen. Hence, coordination of the phenol to the metal center will be

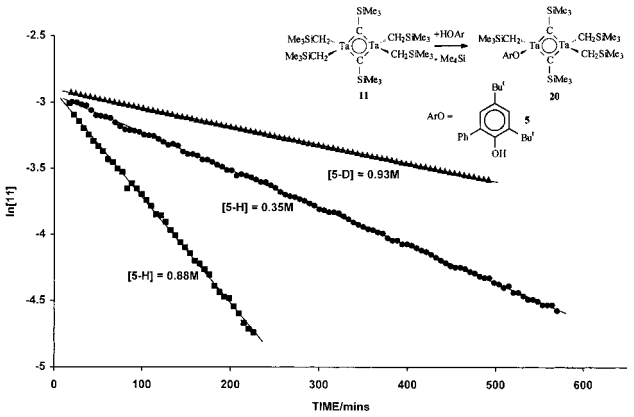
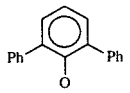
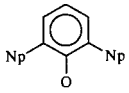
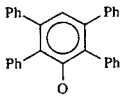
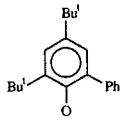
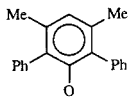
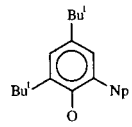
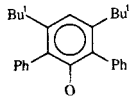


Figure 2. First-order plots of the disappearance of **11** when reacted with excess **5-H** and **5-D** in C_6D_6 solvent at 30 °C, as monitored by ^{1}H NMR spectroscopy. Initial [**11**] = 0.055 M.

Table 2. Relative Rates of Substitution of [11] by Various Phenols

Phenol		Rate	Phenol		Rate
	**12**	1.00		**17**	0.25
	**13**	0.33		**20**	0.014
	**14**	0.45		**21**	0.0057
	**15**	0.040			

favored. However, the final step of the reaction involves proton transfer to the alkyl leaving group. This is shown by the kinetic isotope effect observed upon deuteriation of the phenolic proton. Electron-donating groups would be predicted to decrease the acidity of the phenol.

It can be seen that *o*-naphthyl substituents decrease the substitution rate compared to that for the corresponding phenyl derivatives (Table 2). This is consistent with a greater steric impact of the 1-naphthyl substituent compared to a simple phenyl group.

Structural Studies. We have subjected compounds **16** and **17** to single-crystal X-ray diffraction. It can be seen (Figures 3 and 4) that similar molecular structures are adopted. In the case of the 2,6-bis(1-naphthyl)-phenoxide **17** it can be seen that the chiral form (both enantiomers) of the ligand is present in the solid state. Selected structural parameters are given in Tables 3 and 4**.** In Table 5 the Ta−Ta distance for the compounds obtained in this study is compared to those of previously reported 1,3-dimetallacyclobutadiene derivatives of niobium, tantalum, and other metals.[13−21] It is evident that for the group 5 metals the metal−metal distance is somewhat insensitive to the nature of the terminal ligands.

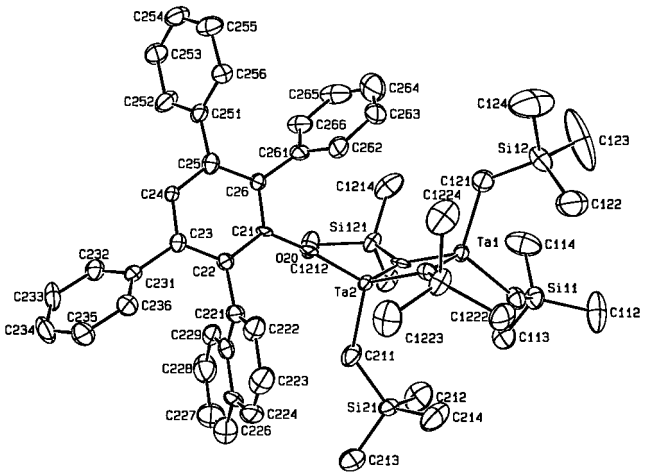


Figure 3. ORTEP view of $[Ta_2(\mu\text{-}CSiMe_3)_2(OC_6HNp\text{-}2\text{-}Ph_3\text{-}3,5,6)(CH_2SiMe_3)_3]$ (**16**).

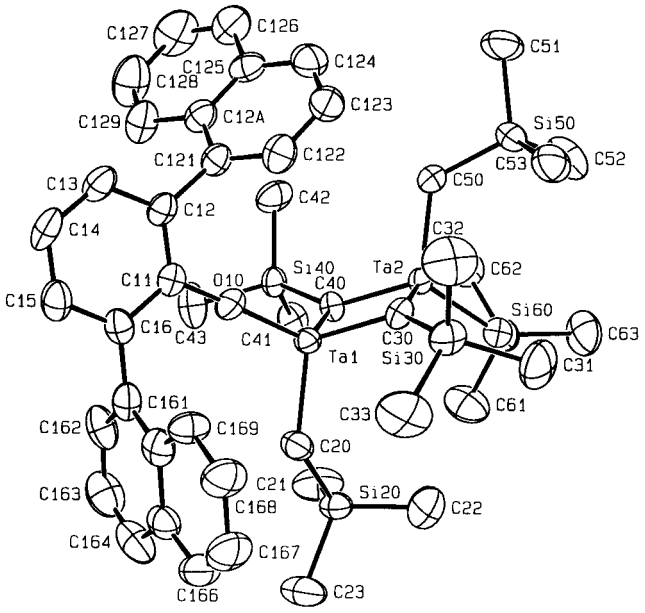


Figure 4. ORTEP view of $[Ta_2(\mu\text{-}CSiMe_3)_2(OC_6H_3Np_2\text{-}2,6)(CH_2SiMe_3)_3]$ (**17**).

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[Ta_2(\mu\text{-}CSiMe_3)_2(OC_6HNp\text{-}2\text{-}Ph_3\text{-}3,5,6)(CH_2SiMe_3)_3]$ (16)

Ta(1)−Ta(2)	2.8943(6)	Ta(2)−O(20)	1.914(8)
Ta(1)−C(1211)	1.98(1)	Ta(2)−C(1211)	1.94(1)
Ta(1)−C(1221)	1.94(1)	Ta(2)−C(1221)	2.00(1)
Ta(1)−C(111)	2.15(1)	Ta(1)−C(121)	2.16(1)
Ta(2)−C(211)	2.12(1)		

O(20)−Ta(2)−C(211)	110.3(4)	C(111)−Ta(1)−C(121)	112.5(5)
Ta(1)−C(1211)−Ta(2)	95.2(5)	Ta(1)−C(1221)−Ta(2)	94.6(5)
Ta(2)−O(20)−C(21)	168.0(8)	Ta(2)−C(211)−Si(21)	133.9(7)
Ta(1)−C(111)−Si(11)	122.7(7)	Ta(1)−C(121)−Si(12)	123.6(8)

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(16) Ogilvy, A. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1987**, *6*, 73.
(17) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C.; Thornton, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1466.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[Ta_2(\mu\text{-}CSiMe_3)_2(OC_6H_3Np_2\text{-}2,6)(CH_2SiMe_3)_3]$ (17)

Ta(1)−Ta(2)	2.8886(7)	Ta(2)−O(10)	1.897(4)
Ta(1)−C(30)	1.993(6)	Ta(2)−C(30)	1.975(6)
Ta(1)−C(40)	1.969(6)	Ta(2)−C(40)	1.980(6)
Ta(1)−C(20)	2.126(6)	Ta(2)−C(50)	2.139(6)
Ta(2)−C(60)	2.128(7)		
O(10)−Ta(1)−C(20)	107.6(2)	C(50)−Ta(2)−C(60)	113.1(3)
Ta(1)−C(30)−Ta(2)	93.4(3)	Ta(1)−C(40)−Ta(2)	94.0(3)
Ta(1)−O(10)−C(11)	177.7(4)	Ta(1)−C(20)−Si(20)	131.1(4)
Ta(2)−C(50)−Si(50)	122.2(3)	Ta(2)−C(60)−Si(60)	120.1(4)

Experimental Section

All operations were carried out under a dry nitrogen atmosphere in a Vacuum Atmospheres Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. The compounds 2,3,5,6-tetraphenylphenol and 2,6-diphenyl-3,5-di-*tert*-butylphenol were obtained by literature methods.[9] The labeled phenol $DOC_6H_2Ph\text{-}2\text{-}Bu^t_2\text{-}4,6$ was obtained by addition of D_2O to the lithium aryloxide in benzene followed by vacuum-drying. The ^1H and ^{13}C NMR spectra were recorded on Varian Associates Gemini 200 and INOVA 300 MHz spectrometers. Microanalyses were obtained in house at Purdue University.

2-Bromo-4,6-di-*tert*-butylphenol. Following a procedure developed by Dilworth,[22] a 1 L conical flask was charged with 25 g (0.12 mol) of 2,4-di-*tert*-butylphenol and 200 mL of concentrated acetic acid. This solution was vigorously stirred as 6.2 mL (0.12 mol) of bromine was slowly added. The solution became noticeably warm as HBr was given off. The mixture was stirred overnight, and 200 mL of water was added. Methylene chloride was added and the organic layer separated, washed three times with H_2O, and dried with $MgSO_4$. The methylene chloride extract was evacuated to dryness, affording 31.4 g (91%) of 2-bromo-4,6-di-*tert*-butylphenol as a white solid. ^1H NMR (C_6D_6, 30 °C): δ 7.00−7.40 (aromatics); 5.53 (s, O*H*); 1.48 (s), 1.14 [s, C(CH_3)$_3$].

2-(3,4-Dihydronaphthyl)-4,6-di-*tert*-butylphenol. A sample of 2-bromo-4,6-di-*tert*-butylphenol (31.4 g, 0.11 mol) was dissolved in 250 mL of Et_2O and cooled to 0 °C using an ice/acetone bath. Under a nitrogen atmosphere 0.22 mol of BuLi (88 mL, 2.5 M hexane solution) was added. The solution became white and was slowly warmed to room temperature over the course of 2 h. To this solution was slowly added 0.11 mol of α-tetralone (14.6 mL dissolved in 50 mL of Et_2O), and the yellow solution which formed was stirred overnight. The solution was hydrolyzed with 300 mL of 6 M HCl and stirred for 1 h. The orange Et_2O layer was separated from the aqueous layer, washed three times with 500 mL of water, dried with $MgSO_4$, and evaporated to dryness, affording an orange oil (62% by GC analysis). This oil was vacuum-distilled to 150 °C to remove unreacted α-tetralone and 2,4-di-*tert*-butylphenol, leaving a yellow oil which was determined by GC analysis to be 99% pure 2-(3,4-dihydronaphthyl)-4,6-di-*tert*-butylphenol. Anal. Calcd for $C_{24}H_{30}O$: C, 86.18; H, 9.04. Found: C, 85.54; H, 9.09. HRMS: calcd, *m*/*z* 335.2375; found, *m*/*z* 335.2375. ^1H NMR ($CDCl_3$, 30 °C): δ 6.90−7.30 (aromatics); 7.40 (d), 7.09 [d, $^4J(^1H-^1H) = 2.4$ Hz, *meta-H*]; 6.26 [t, $^3J(^1H-^1H) = 4.4$ Hz, C*H*CH$_2$]; 5.25 (s, O*H*); 2.97 (m, CHCH$_2$C*H*$_2$); 2.53 (m, CHC*H*$_2$); 1.52 (s), 1.39 [s, C(CH_3)$_3$]. Selected ^{13}C NMR ($CDCl_3$, 30 °C): δ 149.3 (O−*C*); 141.7, 136.2, 135.4, 135.0, 133.9, 130.8, 127.7, 126.8, 125.9, 125.1, 124.9, 123.3 (aromatic *C*); 35.0, 34.3 [*C*(CH$_3$)$_3$]; 31.7, 29.7 [C(*C*H$_3$)$_3$]; 27.9, 23.4 (CH*C*H$_2$*C*H$_2$).

2-(1-Naphthyl)-4,6-di-*tert*-butylphenol (6). A sample of 2-(3,4-dihydronaphthyl)-4,6-di-*tert*-butylphenol was heated in the presence of a catalytic amount of palladium on activated carbon under a nitrogen atmosphere for approximately 30 min. The flask and its contents were cooled, and methylene chloride was added. This solution was filtered to remove Pd/C and the filtrate evacuated to dryness, affording a yellow oil. Dissolving the yellow oil in hot ethanol and slow cooling afforded 9.1 g (25% based on 31.4 g of 2-bromo-4,6-di-*tert*-butylphenol) of 2-(1-naphthyl)-4,6-di-*tert*-butylphenol as a white solid. Anal. Calcd for $C_{24}H_{28}O$: C, 86.70; H, 8.49. Found: C, 86.69; H, 8.52. HRMS: calcd, *m*/*z* 333.2218; found, *m*/*z* 333.2217. ^1H NMR ($CDCl_3$, 30 °C): δ 7.00−7.90 (aromatics); 4.82 (s, O*H*); 1.44 (s), 1.32 [s, C(CH_3)$_3$]. Selected ^{13}C NMR ($CDCl_3$, 30 °C): δ 149.3 (O−*C*); 123.8−141.8 (aromatic *C*); 35.1, 34.4 [*C*(CH$_3$)$_3$]; 31.7, 29.7 [C(*C*H$_3$)$_3$].

2,6-Bis(1-naphthyl)cyclohexanone. Following a procedure developed by Hay,[9] 26 g (0.084 mol) of bis(1-naphthyl)-acetone,[23] 11.5 g (0.036 mol) of Bu_4NBr, 50 mL of a 50% NaOH solution, and 30 mL of chlorobenzene were mixed in a round-bottomed flask. To this suspension was slowly added 8.53 mL (0.084 mol) of $Br(CH_2)_3Br$ under a N_2 atmosphere. The mixture was stirred overnight and then poured into H_2O and extracted with $CHCl_3$. The $CHCl_3$ extract was washed with H_2O and dried with $MgSO_4$. Evacuation of the extract to dryness afforded a yellow oil. Addition of EtOH afforded 9.2 g (31%) of **3** as a white precipitate which was isolated by filtration and washed with hexane. Anal. Calcd for $C_{26}H_{22}O$: C, 89.11; H, 6.33. Found: C, 87.40; H, 6.22. HRMS: calcd, *m*/*z* 351.1749; found, *m*/*z* 351.1748. ^1H NMR ($CDCl_3$, 30 °C): δ 7.20−8.00 (aromatics); 4.81 [dd, $^3J(^1H-^1H) = 11.8$, 5.4 Hz, C*H*, 2H]; 2.20−2.70 (aliphatics, CH_2CH_2, 6H). Selected ^{13}C NMR ($CDCl_3$, 30 °C): δ 207.8 (*C*O); 134.7, 133.7, 131.8 (aromatic *C*); 129.0, 127.6, 125.9, 125.4, 125.30, 125.26, 122.9 (aromatic *C*H); 53.6 (*C*H); 35.3 (CH*C*H$_2$); 26.6 (CH$_2$*C*H$_2$).

2,6-Bis(1-naphthyl)phenol (7). To a round-bottomed flask was added 9.2 g (0.026 mol) of 2,6-bis(1-naphthyl)cyclohexanone and a catalytic amount of Pd/C (10%). The mixture was heated until a melt was formed, and then heating was continued for approximately 15 min until the melted solution ceased frothing. The flask and its contents were then cooled to room temperature, and CH_2Cl_2 was added. The Pd/C was removed by filtration and the CH_2Cl_2 filtrate evacuated to dryness, affording a yellow oil. This oil was dissolved in hot heptane and slowly cooled to room temperature, affording 4.3 g (47%) of **4** as white crystals. Anal. Calcd for $C_{26}H_{18}O$: C, 90.14; H, 5.24. Found: C, 87.50; H, 5.32. HRMS: calcd, *m*/*z* 347.1436; found, *m*/*z* 347.1436. ^1H NMR ($CDCl_3$, 30 °C): δ 6.80−8.20 (aromatics); 4.78 (s), 4.74 (s, O*H*). Selected ^{13}C NMR ($CDCl_3$, 30 °C): δ 150.7, 150.6 (*C*O); 135.1, 135.0, 133.8, 131.95, 131.88, 127.0, 126.93 (aromatic *C*); 131.3, 129.3, 128.4, 128.3, 128.0, 127.8, 126.3, 126.2, 126.0, 125.9, 125.6, 120.3, 120.2 (aromatic *C*H).

2,6-Bis(1-naphthyl)-3,5-diphenylphenol (8). A 1 L round-bottomed flask was charged with 28.9 g (0.093 mol) of bis(1-naphthyl)acetone, 19.5 g (0.093 mol) of *trans*-chalcone, and approximately 400 mL of MeOH. To this suspension was added 2.1 g (0.091 mol) of Na. The yellow solution which formed was stirred for 1 h at room temperature, and then 8.6 g (0.37 mol) of Na was added. The solution was refluxed overnight and then the MeOH removed in vacuo, affording a brown solid. This brown solid was dissolved in CH_2Cl_2 and washed several times with water. The remaining CH_2Cl_2 solution was then dried with $MgSO_4$ and evacuated to dryness, affording 44.0 g of a

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Table 5. Metal−Metal Bond Distances for 1,3-Dimetallacyclobutadiene Compounds

compd	M−M, Å	ref
$[Nb_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$	2.897(2)	13
anti-$[Nb_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_2(OC_6H_3Ph_2\text{-}2,6)_2]$	2.9082(8)	15
$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3(OC_6H_3Ph_2\text{-}2,6)]$	2.8825(6)	16
$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3(OC_6HNp\text{-}2\text{-}Ph_3\text{-}3,5,6)]$ (**16**)	2.8943(6)	*a*
$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3(OC_6H_3Np_2\text{-}2,6)]$ (**17**)	2.8886(7)	*a*
1,1-$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_2(OC_6H_3Bu^t_2\text{-}2,6)_2]$	2.9071(4)	16
$[Nb_2(\mu\text{-}CSiMe_3)_2(cb)_4]$	2.9015(4)	14
$[Ta_2(\mu\text{-}CSiMe_3)_2(cb)_4]$	2.8801(4)	14
$[(Me_3SiCH_2)_2(Cl)W(\mu\text{-}CSiMe_3)_2W(Cl)(CH_2SiMe_3)_2]$	2.760(1)	17
$[(Me_3SiCH_2)_2(Br)W(\mu\text{-}CSiMe_3)_2W(Br)(CH_2SiMe_3)_2]$	2.757(1)	17
$[W_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$	2.521(2), 2.549(2)	18
$[W_2(\mu\text{-}CSiMe_3)_2W(OPr\text{-}i)_4]$	2.618(2)	19
$[W_2(\mu\text{-}CPh)_2W(OBu\text{-}t)_4]$	2.665(1)	20
$[Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$	2.557(1)	21

[a] This work.

yellowish orange solid. A 1 L round-bottomed flask was charged with 20 g of this solid and a catalytic amount of palladium on activated carbon. The neat mixture was melted and then refluxed for 2 h. After the mixtured was cooled to room temperature, methylene chloride was added and the mixture filtered to remove Pd/C. The dark red filtrate was then treated with activated carbon and filtered through silica gel, affording a dark yellow solution that dried to a dark glassy solid. This solid was dissolved in hot toluene, which upon cooling afforded 3.5 g (18%) of 2,6-bis(1-naphthyl)-3,5-diphenylphenol as white crystals which were washed with pentane and dried in vacuo. HRMS: calcd, *m*/*z* 499.2062; found, *m*/*z* 499.2061. ^{1}H NMR ($CDCl_3$, 30 °C): δ 7.00−8.10 (aromatics); 4.95 (s), 4.93 (s, O*H*). Selected ^{13}C NMR ($CDCl_3$, 30 °C): δ 151.43, 151.38 (*C*O); 124.0−141.0 (aromatics).

1-(1-Naphthyl)-3-phenyl-2-propanone. Sodium metal (30 g, 1.3 mol) was dissolved in 500 mL of dry ethanol, and a mixture of (1-naphthyl)acetonitrile (100 g, 0.60 mol) and ethyl phenylacetate (120 mL, 0.74 mol) was added dropwise with rapid stirring. Upon complete addition, a condenser was attached to the flask and the solution was refluxed overnight. After it was cooled to room temperature, the reaction mixture was extracted with diethyl ether and the ether layer discarded. The aqueous solution was acidified using concentrated HCl and extracted with ether. The ether layer was washed with water followed by two washings with a 10% sodium bicarbonate solution and then dried over magnesium sulfate. After filtration, the volume of the solution was reduced in vacuo to yield 1-(1-naphthyl)-1-cyano-3-phenyl-2-propanone as a light brown oil. IR (neat): 2188 cm^{-1} (ν(CN)). The compound prepared above, 1-(1-naphthyl)-1-cyano-3-phenyl-2-propanone, was placed in a 1000 mL round-bottomed flask fitted with a reflux condenser, and 450 mL of an 80% sulfuric acid solution was added. The mixture was heated to reflux overnight, during which time a dark sludge formed. The reaction mixture was cooled to room temperature and extracted with methylene chloride. The methylene chloride solution was washed with water, 10% sodium hydroxide solution, and water, dried over magnesium sulfate and silica gel, filtered through a plug of silica gel, and concentrated in vacuo. The resulting dark oil was dissolved in a mixture of pentane/absolute ethanol and placed in the freezer overnight. The solid was collected by vacuum filtration and washed with a small portion of ice cold ethanol to yield 1-(1-naphthyl)-3-phenyl-2-propanone as off-white crystals. ^{1}H NMR ($CDCl_3$; 30 °C): δ 7.05−7.85 (m, aromatics, 12 H); 4.11 (s, CH_2, 2H); 3.66 (s, CH_2, 2H). ^{13}C NMR ($CDCl_3$, 30 °C): δ 205.9 (*C*═O); 134.0, 133.8, 132.2, 130.7, 129.4, 128.6, 128.4, 128.2, 128.0, 127.9, 127.0, 126.4, 126.3, 125.8, 125.5, 123.7, 48.6 (*C*H$_2$); 47.3 (*C*H$_2$).

2-(1-Naphthyl)-3,5,6-triphenylcyclohex-2-enone. To a mixture of 1-(1-naphthyl)-3-phenyl-2-propanone (52.0 g, 0.20 mol) and *trans*-chalcone (40.0 g, 0.20 mol) in 400 mL of dry methanol was added sodium methoxide (10.6 g, 0.20 mol). The reaction mixture was stirred at room temperature for several hours, more sodium methoxide was added (42.4 g, 0.80 mol), and the solution was heated to reflux for 12 h. The solution was placed in an ice bath, and the solid was collected via vacuum filtration and washed with a small portion of ice-cold methanol to yield 2-(1-naphthyl)-3,5,6-triphenylcyclohex-2-enone as a light tan solid. ^{1}H NMR ($CDCl_3$, 30 °C): δ 7.0−7.8 (aromatics); 4.21 (d, 1H); 3.98 (m, 1H); 3.0−3.5 (m, 1H).

2-(1-Naphthyl)-3,5,6-triphenylphenol (9). A 500 mL round-bottomed flask was charged with 2-(1-naphthyl)-3,5,6-triphenylcyclohex-2-enone, 1 g of 10% palladium on activated carbon, and 200 mL of phenyl ether. The mixture was heated to reflux for 12 h and cooled to room temperature. No solid formed; the phenyl ether was removed by vacuum distillation, and the residue was purified using preparatory TLC. ^{1}H NMR ($CDCl_3$; 30 °C): δ 8.05 (d, 1H); 6.8−7.8 (m, 22H, aromatics); 5.07 (s, 1H, −OH).

2,6-Bis(1-naphthyl)-3,5-di-*tert*-butylphenol (10). To a stirred solution of tris(1-naphthyl)bismuth (20 g, 34 mmol) in CH_2Cl_2 at −78 °C was added dropwise $SOCl_2$ (3 mL, 35 mmol). The reaction mixture was stirred for 30 min and warmed to room temperature, and the solvent was removed under vacuum. To the remaining powder was added benzene (200 mL), 1,1,2,2-tetramethylguanadine (12 mL, 102 mol), and 3,5-di-*tert*-butylphenol (3.3 g, 16 mmol), and the solution was heated under reflux for 20 h., cooled and evaporated. The residue was fractionated by column chromatography (eluant methylene chloride−pentane, 95:5), giving 2,6-bis(1-naphthyl)-3,5-di-*tert*-butylphenol (2.5 g, 43.5%). ^{1}H NMR (C_6D_6, 30 °C): δ 7.9−7.23 (m, aromatics); 4.15 (s, O*H*); 1.18 [s, C(C*H*$_3$)$_3$]. Selected ^{13}C NMR (C_6D_6, 30 °C): δ 151.7 (O−*C*); 148.5, 136.2, 133.5, 129.5, 128.1, 128.0, 126.6, 126.1, 125.9, 125.3, 122.8, 118.0, 109.5 (unsaturated C); 37.2 [*C*(CH$_3$)$_3$]; 32.4 [C(*C*H$_3$)$_3$]. HRMS: calcd for $C_{34}H_{34}O$, *m*/*z* 459.2688; found, *m*/*z* 459.2688.

$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3(OC_6HPh_4\text{-}2,3,5,6)]$ (13). To a benzene (25 mL) solution of $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$ (0.25 g, 0.28 mmol) was added 2,3,5,6-diphenylphenol (0.11 g, 0.28 mmol). The resulting clear red solution was stirred for 11 h before the solvent was removed in vacuo. The resulting orange solid was washed with hexane and dried in vacuo. Yield: 0.11 g (33%). Anal. Calcd for $C_{50}H_{72}OSi_5Ta_2$: C, 50.41; H, 6.09. Found: C, 49.78; H, 5.93. ^{1}H NMR (C_6D_6, 30 °C): δ 7.50−7.00 (aromatics); 1.25, 1.02, −0.24 (s, Ta−C*H*$_2$); 0.52, 0.32, 0.16 (s, CH$_2$Si*Me*$_3$); −0.04 (s, μ-CSi*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): 398.3 (μ-*C*SiMe$_3$); 158.8 (Ta−O−*C*); 79.9, 78.9, 64.5 (Ta−CH$_2$); 5.01 (μ-CSi*Me*$_3$); 3.91, 3.71, 3.51 (CH$_2$Si*Me*$_3$).

$[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_3(OC_6HPh_2\text{-}2,6\text{-}Me_2\text{-}3,5)]$ (14). To a benzene (25 mL) solution of $[Ta_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4]$ (0.25 g, 0.28 mmol) was added 3,5-dimethyl-2,6-diphenylphenol (0.078 g, 0.28 mmol). The resulting clear red solution was stirred for 18 h before the solvent was removed in vacuo to yield the orange product. Yield: 0.16 g (64%). Anal. Calcd for $C_{40}H_{68}OSi_5Ta_2$: C, 45.01; H, 6.42. Found: C, 44.63; H, 6.59.

^{1}H NMR (C_6D_6, 30 °C): δ 7.49−6.82 (aromatics); 2.03 [s, C(CH_3)]; 1.25, 1.01, −0.33 (s, Ta−CH_2); 0.56, 0.34, 0.19 (s, CH_2-SiMe_3); 0.05 (s, μ-CSiMe_3). ^{13}C NMR (C_6D_6, 30 °C): δ 397.6 (μ-*C*SiMe$_3$); 156.4 (Ta−O−*C*); 79.3, 78.1, 63.4 (Ta−CH_2); 21.2 [C(*C*H$_3$)]; 5.05 (μ-CSi*Me*$_3$); 3.95, 3.77, 3.58 (CH_2Si*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3$(OC$_6$HPh$_2$-2,6-Bu$^t_2$-3,5)] (15). To a solution of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] (0.50 g, 0.57 mmol) in benzene (20 mL) was added 2,6-diphenyl-3,5-di-*tert*-butylphenol (0.20 g, 0.57 mmol). The mixture was stirred for 1 day and evacuated to dryness, yielding a red-orange solid. The solid was recrystallized in pentane (1.5 mL), giving orange crystals (0.45 g, 70%). Anal. Calcd for $C_{46}H_{80}OSi_5Ta_2$: C, 48.0; H, 7.00. Found: C, 48.6; H, 7.38. ^{1}H NMR (C_6D_6, 30 °C): δ 7.75−7.03 (aromatics); 1.24 [s, C(CH_3)$_3$]; 1.34, 1.06, −0.50 (s, Ta−CH_2); 062, 0.33, 0.19 (s, CH_2Si*Me*$_3$); −0.02 (s, μ-CSi*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 397.6 (μ-*C*SiMe$_3$); 161.5 (Ta−O−*C*); 79.7, 78.4, 63.9 (Ta−CH_2); 37.8 [*C*(CH$_3$)$_3$]; 33.3 [C(*C*H$_3$)$_3$]; 5.36 (μ-CSi*Me*$_3$); 4.09, 3.69 (CH_2Si*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3${OC$_6$H(1-Np)-2-Ph$_3$-3,5,6}] (16). A toluene solution of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] (0.20 g, 0.23 mmol) was treated with 2-(1-naphthyl)-3,5,6-triphenylphenol (0.11 g, 0.25 mmol) and stirred at room temperature overnight. The solution was layered with a small portion of hexane to induce the formation of bright red-orange crystals of **16**, which were washed with a small portion of hexane and dried in vacuo. The crystals were submitted for an X-ray diffraction study. ^{1}H NMR (C_6D_6, 30 °C): δ 6.80−8.05 (m, aromatics); 1.10 (AB pattern, 2H, CH_2SiMe$_3$); 1.18 (s, 2H, CH_2-SiMe$_3$); 0.49 (s, 9H, CH_2Si*Me*$_3$); 0.24 (s, 9H, CH_2Si*Me*$_3$); 0.16 (s, 9H, CH_2Si*Me*$_3$); −0.11 (s, 18H, CSi*Me*$_3$); −1.14 (d), −1.34 [d, ^2J(H−H) = 12.4 Hz, 2H, CH_2SiMe$_3$ adjacent to phenoxy]. ^{13}C NMR (C_6D_6, 30 °C): δ 398.7 (CSiMe$_3$); 397.9 (CSiMe$_3$); 159.4 (Ta−O−C); 79.4 (*C*H$_2$SiMe$_3$); 78.9 (*C*H$_2$SiMe$_3$); 64.4 (*C*H$_2$-SiMe$_3$, adjacent to the phenol); 5.1 (CH_2Si*Me*$_3$); 4.8 (CH_2Si*Me*$_3$); 3.7 (CH_2Si*Me*$_3$); 3.48 (CSi*Me*$_3$); 3.42 (CSi*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3${OC$_6$H$_3$(1-Np)$_2$-2,6}] (17). A round-bottomed flask was charged with 200 mg (0.23 mmol) of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] and benzene. To this solution was added 78.6 mg (0.23 mmol) of a 50/50 mixture of the *meso* and *dl* forms of 2,6-bis(1-naphthyl)phenol. The mixture was allowed to react at room temperature for 1 day and then evacuated to dryness, affording an orange solid. This solid was recrystallized from pentane over the course of 4 days, affording orange crystals (140 mg, 54%). Anal. Calcd for $Ta_2C_{46}H_{68}OSi_5$: C, 48.49; H, 6.02. Found: C, 48.20; H, 5.84. ^{1}H NMR (C_6D_6, 30 °C): δ 6.80−8.10 (aromatics); 1.17 (s), 0.95 (s, Ta−CH_2, *meso*); 0.41 (s), 0.38 (s), 0.22 (s), 0.21 (s), 0.19 (s), 0.13 (s, CH_2Si*Me*$_3$); −0.11 (s), −0.43 (s, μ-CSi*Me*$_3$, *dl*); −0.31 (s, μ-CSi*Me*$_3$, *meso*); −1.15 [d, ^2J(^{1}H−^{1}H) = 12.4 Hz], −1.24 [d, ^2J(^{1}H−^{1}H) = 12.3 Hz, O−Ta−CH_2, *dl*]; −1.25 (s, O−Ta−CH_2, *meso*). ^{13}C NMR (C_6D_6, 30 °C): δ 399.8, 396.2 (μ-*C*SiMe$_3$, *dl*); 396.4 (μ-*C*SiMe$_3$, *meso*); 159.3 (Ta−O−*C*); 79.6, 79.3, 78.0, 77.1, 64.2, 63.8 (Ta−CH_2); 3.4, 3.3, 3.2 (μ-CSi*Me*$_3$); 5.1, 4.5, 4.5, 4.1, 3.6, 3.6 (CH_2Si*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3${OC$_6$H$_3$(1-Np)$_2$-2,6-Ph$_2$-3,5}] (18). A round-bottomed flask was charged with 250 mg (0.28 mmol) of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] and benzene. To this solution was added 156 mg (0.31 mmol) of a 50/50 mixture of the *meso* and *dl* forms of 2,6-bis(1-naphthyl)-3,5-diphenylphenol. The mixture was heated at 100 °C for 3 h and then evacuated to dryness, affording an orange solid. A minimal amount of pentane was added to this solid and the mixture left undisturbed for several days, affording orange crystals. Anal. Calcd for $Ta_2C_{58}H_{75}OSi_5$: C, 53.98; H, 5.86. Found: C, 52.46; H, 5.45. ^{1}H NMR (C_6D_6, 30 °C): δ 6.69−8.11 (aromatics); 1.37 [d, ^2J(^{1}H−^{1}H) = 12.8 Hz, Ta−CH_2, *dl*]; 1.22 [d, ^2J(^{1}H−^{1}H) = 13.1 Hz, Ta−CH_2, *dl*]; 1.18 (s), 0.92 (s, Ta−CH_2, *meso*); 0.41 (s), 0.36 (s), 0.16 (s), 0.13 (s), 0.12 (s), 0.07 (s, CH_2Si*Me*$_3$); −0.10 (s), −0.45 (s, μ-CSi*Me*$_3$, *dl*); −0.34 (s, μ-CSi*Me*$_3$, *meso*); −1.37 [d, ^2J(^{1}H−^{1}H) = 12.3 Hz], −1.56 [d, ^2J(^{1}H−^{1}H) = 12.3 Hz, O−Ta−CH_2, *dl*]; −1.50 (s, O−Ta−CH_2, *meso*). ^{13}C NMR (C_6D_6, 30 °C): δ 399.8, 396.0 (μ-*C*SiMe$_3$, *dl*); 398.0 (μ-*C*SiMe$_3$, *meso*); 159.9, 159.7 (Ta−O−*C*); 79.6, 79.2, 77.8, 77.1, 64.2, 64.0 (Ta−*C*H$_2$); 3.2, 3.0, −0.3 (μ-CSi*Me*$_3$); 5.1, 4.4, 4.0, 3.4, 3.3, 3.2 (CH_2Si*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3${OC$_6$H(1-Np)$_2$-2,6-Bu$^t_2$-3,5}] (19). To a solution of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] (0.090 g, 0.1 mmol) in benzene (1.5 mL) was added 2,6-bis(1-naphthyl)-3,5-di-*tert*-butylphenol (0.050 g, 0.1 mmol). The mixture was allowed to react in a Solv-Seal NMR tube at 100 °C for 1 day, and the product was analyzed by ^{1}H and ^{13}C NMR. ^{1}H NMR (C_6D_6, 30 °C): 7.90 − 7.15 (aromatics); 1.07 [s, C(CH_3)$_3$]; 0.46, −0.14, −0.46 (s, CH_2Si*Me*$_3$); −0.04 (s, μ-CSi*Me*$_3$); −1.64 [d, ^2J(^{1}H−^{1}H) = 12.4 Hz, Ta−CH_2]; −1.90 [d, ^2J(^{1}H−^{1}H) = 12.4 Hz, Ta−CH_2]. ^{13}C NMR (C_6D_6, 30 °C): δ 399.5, 396.0 (μ-*C*SiMe$_3$); 160.6 (Ta−O−*C*); 79.9, 79.0, 64.0 (Ta−CH_2); 37.9 [*C*(CH$_3$)$_3$]; 33.0 [C(*C*H$_3$)$_3$]; 5.57, 4.73 (μ-CSi*Me*$_3$); 3.69, 3.67, 3.65 (CH_2Si*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3$(OC$_6$H$_2$Ph-2-Bu$^t_2$-4,6)] (20). A round-bottomed flask was charged with 750 mg (0.85 mmol) of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] and benzene. To this solution was added 240 mg (0.85 mmol) of 2-phenyl-4,6-di-*tert*-butylphenol. The mixture was heated at 115 °C for 3 h and then evacuated to dryness, affording a reddish oil. This oil was redissolved in pentane, and upon standing an orange solid had formed (100 mg, 11%), which was washed with pentane and dried in vacuo. ^{1}H NMR (C_6D_6, 30 °C): δ 7.72 (d, ^4J(^{1}H−^{1}H) = 2,6 Hz, *m-H*); 7.06−7.17 (aromatics); 2.30 (s), 1.29 [s, C(CH_3)$_3$]; 1.44 (s), 0.97 (s), −0.14 (s, Ta−CH_2); 0.54 (s), 0.40 (s), 0.20 (s, CH_2Si*Me*$_3$); 0.00 (s, μ-CSi*Me*$_3$). ^{13}C NMR (C_6D_6, 30 °C): δ 397.9 (μ-*C*SiMe$_3$); 158.7 (Ta−O−*C*); 79.8, 77.5, 66.9 (Ta−CH_2); 36.6, 34.6 [*C*(CH$_3$)$_3$]; 32.3, 31.7 [C(*C*H$_3$)$_3$]; 5.0 (μ-CSi*Me*$_3$); 3.86, 3.75, 3.39 (CH_2Si*Me*$_3$).

[Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_3${OC$_6$H$_2$(1-Np)-2-Bu$^t_2$-4,6}] (21). A round-bottomed flask was charged with 500 mg (0.57 mmol) of [Ta$_2$(μ-CSiMe$_3$)$_2$(CH$_2$SiMe$_3$)$_4$] and benzene. To this solution was added 207 mg (0.62 mmol) of 2-(1-naphthyl)-4,6-di-*tert*-butylphenol. The mixture was heated at 115 °C for 3 h and then evacuated to dryness, affording a reddish oil. This oil was redissolved in pentane and cooled to 0 °C, affording red crystals (460 mg, 42%). ^{1}H NMR (C_6D_6, 30 °C): δ 7.09−7.92 (aromatics); 2.49 (s), 1.34 [s, C(CH_3)$_3$]; 1.97 [d, ^2J(^{1}H−^{1}H) = 13.0 Hz, Ta−CH_2]; 0.97 [d, ^2J(^{1}H−^{1}H) = 12.8 Hz, Ta−CH_2]; 1.82 [d, ^2J(^{1}H−^{1}H) = 12.8 Hz, Ta−CH_2]; 0.62 [d, ^2J(^{1}H−^{1}H) = 12.8 Hz, Ta−CH_2]; 0.61 (s), 0.30 (s), 0.28 (s, CH_2Si*Me*$_3$); −0.01 (s), −0.04 (s, μ-CSi*Me*$_3$); −1.38 [d, ^2J(^{1}H−^{1}H) = 12.3 Hz], −1.64 [d, ^2J(^{1}H−^{1}H) = 12.3 Hz, O−Ta−CH_2]. ^{13}C NMR (C_6D_6, 30 °C): δ 399.6, 396.4 (μ-*C*SiMe$_3$); 159.7 (Ta−O−*C*); 79.2, 78.4, 67.0 (Ta−CH_2); 36.6, 34.6 [*C*(CH$_3$)$_3$]; 32.5, 31.8 [C(*C*H$_3$)$_3$]; 5.3, 4.9 (μ-CSi*Me*$_3$); 3.64, 3.57, 3.46 (CH_2Si*Me*$_3$).

Kinetic Studies. Kinetic studies were carried out in C_6D_6 solvent containing a known concentration of H_2CPh_2. To a standard solution of **11** (0.055 M) in this solvent was added various amounts of phenol **5** in a 5 mm NMR tube. The progress of the reaction was then monitored over time by ^{1}H NMR spectroscopy while the sample was maintained in the probe of an INOVA300 spectrometer. The concentration of **11** was determined by integration versus the H_2CPh_2 proton signal.

Acknowledgment. We thank the National Science Foundation (Grant CHE-9700269) for financial support of this research.

Supporting Information Available: Text giving a description of the experimental procedures for X-ray diffraction studies and tables of thermal parameters, bond distances and angles, intensity data, torsion angles, and mutiplicities for **7**, **8**, **16**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990015+