Mechanistic Study of the Cyclometalation of *o*-Arylphenoxide Ligands at Group 5 Metal Centers

Robert W. Chesnut, Gayatry G. Jacob, Joyce S. Yu, Phillip E. Fanwick, and Ian P. Rothwell*

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907

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A series of 4-methylbenzyl derivatives of niobium and tantalum of general formula $M(OAr)_2$ - $(CH_2C_6H_4-4-Me)_3$ (OAr = various 2,6-diaryl- or 2,4,6-triarylphenoxides) have been synthesized. Thermolysis of these compounds at temperatures ranging from 100 to 150 °C is found to lead to the elimination of 1 equiv of *p*-xylene and formation of a series of cyclometalated compounds in which intramolecular activation of the aromatic CH bond of one of the substituent aryl rings of an aryl oxide ligand had taken place. A mechanistic investigation of the reactivity was carried by utilizing 2,4,6-triarylphenoxide groups in which the 2-aryl group contained the para substituent CH₃, CH₃O, and Cl. The product distribution of these competitive ring-closure reactions was estimated by using ¹H NMR spectroscopy. The effect of substituents within the aryl ring upon the rate of ring closure was found to be slight. It was found, however, that irrespective of whether an electron-donating (CH₃) or electron-withdrawing (Cl) substituent was used the substituted ring underwent metalation preferentially over the nonsubstituted ring. The results of this study are inconsistent with these reactions following an electrophilic aromatic substitution pathway proceeding via an arenium ion intermediate being operative for these reactions. A structural study of the tris(4-methylbenzyl) substrates $M(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4Me)_3$ (M = Nb, Ta) showed the compounds to be isomorphous in the solid state with trans, axial aryl oxide ligands and three equatorial 4-methylbenzyl groups about the metal center. Crystal data at 22 °C for Nb(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4Me)_3 are as follows: a = 13.008 (3) Å, b = 14.356 (3) Å, c = 15.235 (2) Å, $\alpha = 105.49$ (1)°, $\beta = 100.98$ (1)°, $\gamma = 91.46$ (2)°, Z = 2, $d_{calcd} = 1.227$ g cm⁻³ in space group PI. Crystal data for Ta(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4Me)_3 at 20 °C are as follows: a = 12.982 (2) Å, b = 14.348 (2) Å, c = 15.210 (5) Å, $\alpha = 105.49$ (2)°, $\beta = 100.81$ (2)°, γ

Introduction

During our studies of the transition-metal organometallic chemistry associated with bulky aryl oxide ligands,¹⁻⁹ we

have recently paid considerable attention to the ligand 2,6-diphenylphenoxide.¹⁰⁻¹² This ligand has demonstrated a range of possible coordination modes at d-block metal centers. Besides simple terminal or bridging coordination to metal centers through the oxygen atom, the ligand is found to be also capable of chelation to the metal center via formation of either a σ -bond or a π -interaction with one of the substituent aryl rings.¹⁰ The parent 2,6-diphenylphenol has also been found to π -bond directly to transition-metal centers through either the substituent aryl rings or the central phenoxy ring itself.^{10c,11}

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Furthermore, intramolecular hydrogenation of the substituent aryl groups has been observed.¹² With high-valent, early d-block metal centers, one of the characteristic reactions of this ligand is its cyclometalation to form a sixmembered metallacycle.¹ This reaction typically takes place when either alkyl or aryl leaving groups are present within the metal coordination sphere. Closely related reactivity has also been observed at Sn(IV) metal centers. although in the case of this p-block metal it is found that halide and dialkylamido leaving groups are necessary.¹³

An important question concerning these intramolecular ring-closure reactions concerns the mechanistic pathway leading to the metallacyclic rings. Given the high-valent, electron-deficient, Lewis acidic nature of the early d-block metal centers involved (Nb⁵⁺, Ta⁵⁺, Ti⁴⁺, Zr⁴⁺), it seems reasonable that the reaction may proceed via initial electrophilic attack of the metal center at the aromatic ring (Scheme I).¹³ Previous mechanistic work dealing with the intramolecular activation of the aromatic CH bonds of benzyl groups by $Hf^{4+14,15}$ and the intermolecular metal-lation of arenes by Sc^{3+16} has indicated little sensitivity of the reactions to the electronic nature of substituents within the aromatic ring. This behavior contrasts markedly with the metallation of arene rings by reagents such as $[(OEP)Rh]^+$ (OEP = octaethylporphyrin) where the use of substituted benzene substrates leads to a somewhat linear Hammett plot and $\rho = 5.43$.¹⁷ The lack of sensitivity to the electronic nature of any ring substituents during cyclometalation at high-valent early d-block metal centers has been argued to be due to the reactions occurring in a concerted fashion via a four-center, fourelectron transition state in which the aromaticity of the substrate ring remains intact (Scheme I).14-16

In order to probe mechanistic questions of this type for the cyclometalation of o-arylphenoxides at various d- and



p-block metal centers, we have used the synthetic methodologies of Dimroth¹⁸ to produce the 2,4,6-triarylphenoxides



The nonsymmetrically substituted compounds offer the possibility for two ring-closure products depending on whether the substituted or nonsubstituted ring is metalated. Assuming that one can demonstrate that the conditions of cyclometalation do not lead to thermodynamic control (i.e., interconversion of isomers does not occur), then simple spectroscopic analysis of the product mixture will give information on the importance of substituents on the reaction.¹⁹

Results and Discussion

Synthesis and Characterization of Compounds. The trichloride compounds $M(OC_6H_3Ph_2-2,6)_2Cl_3$ (M = Nb, Ta)^{10g} react with the magnesium reagent Mg- $(CH_2C_6H_4-4-Me)_2$ in benzene solution to generate the corresponding tris(4-methylbenzyl) compounds 1 and 2 as shown in Scheme II. The NMR spectroscopic properties of 1 and 2 are consistent with their formation. In the ${}^{1}H$ NMR spectrum, a sharp singlet due to three, equivalent methylene groups, $M-\dot{C}H_2C_6H_4$ -4-Me, is evident upfield of the 4-methyl resonance. The shift to higher frequency

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Table I. Fractional Coordinates and Isotropic Thermal Parameters for $Nb(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4-4-Me)_3$ (1)^a

atom	x	У	z	<i>B</i> , Å ²
Nb	0.18945 (3)	0.17140 (3)	0.28152 (3)	2.676 (8)
O(10)	0.0568 (2)	0.2252 (2)	0.2878(2)	2.94 (6)
O(20)	0.3149 (2)	0.1067(2)	0.2686(2)	3.44 (7)
C(11)	-0.0353(3)	0.2575(3) 0.2574(3)	0.3094(3)	2.84(9)
C(12) C(13)	-0.0300(4)	0.3921(4)	0.3590 (4)	42(1)
C(14)	-0.2134(4)	0.3313(4)	0.3734(4)	4.7 (1)
C(15)	-0.2001 (4)	0.2326 (4)	0.3538 (4)	4.1 (1)
C(16)	-0.1130 (4)	0.1946 (3)	0.3208 (3)	3.1 (1)
C(21)	0.4036 (3)	0.0594 (4)	0.2618(3)	3.3(1)
C(22)	0.4783(4)	0.0894(4)	0.2170(4)	4.3(1)
C(23)	0.5759 (5)	-0.027 (5)	0.2218(5) 0.2660(5)	5.6 (2) 6 2 (2)
C(25)	0.5188(5)	-0.0573(4)	0.3048(5)	5.3(1)
C(26)	0.4216 (4)	-0.0190 (4)	0.3002 (4)	3.8 (1)
C(30)	0.2789(4)	0.3105 (4)	0.3099 (4)	3.8 (1)
C(31)	0.3483 (4)	0.3414 (3)	0.4038 (3)	3.6 (1)
C(32)	0.3213(4)	0.4136(4)	0.4750(4)	4.3(1)
C(33)	0.3870(5) 0.4828(5)	0.4456(4) 0.4069(4)	0.5609(4) 0.5800(4)	3.2(2)
C(35)	0.5095(4)	0.3347(5)	0.5113(4)	5.1(1)
C(36)	0.4425(4)	0.3005 (4)	0.4240 (4)	4.2 (1)
C(37)	0.5551 (7)	0.4440 (7)	0.6747 (5)	7.8 (2)
C(40)	0.1267(4)	0.0877 (4)	0.1370 (3)	3.7 (1)
C(41)	0.0926(4)	0.1541(4)	0.0792(3)	3.4(1)
C(42) C(43)	-0.0116(4)	0.1534(4) 0.2163(4)	-0.0325(3)	4.1(1) 4.6(1)
C(43) C(44)	0.0314(5)	0.2841(4)	-0.0282(4)	4.8 (1)
C(45)	0.1348 (5)	0.2859(4)	0.0158(4)	4.5 (1)
C(46)	0.1650 (4)	0.2230 (4)	0.0692 (4)	4.1 (1)
C(47)	-0.0010 (7)	0.3548 (5)	-0.0851 (5)	7.2 (2)
C(50)	0.1699(4)	0.1152(3)	0.3975(3)	3.4(1)
C(51)	0.1919(4) 0.1170(4)	0.1881(3) 0.2471(4)	0.4902(3) 0.5235(4)	3.3(1)
C(52) C(53)	0.1366(5)	0.3104(4)	0.6116(4)	4.8 (1)
C(54)	0.2343 (5)	0.3171(4)	0.6708 (4)	5.1 (1)
C(55)	0.3090 (5)	0.2596 (4)	0.6380 (4)	5.0 (1)
C(56)	0.2897(4)	0.1965 (4)	0.5498 (4)	4.0 (1)
C(57)	0.2558 (8)	0.3863(6)	0.7670 (6)	8.6 (3)
C(121) C(122)	0.0252(4) 0.0476(4)	0.4276 (3)	0.3092(3)	3.3(1)
C(122) C(123)	0.1110(5)	0.4855(4)	0.2054(4)	4.8 (1)
C(124)	0.1539 (5)	0.5669 (4)	0.2766 (4)	5.0 (1)
C(125)	0.1335 (5)	0.5783 (4)	0.3637(4)	4.8 (1)
C(126)	0.0697(4)	0.5096 (4)	0.3796(4)	4.1 (1)
C(161)	-0.1090(4)	0.0870(3)	0.2972(3)	3.3(1)
C(102) C(163)	-0.1193(5)	-0.0671(4)	0.1824(5)	5.8(2)
C(164)	-0.1189 (5)	-0.1143 (4)	0.2494 (5)	5.9 (2)
C(165)	-0.1127 (5)	-0.0628 (4)	0.3393 (4)	5.6 (1)
C(166)	-0.1080(4)	0.0382(4)	0.3648(4)	4.5 (1)
C(221)	0.4576(4)	0.1570(4)	0.1572(4)	4.9 (1)
C(222) C(223)	0.4931(0) 0.4782(7)	0.2341(5) 0.3116(5)	0.1880(5) 0.1234(6)	(.1(2)) 9.2(2)
C(224)	0.4338(7)	0.2719(7)	0.0339(6)	8.9 (2)
C(225)	0.3992 (7)	0.1761 (7)	0.0026 (6)	8.7 (2)
C(226)	0.4102 (6)	0.1195 (6)	0.0631 (5)	6.9 (2)
C(261)	0.3379(4)	-0.0650 (4)	0.3324(4)	4.3 (1)
C(262)	0.3040 (6)	-0.0816 (5)	0.4200 (5)	6.2 (2) 8 2 (2)
C(263)	0.1819(7)	-0.1574(5)	0.3886 (6)	8.6 (2)
C(265)	0.1636 (6)	-0.1445 (5)	0.2999 (6)	7.1(2)
C(266)	0.2405 (5)	-0.0988 (4)	0.2721 (4)	4.9 (1)
C(701)	0.303 (1)	0.737 (1)	-1.011 (1)	14.4 (4)*
C(702)	0.3531(8)	0.7509(7)	-0.9223(7)	8.6 (2)*
C(703) C(704)	0.308(1) 0.328(1)	0.691 (1)	-0.873(1) -0.918(1)	14.4 (4)* 154 (5)*
C(705)	0.276(1)	0.574(1)	-1.005 (1)	15.3 (5)*
C(706)	0.2583 (9)	0.6421 (8)	-1.0626 (8)	10.3 (3)*
C(707)	0.295 (1)	0.8144 (9)	-1.0496 (9)	11.3 (3)*

^aStarred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $4/_3[a^2B(11) + b^2B(22) + c^2B(33) + ab(\cos \gamma)B(12) + ac(\cos \beta)B(13) + bc(\cos \alpha)B(23)].$

Table II.	Fractional	Coordinates	and Isotr	opic Thermal
Paramet	ers for Ta(0C ₆ H ₃ Ph ₂ -2,6	(CH_2C_6H)	$I_4-4-Me)_3 (2)^a$

1 ai ain	eters tor Tal	0061131 112-2,0	/2(011206114-4	-me)3 (2)
atom	x	у —	z	B, \tilde{A}^2
Та	0.18962 (2)	0.17098 (2)	0.28190 (2)	2 780 (5)
$\dot{0}$ (10)	0.10002(2)	0.2243(3)	0.20100(2) 0.2870(3)	32(1)
O(20)	0.3147(3)	0.2248(0)	0.2610(3)	36(1)
C(11)	-0.0348(5)	0.1000(0)	0.3096 (4)	29(1)
C(12)	-0.0487(5)	0.3565(5)	0.3261(4)	33(2)
C(13)	-0.1381(6)	0.3914(5)	0.3585(5)	44(2)
C(14)	-0.2132(6)	0.3309(6)	0.3733(6)	4.9(2)
$\tilde{C}(15)$	-0.1996 (6)	0.2323(5)	0.3537(5)	4.2 (2)
C(16)	-0.1118(5)	0.1936(5)	0.3207(4)	3.2(2)
C(21)	0.4034 (5)	0.0592(5)	0.2623(5)	3.6(2)
C(22)	0.4783 (6)	0.0892 (6)	0.2170(5)	4.4 (2)
C(23)	0.5748 (6)	0.0477(7)	0.2216(7)	6.0 (2)
C(24)	0.5959 (7)	-0.0235(7)	0.2659(7)	6.4 (3)
C(25)	0.5187 (6)	-0.0583(6)	0.3041 (6)	5.3 (2)
C(26)	0.4217 (5)	-0.0190 (5)	0.3005 (5)	3.8 (2)
C(30)	0.2777(6)	0.3085 (5)	0.3101 (5)	4.0 (2)
C(31)	0.3482(5)	0.3404 (5)	0.4040 (5)	3.8(2)
C(32)	0.4422 (6)	0.2994 (6)	0.4245(5)	4.5 (2)
C(33)	0.5093 (6)	0.3319 (6)	0.5107 (6)	5.2(2)
C(34)	0.4830 (7)	0.4061 (6)	0.5803 (6)	5.3 (2)
C(35)	0.3883(7)	0.4452 (6)	0.5609(6)	5.4 (2)
C(36)	0.3217 (6)	0.4136 (5)	0.4755(5)	4.6 (2)
C(37)	0.5558 (9)	0.4430 (8)	0.6749 (7)	8.2 (3)
C(40)	0.1266(5)	0.0888(5)	0.1381(5)	3.8(2)
C(41)	0.0926 (6)	0.1545 (5)	0.0800 (4)	3.8(2)
C(42)	0.1644 (6)	0.2230(5)	0.0697(5)	4.3 (2)
C(43)	0.1340 (7)	0.2862(6)	0.0157(5)	4.8 (2)
C(44)	0.0311(7)	0.2838(6)	-0.0286 (5)	5.0 (2)
C(45)	-0.0416 (6)	0.2153 (6)	-0.0200 (5)	5.1(2)
C(46)	-0.0113 (6)	0.1521(6)	0.0320(5)	4.2 (2)
C(47)	-0.0017 (9)	0.3548 (7)	-0.0843 (6)	7.7 (3)
C(50)	0.1716(6)	0.1163(5)	0.3979(5)	3.8 (2)
C(51)	0.1923(5)	0.1881(5)	0.4906 (4)	3.5 (2)
C(52)	0.2886 (6)	0.1961(5)	0.5505(5)	4.5 (2)
C(53)	0.3072(7)	0.2610(6)	0.6395 (6)	5.5 (2)
C(54)	0.2318(7) 0.1961(7)	0.3186(6)	0.6711(5)	5.4(2)
C(55)	0.1301(7) 0.1170(6)	0.3112(0) 0.9474(5)	0.0108 (0)	4.9 (2)
C(50)	0.1170(0)	0.2474(0) 0.2975(9)	0.5229(5) 0.7676(7)	4.2(2)
C(01)	0.204(1) 0.0254(5)	0.3013(0) 0.4974(5)	0.7070 (7)	9.1(4) 9.1(9)
C(121)	0.0204(0)	0.4274(0)	0.3007 (5)	3.4(2)
C(122)	0.0471(0) 0.1103(7)	0.4154 (5)	0.2203(0)	$\frac{4.2}{50}$
C(123)	0.1103(7) 0.1541(7)	0.5667 (6)	0.2051(0)	5.0(2)
C(125)	0.1348(6)	0.5781(5)	0.2104(0) 0.3634(6)	51(2)
C(126)	0.0708(6)	0.5083(5)	0.3790(5)	4.1(2)
C(161)	-0.1079(5)	0.0867(5)	0.2970(5)	3.6 (2)
C(162)	-0.1154(6)	0.0331(5)	0.2062(5)	4.5 (2)
C(163)	-0.1204(7)	-0.0676 (6)	0.1821(6)	5.9 (2)
C(164)	-0.1194 (7)	-0.1142 (6)	0.2482 (7)	6.1 (2)
C(165)	-0.1121 (7)	-0.0646 (6)	0.3383 (6)	6.0 (2)
C(166)	-0.1071 (6)	0.0375 (6)	0.3646 (5)	4.8 (2)
C(221)	0.4578 (6)	0.1574 (6)	0.1568 (6)	5.2(2)
C(222)	0.4935 (8)	0.2539(7)	0.1884(7)	7.5 (3)
C(223)	0.4810 (9)	0.3138 (8)	0.1282 (8)	9.9 (3)
C(224)	0.4346 (9)	0.2747 (8)	0.0372 (8)	10.0 (3)
C(225)	0.3991 (9)	0.1786 (9)	0.0035 (7)	9.1 (3)
C(226)	0.4106 (8)	0.1205(8)	0.0644(7)	7.0 (3)
C(261)	0.3384 (6)	-0.0657 (5)	0.3321(5)	4.5 (2)
C(262)	0.2416 (6)	-0.0989 (6)	0.2727 (6)	4.9 (2)
C(263)	0.1635 (8)	-0.1447 (7)	0.3001(7)	7.3 (3)
C(264)	0.1789 (8)	-0.1578 (7)	0.3865 (8)	8.2 (3)
C(265)	0.2731 (9)	-0.1269 (7)	0.4475 (7)	8.8 (3)
C(266)	0.3549 (8)	-0.0811 (6)	0.4212 (6)	6.5 (2)
C(1001)	0.293 (2)	0.728 (2)	-0.026(2)	19.1 (8)*
C(1002)	0.353 (1)	0.7608 (9)	0.0721 (9)	9.4 (3)*
C(1003)	0.310(1)	0.595 (1)	0.120(1)	10.1 (6)* 16.2 (6)*
C(1004) C(1005)	0.000 (2) 0.278 (2)	0.000 (1)	-0.001(1)	10.3 (b)* 15 8 (c*
C(1000)	0.270(2) 0.258(1)	0.074 (1)	-0.002 (I) 0.0613 (9)	10.7 (4)*
C(1000)	0.295(1)	0.816(1)	-0.049(1)	12.3 (4)*

^aStarred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $\frac{4}{3}[a^2B(11) + b^2B(22) + c^2B(33) + ab(\cos \gamma)B(12) + ac(\cos \beta)B(13) + bc(\cos \alpha)B(23)].$

Table III. Selected Bond Distances (Å) and Angles (deg) for 1 and 2 (M = Nb (1), Ta (2))



Figure 1. ORTEP view of $Ta(OC_6H_4Ph_2-2,6)_2(CH_2C_6H_4-4-Me)_3$ (2) emphasizing the central coordination sphere. The numbering scheme used for the isomorphous niobium compound 1 is identical.

of the methylene protons is a direct consequence of the 2,6-diphenylphenoxide ligation. The conformation and diamagnetic anisotropy of the 2,6-substituent aryl rings generally causes a shielding of the protons of other ligands adjacent to these groups in the coordination sphere.^{10g} The aromatic protons of the 4-methylbenzyl ligands are also well resolved, as a singlet in compound 1 and an AB pattern in compound 2. In the ¹³C NMR spectrum, the $M-CH_2$ carbon resonates at δ 72.5 ppm for 1 and δ 78.4 ppm for 2.

In order to gain more insight into the molecular structure of the benzyl compounds 1 and 2, a single-crystal X-ray diffraction analysis of both compounds was performed. The two compounds were found to be isomorphous (Figure 1). The fractional coordinates for 1 and 2 are contained in Tables I and II, while some selected bond distances and angles are collected in Table III. Both molecules can be seen to adopt a trigonal bipyramidal environment about the metal center with trans axial aryl oxide oxygen atoms. The three 4-methylbenzyl groups occupy the equatorial positions.²⁰

The M–O and M–C distances (Table III) are consistent with previously reported compounds of Nb(V) and Ta(V)containing related ligands.^{20,21} The Nb-O and Nb-C distances are slightly longer, 0.01-0.03 Å, than the corresponding Ta-O and Ta-C distances. The large M-O-Ar angles found in these compounds are a characteristic

	x x - y -	- (-))
M-C(4)	2.192 (4)	2.179 (6)
M - C(50)	2.181(3)	2.161 (6)
O(20) - M - C(50)	92.0 (1)	92.0 (2)
C(30)-M-C(40)	119.5 (1)	119.4 (3)
C(30-M-C(50))	119.3 (1)	118.6 (3)
C(40)-M-C(50)	121.2(1)	121.9 (3)
M-O(10)-C(11)	167.7 (2)	167.1 (4)
M-O(20)-C(21)	178.1(2)	177.5 (4)

property of aryl oxide ligands bound to high-valent, early d-block metal centers.²¹ The M-CH₂-C angles at the methylene group range from 110 to 116°, typical of pure σ -bound benzyl ligands.²²

Both compounds 1 and 2 exhibit thermal instability at temperatures above 100 °C in toluene solution. Monitoring the thermal reactions by ¹H NMR spectroscopy showed that in both cases the elimination of *p*-xylene occurred with concomitant formation of cyclometalated products. For the niobium complex 1, although the reaction was faster than for 2, a number of products were observed. In the case of the tantalum compound 2, however, thermolysis at temperatures of 100-150 °C was found to be clean, leading to an almost quantitative (as judged by ¹H NMR spectroscopy) yield of a monocyclometalated product (vide infra). It was hence decided that the tantalum system would be more amenable to detailed study with the nonsymmetrically substituted aryl oxide ligands.

The corresponding 2,4,6-triarylphenoxide derivatives of tantalum, 4^{H} , 4^{Me} , 4^{OMe} , and 4^{Cl} were synthesized by using very similar procedures to those used to obtain 1 and 2 (Scheme II). Initially, $TaCl_5$ is reacted with the parent phenol (2 equiv) in refluxing toluene to produce the corresponding trichloride compounds 3 (Scheme II). In the case of 3^H and 3^{Cl}, it was found necessary to purify the trichloride compounds as their monoetherate adducts. Treatment of 3 with $Mg(CH_2C_6H_4-4-Me)_2$ then led to the required tris(4-methylbenzyl) compound 4 (Scheme II). The NMR spectroscopic properties of compounds 4 are very similar to those of the 2,6-diphenylphenoxide derivatives 2. The chemical shifts for the 4-methylbenzyl ligands are almost identical, lending support for the adoption of identical structures in all cases. The only differences in the ¹H NMR spectra of 4 arise from the more complex aromatic pattern and the presence of resonances for the CH_3 and OCH_3 protons in the spectra of 4^{Me} and 4^{OMe} , respectively. One noticeable effect of the introduction of the extra aryl groups in 4 compared to 2 was the decrease in solubility in hydrocarbon solvents. Hence, ¹³C NMR spectra of compounds 4 were recorded in CDCl₃. The Ta-CH₂ carbon atoms were found to resonate at δ 77.8, 77.9, 77.8, and 77.8 ppm for 4^H, 4^{Me}, 4^{OM}e, and 4^{Cl}, respectively.

The 2,6-diphenylphenoxide compound 2 was found to undergo cyclometalation of one of the aryl oxide ligands on thermolysis in hydrocarbon solvents. The reaction was monitored by heating sealed 5-mm NMR tubes of 2 in toluene- d_8 and following the changes by ¹H NMR spectroscopy. At temperatures between 100 and 150 °C, the disappearance of signals due to 2 was observed with the buildup of signals assignable to p-xylene and the monocyclometalated compound 5. On the basis of previous structural studies of niobium and tantalum compounds containing cyclometalated aryl oxide ligands,¹ we assign

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compound 5 the geometry shown in Scheme III. The NMR spectroscopic data of 5 are also consistent with this formulation. In the ¹H NMR spectrum, the two 4methylbenzyl ligands on 5 appear as two AB patterns and a singlet. The singlet due to the 4-methyl group, Ta- $CH_2C_6H_4Me$, is slightly shifted from the position found in the tris(benzyl) substrate 2. The methylene protons, Ta- $CH_2C_6H_4Me$, appear as a well-resolved AB pattern at δ 1.57 and 1.69 ppm. The ortho and meta protons of the 4methylbenzyl ligands also appear as an AB pattern slightly upfield of the normal aromatic region.^{21,22} In the ¹³C NMR spectrum of 5, the new Ta-C(ipso) bond is indicated by the presence of this carbon atom resonating at δ 201.7 ppm. the region typical for tantalum aryl groups.

Another important aspect of the ¹H NMR spectrum of 5 concerns the presence of three well-resolved, equal intensity doublets at δ 7.78, 7.85, and 7.96 ppm. Similar downfield doublets have also been observed for other dblock metal compounds containing cyclometalated 2,6diphenylphenoxide ligands.^{10b} The origin of these three doublets can be understood by studying the conformation adopted by the new metallacycle ring.



In non-metalated, terminal 2,6-diphenylphenoxide ligands, the aryl substituents typically are oriented so that there is a dihedral angle of 35-55° between themselves and the central phenoxy ring (Figure 1).¹⁰ Formation of a sixmembered metallacycle via cyclometalation of this ligand forces the metalated aryl group to be almost coplanar (typically $5-15^{\circ}$) with the phenoxy ring. This has the effect of causing protons H_3 and H_{26} to become deshielded due to the combined diamagnetic anisotropy of the two, coplanar aromatic rings. Hence, two of the downfield doublets can be assigned to H_3 and H_{26} . The remaining doublet can be attributed to H_{23} . It has been well documented that protons ortho to a Ta-C(aryl) bond are typically found to resonate downfield of the normal aromatic region in the ¹H NMR spectrum.^{23,24} Support for the

m.L1. XX7 Constal Data and Data Callestian Demonstration

Table IV. Crys	stal Data allu Dat	ta conection rarameters
formula	NbO ₂ C ₆₇ H ₆₁	$TaO_2C_{67}H_{61}$
fw	991.14	1079.18
space group	PĨ	PĪ
a, Å	13.008 (3)	12.982 (3)
b, Å	14.356 (3)	14.348 (2)
c, Å	15.235 (2)	15.210 (5)
β, deg	100.98 (1)	100.81 (2)
V, Å ³	2683 (2)	2673 (2)
Ζ	2	2
$ ho_{ m calcd}, { m g}/{ m cm}^3$	1.227	1.341
cryst size, mm	$0.56 \times 0.45 \times 0.40$	$0.40 \times 0.34 \times 0.30$
temp, °C	22.0	20.0
radiation (λ, \mathbf{A})	Μο Κα	Μο Κα (0.71073)
	(0.71073)	
linear abs coeff, cm ⁻¹	2.56	20.73
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
scan method	$\theta - 2\theta$	$\omega - 2\theta$
hkl limits	-13 to 13, -15 to 14, 0 to 16	-13 to 13, -15 to 14, 0 to 16
2θ range, deg	4.00-45.00	4.00-45.00
take-off angle, deg	$0.50 + 0.35 \tan \theta$	$0.41 + 0.35 \tan \theta$
Fnon	1040.0	1104.0
ρ factor used in weighting	0.060	0.040
no. of unique data	6988	7002
no. of data width $I > 3.0\sigma(I)$	5585	5695
no. of variables	596	596
largest Δ/σ	0.14	0.29
$R(\bar{F})$	0.055	0.037
$R_w(F)$	0.073	0.046
GOF	2.227	1.193

assignment arises from analysis of the ¹H NMR spectra obtained upon thermolysis of the 2,4,6-triphenylphenoxide compound 4^{H} . The cyclometalated compound formed in this case, 6^H, displays essentially identical chemical shifts for the protons of the 4-methylbenzyl ligands. However, the pattern downfield of the aromatic region has now changed from three doublets to two doublets and a very narrow doublet. The narrow doublet can be assigned to H_3 (meta coupling to H_5), consistent with our initial assignments. The appearance of these three protons in a region well separated from the remaining aryl protons is crucial to our ability to quantify the competitive ring-closure reactions utilizing 4^{Me} , 4^{OMe} , and 4^{Cl} . In these cases, two possible metallacycles can be formed depending whether the substituted or nonsubstituted aryl ring is metalated. In the case of attack on the nonsubstituted ring, the position and appearance of protons H₃, H₂₆, and H_{23} should be similar to those observed for compound 6^{H} . Metallation of the substituted ring will lead to a metallacycle in which proton H_{23} will have no ortho coupling and hence will appear as either a broad singlet or narrow doublet (meta coupling to H_{25}). Furthermore, the presence of the substituent within the metalated ring will lead to changes in the chemical shift of protons H_{23} and H_{26} . Thermolysis of the methyl-substituted compound 4^{Me}

in toluene- d_8 at 150 °C results in a spectrum indicative of the formation of two compounds. The ¹H NMR spectrum is consistent with formation of a mixture of monocyclometalated compounds in which the substituted 6_s^{Me} and unsubstituted 6_u^{Me} rings are metalated (Table IV). In the aliphatic region of the spectrum, two resolvable AB patterns due to the Ta- $CH_2C_6H_4$ -4-Me groups of 6_s^{Me} and 6_u^{Me} are observed. Similarly, there are two AB pratterns upfield of the normal aromatic region due to the ortho and meta protons of these groups. The intensity ratio of these AB

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patterns indicates that one of the isomers predominates over the other in an approximately 3:2 ratio. Assignment of the predominant isomer, in which metalation of the substituted ring has occurred, 6_s^{Me} , can be achieved by studying the pattern due to protons H_3 , H_{26} , and H_{23} . In this region of the spectrum, a set of three peaks can be seen at identical positions to those observed for 6^H. The similarity in their intensity and identical position to those observed for $6^{\rm H}$ allows them to be assigned to the metallacycle formed by metalation of the unsubstituted ring, i.e., due to 6_u^{Me} . Also in this region of the spectrum are three more intense signals, two broad singlets and a doublet. These can be assigned to H₃, H₂₆, and H₂₃ of the metallacycle formed by metalation of the substituted ring, 6_s^{Me} . The methyl substituent within the metalated ring reduce H_{23} to a broad singlet. The ratio of 6_s^{Me} to 6_u^{Me} at 150 °C was determined by expanding the ¹H NMR spectra both in the aliphatic and aromatic regions and cutting and weighting peaks due to the corresponding isomers. The isomer ratio was cross-checked by using the intensity ratio of as many signals as possible. The ratio of 6_s^{Me} to 6_u^{Me} was also determined for reaction temperatures of 120 and 103 °C (Scheme IV). In the case of thermolysis of 4^{OMe} and 4^{Cl}, ¹H NMR spectra consistent with the formation of two isomeric compounds were also obtained. In the low-field, aromatic region, the intensities and chemical shifts due to the isomer formed by attack of the unsubstituted aryl ring were found to be almost identical with those observed for $6^{\rm H}$. The remaining patterns were readily identifiable with that expected for metalation of the substituted ring. The proportions of the two isomers were determined as for the methyl compound at 109, 120, and 150 °C and are tabulated (Scheme IV).

Mechanistic Discussion. Thermolysis of the 2,6-diphenylphenoxide compound 2 at 120 °C leads to the formation of the monocyclometalated compound 3 with a half-life of 20 (2) h. Under identical conditions, cyclometalation of the 2,4,6-triphenylphenoxide compound 4^{H} occurs at a slightly faster rate, with a half-life of 11 (1) h. All three substituted compounds 4^{Me} , 4^{OMe} , and 4^{Cl} cyclometalate at rates slightly faster than the symmetrical aryl oxide compound 4^H. The isomer ratios determined for the products of thermolysis of 4^{Me}, 4^{OMe}, and 4^{Cl} at temperatures of 103, 120, and 150 °C are collected in Scheme IV. It can be seen that, within the experimental errors, the percentage of each of the product metallacycle compounds is essentially unperturbed over this temperature range.



Furthermore, it can be seen that the preference for formation of a substituted versus unsubstituted metallacycle is only slight. The use of para substituents within only one of the aryl rings suggests that on a statistical basis a 50/50 mixture of 6_u^x and 6_s^x will be formed in the absence of any steric or electronic effects. Attack upon the ring carrying the substituent will lead to a new metal-aryl linkage in which the substituent is meta to the new metal-carbon bond. Molecular models based upon related compounds containing cyclometalated 2,6-diphenylphenoxide ligation show that substituents such as Me, OMe, and Cl should have minimal steric impact upon other ligation within the coordination sphere. Hence, any departure from a 50/50 ratio of isomers can be ascribed to the electronic influence of the substituent.

It can be seen in Scheme IV that the introduction of either a methyl, methoxy, or chloro substituent results in preferential attack upon the substituted ring. This is despite the fact that CH_3 is generally considered electron donating while Cl is electron withdrawing.²⁴ If the reactivity proceeds via an arenium ion intermediate formed by electrophilic attack of Ta on the aromatic ring, then one would predict that the ratio of metallacycles formed would correlate with σ_m values of the substituents with a negative ρ value. Based upon the data in Scheme IV, this is not the case. A related study involving cyclometalation of the same ligands at Sn(IV) metal centers with a dialkylamido leaving group (Scheme V) does show a correlation between σ_m of the substituent and the ratio of substituted to unsubstituted metallacycles formed.²⁵ In the case of tin, use of the Cl substitutent inhibits attack on the aromatic ring. Hence, these data can be accommodated into a mechanism involving electrophilic attack by the Sn metal on the aromatic ring followed by intramolecular proton transfer to an NMe2 group to produce a dimethylamine ligand. The use of only a limited number of substituents leads to a ρ value of -1.0 (1) for the reaction. showing that the sensitivity of the reaction to substituents is less than typically found for reactions such as aromatic mercuration ($\rho = -4$ to -6).²⁶

In the case of the tin system, it is possible to demonstrate that the observed product ratios are kinetic and not thermodynamically controlled. This was achieved by selective precipitation of the compound in which metalation of the chloro-substituted aryl ring had occurred. Thermolysis of this compound at 100 °C showed no equilibration with the other metalation product. In the case of tantalum, no such evidence was obtained. However, monitoring the ¹H NMR spectra of the reactions carried out at 103 °C showed the initial product ratios to be the same as these in Scheme IV even when the reactions were

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less than 1% complete. Furthermore, we believe that an equilibration process involving rapid ring opening and closing is unlikely for this system. A much more reasonable outcome of further CH bond activation would be the formation of biscyclometalated products with elimination of the *p*-xylene. However, the work of Bercaw et al. has clearly demonstrated that thermodynamic equilibration of metallacycle rings is possible at Sc^{3+} metal centers.²⁷

Hence, for the tantalum system, a straightforward analysis of the data leading to a mechanistic conclusion is not possible. It is interesting to note not only that cyclometalation of benzyl ligands at Hf(IV) metal centers demonstrated a very small dependence on substituents but also that the reaction was accelerated slightly by both electron-donating $(p-NMe_2)$ and -withdrawing $(p-CF_3)$ groups.¹⁵ There is a possible complication in the 2,6-diarylphenoxide systems, which may in fact be dominating the reactivity. As can be seen from the solid-state structure of substrates 1 and 2 (Figure 1), substituent aryl rings in non-metalated 2,6-diphenylphenoxide ligands adopt conformations that are twisted with respect to the central phenoxy ring. In order for aromatic CH bond activation to occur, this ring must be rotated approximately coplanar with the central ring. There will be a barrier to this rotation, as one would expect the coplanar arrangement (as found in the final metallacycle) to generate unfavorable steric interactions between H_3 and H_{26} . This rotation prior to actual CH bond activation may indeed be an important contribution to the activation energy. It is highly likely that there will be a subtituent effect upon this barrier to rotation. In this context, it is important to note that there have been studies dealing with the effect of substituents upon the rate of racemization of optically active biphenyl compounds.²⁸ In one particular series of studies, the effect of substituents para to the central aryl-aryl bond was investigated.^{28a} It was discovered that the substituent effect for racemization of 4'-substituted, 2-nitro-6carboxy-2'-methoxybiphenyl followed the trend, $NO_2 > Br$ > Cl > CH₃ > OCH₃ > H. It was argued from this study that the presence of the substituents led to an electronic stabilization of the coplanar structure by inter-annular conjugation.^{28b} Hence, both electron-donating and electron-withdrawing substituents will electronically stabilize the adoption of a coplanar conformation for biphenyl systems over an unsubstituted ring.²⁸ This idea can be directly applied to the cyclometalation reactions in this study. If one assumes that rotation of the aryl ring to be metalated into a coplanar conformation is a contributing factor, then the presence of para substituents in one of the rings will lead (in the absence of the other factors) to preferential metalation of that particular ring. This is especially true if the metalation reaction itself proceeds through a transition state/intermediate that is insensitive to substituents. It has been known since the early part of this century that ring-closure reactions can be accelerated by the introduction of substituents onto the backbone of the precursor molecule.²⁹ This is so-called "gem-dimethyl" or "Thorpe-Ingold" effect was recognized as being important in cyclometalation chemistry by Shaw.³⁰ The presence of bulky substituents on phosphine ligands was shown to facilitate their cyclometalation, and entropic argument has been used to explain this effect.²⁹ In the present case of the cyclometalation of o-arylphenoxide ligands at tantalum, it would appear that formation of the metallacycle is accelerated electronically. It must be recognized that the presence of substituents within the aryl ring may be promoting the reaction by favoring a conformation in which the CH bond about to be activated is being brought close to the metal center.

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or in vacuo either 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 $M(OC_6H_3Ph_2-2,6)_2Cl_3$ (M = Nb, Ta) were obtained by published procedures.^{10g} 2,4,6-Triphenylphenol and the substituted derivatives were obtained by the methods of Dimroth.¹⁸ ¹H and ¹³C NMR spectra were recorded by using a Varian Associates Gemini 200 spectrometer. Microanalytical data were obtained in-house at Purdue.

 $Nb(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4-4-Me)_3$ (1). To a solution of $Nb(OC_6H_3Ph_2-2,6)_2Cl_3$ (1.0 g, 1. mmol) in benzene (20 mL) was added $Mg(CH_2C_6H_4-4-Me)_2$ (1.36 g, 5.8 mmol). The mixture was stirred for 1 h at room temperature and filtered. The solvent was removed from the red filtrate, and the crude solid was dissolved in a minimum amount of toluene. Slow cooling of this solution yielded the pure product as large red crystals that were isolated, washed with hexane, and dried. Yield = 0.66 g (48%). Anal. Calcd for NbO₂C₆₇H₆₁·C₇H₈: C, 81.28; H, 6.11. Found: C, 80.95; H, 6.20. ¹H NMR (C₆D₆, 30 °C): δ 2.02 (s, NbCH₂); 2.17 (s, 4-*Me*); 6.66 (s, ortho and meta protons on NbCH₂C₆ H_4 -4-Me); 6.9-7.5 (m, aromatics). ¹³C NMR (C_6D_6 , 30 °C): δ 72.5 (NbCH₂); 21.1 (4-Me).

 $Ta(OC_6H_3Ph_2-2,6)_2(CH_2C_6H_4-4-Me)_3$ (2). An essentially identical procedure to that used for 1 above yielded pure yellow crystals of $2 \cdot C_7 H_8$ from toluene solution. Anal. Calcd for $TaO_2C_{67}H_{61}\cdot C_7 H_8$: C, 74.57; H, 5.70. Found: C, 74.51; H, 5.72. ¹H NMR (C_6D_6 , 30 °C): δ 1.22 (s, TaCH₂); 2.09 (s, 4-Me); 6.53 (d), 6.38 (d, $\check{T}a\check{C}H_2C_6H_4$ -4-Me); 6.8–7.4 (m, aromatics). ¹³C NMR $\begin{array}{l} (C_6 D_6, \ 30\ ^\circ C): \ \delta \ 78.4 \ (Ta CH_2); \ 20.9 \ (4\text{-}Me). \\ Ta (OC_6 H_2 Ph_3\text{-}2,4,6)_2 Cl_3 \ (3^H). \ To \ a \ suspension \ of \ Ta Cl_5 \ (2.36) \end{array}$

g, 6.59 mmol) in toluene (25 mL) was added a solution of 2,4,6triphenylphenol (HOC₆H₂Ph₃-2,4,6; 4.49 g, 14 mmol) in toluene (40 mL). The resulting mixture was refluxed for 4 h and cooled, and the solvent was removed in vacuo. The resulting crude product was dissolved in a minimum quantity of Et₂O and the clear yellow solution allowed to stand whereupon crystals of the monoetherate adduct of 3 slowly came out of solution. Yield = 3.89 g (59%). Additional product was obtained by slow evaporation of the supernatant. Anal. Calcd for TaO₃Cl₃C₅₂H₄₄·Et₂O: C, 62.19; H, 4.42; Cl, 10.59. Found: C, 62.32; H, 4.80; Cl, 10.39. The NMR spectra of 3^H·Et₂O are not particularly informative: ¹H NMR (C_6D_6): δ 3.60 (br, OCH₂CH₃); 0.66 (br, OCH₂CH₃).

 $Ta(OC_6H_2Ph_2C_6H_4Me)_2Cl_3$ (3^{Me}). A mixture of $TaCl_5$ (2.32 g, 6.48 mmol) and $HOC_6H_2Ph_2C_6H_4Me$ (4.47 g, 13.3 mmol) was refluxed in toluene (35 mL). On cooling, the product was formed as a yellow microcrystalline precipitate. Yield = 4.32 g (71%). Evaporation of the supernatant yielded additional product. Anal. Calcd for $TaO_2Cl_3C_{50}H_{38}$: C, 62.68; H, 4.00; Cl, 11.10. Found: C, 62.15; H, 4.18; Cl, 11.37. ¹H NMR (C₆D₆, 30 °C): δ 2.50 (s, CH_3 ; 7.0-7.5 (m, aromatics).

 $Ta(OC_6H_2Ph_2C_6H_4OMe)_2Cl_3$ (3^{OMe}). An essentially identical procedure to that used to prepare 3^{Me} yielded 5.02 g (80% yield) of 3^{OMe} . Anal. Calcd for TaO₄C₅₀H₃₈: C, 60.65; H, 3.87; Cl, 10.87. Found: C, 60.08; H, 4.18; Cl, 11.34. ¹H NMR (C₆D₆, 30 °C): δ 3.30 (s, OMe); 6.8-7.5 (m, aromatics)

 $Ta(OC_6H_2Ph_2C_6H_4Cl)_2Cl_3$ (3^{Cl}). An identical procedure to that used for 3^{H} only using TaCl₅ (2.38 g, 6.64 mmol) and $HOC_6H_2Ph_2C_6H_4Cl$ (4.74 g, 13.3 mmol) yielded the etherate 3^{Cl} . Anal. Calcd for 3^{Cl} . Et₂O: C, 58.20; H, 3.94; Cl, 16.52. Found: C, 58.71; H, 4.44; Cl, 15.60. ¹H NMR (C₆D₆, 30 °C): δ 3.39 (br, OCH_2CH_3 ; 0.57 (br, OCH_2CH_3), 7.0-7.5 (m, aromatics).

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Tris(4-methylbenzyl) Compounds 4. Identical procedures were used for the formation of compounds 4^H, 4^{M3}, 4^{OMe}, and 4^{CI} as were used for 1 and 2. Analytical and spectroscopic data for these four compounds follow.

4^H. Anal. Calcd for $TaO_2C_{72}H_{61}$: C, 75.91; H, 5.40. Found: C, 755.17; H, 5.28. ¹H NMR (C_6D_6 , 30 °C): δ 1.459 (s, $TaCH_2$); 2.15 (s, 4-*Me*); 6.49 (d), 6.63 (d, $TaCH_2C_6H_4$ -4-Me); 7.0–7.6 (m, aromatics). ¹³C NMR (CDCl₃, 30 °C): δ 77.8 ($TaCH_2$); 20.7 (4-Me).

4^{Me}. Anal. Calcd for TaO₂C₇₄H₆₅: C, 76.14; H, 5.61. Found: C, 75.77; H, 5.61. ¹H NMR (C₆D₆, 30 °C): δ 1.46 (s, TaCH₂); 2.30 (s, 4-*Me*); 2.15 (s, CH₃); 6.53 (d), 6.63 (d, TaCH₂C₆H₄-4-Me); 7.0–7.6 (m, aromatics). ¹³C NMR (CDCl₃, 30 °C): δ 77.9 (TaCH₂); 21.3 (4-*Me*); 20.8 (CH₃).

4^{OMe}. Anal. Calcd for TaO₄C₇₄H₆₆: C, 74.11; H, 5.46. Found: C, 73.05; H, 5.80. ¹H NMR (C₆D₆, 30 °C): δ 1.50 (s, TaCH₂); 2.18 (s, 4-Me); 3.58 (s, OCH₃); 6.57 (d), 6.63 (d, TaCH₂C₆H₄-4-Me); 7.0–7.7 (m, aromatics). ¹³C NMR (CDCl₃, 30 °C): δ 77.8 (TaCH₂); 20.8 (4-Me); 55.2 (OCH₃).

 $4^{\rm Cl}$. Anal. Calcd for TaO₂Cl₂C₇₂H₅₉: C, 71.58; H, 4.92; Cl, 5.87. Found: C, 71.63; H, 5.23; Cl, 5.56. ¹H NMR (C₆D₆, 30 °C): δ 1.47 (s, TaCH₂); 2.10 (s, 4-*Me*); 6.49 (d), 6.60 (d, TaCH₂C₆H₄-4-Me); 7.0–7.6 (m, aromatics). ¹³C NMR (C₆D₆, 30 °C): δ 77.8 (TaCH₂); 20.7 (*Me*).

Cyclometalated Compounds 5 and 6. The tris(4-methylbenzyl) compounds 2 and 4 were converted to the corresponding monocyclometalated compounds by thermolysis at temperatures between 100 and 150 °C in toluene- d_g solution within sealed 5-mm ¹H NMR tubes. Compound 5 was also obtained on a preparative scale by thermolysis of 2 in toluene at 150 °C in a sealed flask for 24 h. Removal of a solvent generated *p*-xylene in vacuo followed by washing with hexane to yield 5 as a pale yellow solid. Selected spectroscopic properties of the cyclometalated compounds follow.

5. Anal. Calcd for TaO₂C₅₂H₄₃: C, 70.91; H, 4.89. Found: C, 70.58; H, 4.81. ¹H NMR (C₆D₅CD₃, 30 °C): δ 1.57 (d), 1.69 (d, TaCH₂); 6.11 (d), 6.69 (d, TaCH₂C₆H₄-4-Me); 2.12 (s, 4-Me); 7.79 (d), 7.86 (d), 7.97 (d, H₃, H₂₃, H₂₆). ¹³C NMR (C₆D₆, 30 °C): δ 201.7 (TaC); 74.6 (TaCH₂); 21.0 (4-Me).

6^H. ¹H NMR ($C_6D_5CD_3$, 30 °C): δ 1.55 (d), 1.79 (d, TaC H_2 ; 6.09 (d), 6.73 (d, TaC $H_2C_6H_4$ -4-Me); 2.18 (s, 4-Me); 7.95 (d), 8.05 (d, H_{23} and H_{26}); 8.24 (br s, H_3).

(d, H_{23} and H_{26}); 8.24 (br s, H_3). 6_s^{Me} . ¹H NMR ($C_6D_5CD_3$, 30 °C): δ 1.69 (d), 1.78 (d, TaCH₂); 6.10 (d), 6.72 (d, TaCH₂ C_6H_4 -4-Me); 2.15 (s, 4-Me); 7.70 (br s, H_{23}), 7.97 (d, H_{26}); 8.29 (br s, H_3).

 $\begin{array}{l} \mathbf{6}_{u}^{\mathsf{Me}} \cdot \ ^{1}\mathsf{H}\ \mathsf{NMR}\ (\mathsf{C}_{6}\mathsf{D}_{5}\mathsf{C}\mathsf{D}_{3},\ 30\ ^{\circ}\mathsf{C}):\ \delta\ 1.72\ (d),\ 1.84\ (d,\ \mathsf{Ta}\mathsf{C}H_{2});\\ 6.20\ (d),\ 6.72\ (d,\ \mathsf{Ta}\mathsf{C}H_{2}\mathsf{C}6H_{4}\text{-}4\text{-}\mathsf{Me});\ 2.15\ (s,\ 4\text{-}Me);\ 7.94\ (d),\ 8.04\ (d,\ H_{23}\ \mathsf{and}\ H_{26});\ 8.23\ (\mathsf{br}\ s,\ H_{3}).\\ \mathbf{6}_{s}^{\mathsf{OMe}} \cdot \ ^{1}\mathsf{H}\ \mathsf{NMR}\ (\mathsf{C}_{6}\mathsf{D}_{5}\mathsf{C}\mathsf{D}_{3},\ 30\ ^{\circ}\mathsf{C}):\ \delta\ 1.85\ (s,\ \mathsf{Ta}\mathsf{C}H_{2});\ 6.18\ (d),\\ \mathbf{6}_{s}^{\mathsf{OMe}} \cdot \ ^{1}\mathsf{H}\ \mathsf{NMR}\ (\mathsf{C}_{6}\mathsf{D}_{5}\mathsf{C}\mathsf{D}_{3},\ 30\ ^{\circ}\mathsf{C}):\ \delta\ 1.85\ (s,\ \mathsf{Ta}\mathsf{C}H_{2});\ 6.18\ (d),\\ \end{array}$

6^{OMe}. ¹H NMR (C₆D₅CD₃, 30 °C): δ 1.85 (s, TaCH₂); 6.18 (d), 6.75 (d, TaCH₂C₆H₄-4-Me); 2.15 (s, 4-Me); 3.47 (s, OMe); 7.60 (s, H₂₃); 7.95 (d, H₂₆); 8.21 (br s, H₃). **6**^{OMe}. ¹H NMR (C₆D₅CD₃, 30 °C): δ 1.74 (d), 1.81 (d, TaCH₂);

 6_{u}^{OMe} . ¹H NMR (C₆D₅CD₃, 30 °C): δ 1.74 (d), 1.81 (d, TaCH₂); 6.25 (d), 6.71 (d, TaCH₂C₆H₄-4-Me); 2.14 (s, 4-Me); 23.46 (s, OMe); 7.96_(d), 8.05 (d, H₂₃ and H₂₆); 8.22 (br s, H₃).

6₁^{Cl} ¹H NMR ($C_6D_5CD_3$, 30 °C): δ 1.81 (d), 1.88 (d, TaCH₂); 6.12 (d), 6.70 (d, TaCH₂ C_6H_4 -4-Me); 2.15 (s, 4-Me); 7.59 (d, H₂₆); 7.68 (br s, H₂₃); 8.10 (br s, H₃).

 6_{u}^{Cl} . ¹H NMR (C₆D₅CD₃, 30 °C); δ 1.75 (d), 1.80 (d, TaCH₂);

6.19 (d), 6.75 (d, TaCH₂C₆ H_4 -4-Me); 2.15 (s, 4-Me); 7.90 (d), 7.93 (d, H₂₃ and H₂₆); 8.25 (br s, H₃).

Crystallographical Studies. Selected crystal data and data collection parameters are collected together in Table IV.

A suitable crystal for each of the two compounds was mounted in a glass capillary in a random orientation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, with the scattering angle of 25 reflections in the range $17.0^{\circ} < 2\theta < 22.0^{\circ}$ for 1 and $15^{\circ} < 2\theta < 18^{\circ}$ for 2 as measured by the computer-controlled diagonal-slit method of centering. Systematic absences and subsequent least-squares refinement indicated the space group $P\overline{1}$ for both 1 and 2. The data were collected at room temperature by using θ -2 θ scan techniques. Mo K α radiation was used for both 1 and 2. The scan rate varied from 1 to 20 deg/min in ω , and data were collected to a maximum 2θ of 45° for both 1 and 2. Moving-crystal, moving-counterbackground counts were made by scanning an additional 25% above and below the scan width. The counteraperture was adjusted as a function of θ . For intense reflections, an attenuator (factor 12.9) was automatically inserted in front of the detector. As a check on crystal and electronic stability, three standard reflections were remeasured every 5000 s of beam time. No decay in standards was observed for both samples.

The structures were solved by using the Paterson heavy-atom method to reveal the positions of niobium and tantalum atoms. The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structures, but their positions were not refined. All calculations including the full-matrix least-squares refinement were perfromed with use of the Enraf-Nonus SDP program on a VAX computer.

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Registry No. 1, 130096-30-9; 2, 130192-95-9; 3^H, 130096-31-0; 3^{Me}, 130096-32-1; 3^{OMe}, 130096-33-2; 3^{Cl}, 130096-34-3; 4^H, 130096-35-4; 4^{Me}, 130096-36-5; 4^{OMe}, 130096-37-6; 4^{Cl}, 130096-38-7; 5, 119705-33-8; 6^H, 130096-39-8; 6^{Se}, 130096-40-1; 6^{Me}, 130120-84-2; 6^{SOMe}, 130120-85-3; 6^{OMe}, 130120-86-4; 6^{Cl}, 130096-41-2; 6^{Cl}, 130096-42-3; Ta(OC₆H₃Ph₂-2,6)₂Cl₃, 116642-99-0; Nb-(OC₆H₃Ph₂-2,6)₂Cl₃, 116642-98-9; TaCl₅, 7721-01-9; Mg-(CH₂C₆H₄-4-Me)₂, 119650-98-5; HOC₆H₂Ph₃-2,4,6, 3140-01-0; HOC₆H₂Ph₂C₆H₄Me, 130096-26-3; HOC₆H₂Ph₂C₆H₄OMe, 130096-27-4; HOC₆H₂Ph₂C₆H₄Cl, 130096-28-5.

Supplementary Material Available: Tables of crystal data and data collection parameters, fractional coordinates of hydrogen atoms, anisotropic thermal parameters, and complete bond distances and angles for 1 and 2 (32 pages); tables listing observed and calculated structure factors for 1 and 2 (79 pages). Ordering information is given on any current masthead page.