interunit Pd···I bonding interaction (Figure 2). The average Pd–I distance, 2.591 (1) Å, is comparable to those observed in other Pd(II)–I complexes: 2.492 (3) Å in the yellow form of *trans*-$Pd(PPhMe_2)_2I_2$[14] and 2.58 (1) Å in *trans*-$Pd(PPh_3)_2I_2$,[15] where the palladium atoms have four nearest neighbors, and 2.638 (3) and 2.619 (3) Å in the red form of *trans*-$Pd(PPhMe_2)_2I_2$,[14] where the palladium atom has five near neighbors.

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Registry No. $[Pd_2(DMB)_4Cl][ClO_4]_3$, 90857-67-3; $[Pd_2(DMB)_4Cl][PF_6]_3$, 90839-43-3; $[Pd_2(DMB)_4Br][ClO_4]_3$, 90839-45-5; $Pd_2(DMB)_2I_4$, 90839-46-6; $[Pd_2(DMB)_4][ClO_4]_4$, 90839-48-8.

Supplementary Material Available: Tables of anisotropic thermal parameters, hydrogen positional parameters, bond angles involving disordered atoms, and observed and calculated structure factor amplitudes (24 pages). Ordering information is given on any current masthead page.

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Chemistry of Sterically Crowded Aryloxide Ligands. 4.[1] Synthesis and Structure of Mixed Chloro Aryloxides of Tantalum

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The reaction of tantalum pentachloride with a number of lithium 2,6-dialkylphenoxides has been investigated. The degree of substitution of OAr for Cl depends on the bulk of the alkyl substituents; for 2,6-dimethylphenoxide total substitution occurs to yield $Ta(OC_6H_3Me_2\text{-}2,6)_5$, while for the sterically very demanding 2,6-di-*tert*-butylphenoxide the disubstituted, mononuclear $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ is given. Structural analysis of this compound shows a square-pyramidal arrangement about the tantalum with one aryloxide ligand occupying the apex and the other a basal position of the square pyramid. One of the *tert*-butyl groups of the basal aryloxide occupies the "open" site trans to the apical aryloxide, and one of the hydrogen atoms approaches within 2.67 Å of the metal center. The molecule crystallizes in space group $C2/c$ with $a = 17.477$ (6) Å, $b = 11.909$ (3) Å, $c = 28.319$ (11) Å, $\beta = 97.71$ (1)°, $Z = 8$, and $d_{calcd} = 1.587$ g cm^{-3}.

Introduction

Early-transition-metal alkoxides and phenoxides have been known for some time.[2,3] In particular the pentaphenoxides of niobium and tantalum were first isolated as early as 1937 by Funk and co-workers.[3] All of the mixed chloro phenoxides of these two metals, $M(OPh)_xCl_{5-x}$ (M = Nb, Ta) have also been synthesized.[4] It has been concluded, primarily on the basis of infrared spectral data and a comparison with the more extensively studied alkoxide chemistry, that all of these phenoxides are dimeric both as solids and in noncoordinating solvents and have phenoxide bridges.[5] A common feature observed for the few structurally characterized early-transition-metal chloro phenoxides is the preference of μ-phenoxo rather than μ-chloro linkages.[2,6,7] During our studies of the early-transition-metal organometallic chemistry associated with bulky aryloxides as ancillary ligands,[8-11] we have investigated the reaction of tantalum pentachloride with a number of 2,6-dialkylphenoxides to generate possible starting materials. The results of this study and their relevance to other areas of early-transition-metal chemistry are discussed in this paper.

Results and Discussion

Treatment of $TaCl_5$ with an excess of the lithium salts of various 2,6-dialkylphenoxides in benzene solvent leads to different degrees of substitution depending on the bulk of the alkyl substituents. With the relatively undemanding ligand 2,6-dimethylphenoxide ($OC_6H_3Me_2\text{-}2,6$) total substitution takes place to yield the white, crystalline $Ta(OC_6H_3Me_2\text{-}2,6)_5$ (I). However, with increasing alkyl bulk the degree of substitution drops off (eq 1). All of the partially substituted

$$TaCl_5 + LiOAr\ (\text{excess}) \rightarrow Ta(OAr)_xCl_{5-x} \qquad (1)$$

OAr	x	
$OC_6H_3Me_2\text{-}2,6$	5	I
$OC_6H_3Me\text{-}t\text{-}Bu\text{-}2,6$	3	II
$OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6$	2	III
$OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6$	2	IV

compounds are yellow-orange solids, slightly soluble in hexane but more soluble in benzene or toluene. Mass spectral analysis of compounds I and IV shows a strong parent molecular ion with distinctive fragmentation due to loss of Cl (when present) or OAr. However, for compounds II and III, ions such as $Ta(OC_6H_3Me\text{-}t\text{-}Bu\text{-}2,6)_4Cl^+$ and $Ta(OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)_3Cl_2^+$ were observed in low abundance. These we believe either to be indicative of the dimeric nature of these compounds in the solid state or else to be due to ligand exchange occurring within the mass spectrometer. Due to the low solubility of II and III solution molecular weight measurements were precluded.

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Table I. Summary of the Crystallographic Data for the Compound $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$

formula	$TaCl_3O_2C_{28}H_{42}$
fw	697.95
space group	$C2/c$
a, Å	17.477 (6)
b, Å	11.909 (3)
c, Å	28.319 (11)
β, deg	97.71 (1)
Z	8
V, Å^3	5840.41
d_{calcd}, g/cm^3	1.587
cryst size, mm	0.05 × 0.05 × 0.07
cryst color	orange
radiation	Mo Kα (λ = 0.710 69 Å)
linear abs coeff, cm^{-1}	40.182
t, °C	−160
detector aperture	3.0 mm wide × 4.0 mm high, 22.5 cm from cryst
sample to source dist, cm	23.5
takeoff angle, deg	2.0
scan speed, deg/min	4.0
scan width, deg	2.0 + 0.692 tan θ
bkgd counts, s	6 at each end of scan
2θ range, deg	6–45
no. of data collected	3943
no. of unique data	3675
no. of params	475
no. of unique data with $F_o > 2.33\sigma(F)$	3288
$R(F)$	0.0324
$R_w(F)$	0.0347
goodness of fit	1.024
largest Δ/σ	0.05

Table II. Fractional Coordinates and Isotropic Thermal Parameters for $Ta(OC_6H_3\text{-}t\text{-}Bu\text{-}2,6)_2Cl_3$

atom	10^4x	10^4y	10^4z	$10B_{iso}$
Ta(1)	1404.2 (1)	1102.2 (2)	1150.5 (1)	11
Cl(2)	984 (1)	1442 (2)	1887 (1)	18
Cl(3)	1567 (1)	3067 (1)	1137 (1)	22
Cl(4)	1064 (1)	1271 (2)	327 (1)	19
O(5)	846 (2)	−243 (4)	1126 (2)	14
C(6)	367 (4)	−1051 (5)	1272 (2)	12
C(7)	−326 (4)	−730 (6)	1435 (2)	17
C(8)	−649 (4)	−1563 (7)	1709 (3)	23
C(9)	−340 (4)	−2612 (6)	1776 (3)	23
C(10)	272 (4)	−2940 (6)	1540 (3)	21
C(11)	631 (3)	−2169 (6)	1271 (2)	12
C(12)	−834 (4)	307 (6)	1300 (3)	20
C(13)	−518 (4)	1115 (6)	950 (3)	21
C(14)	−1013 (4)	947 (7)	1740 (3)	25
C(15)	−1599 (4)	−132 (7)	1025 (3)	29
C(16)	1235 (4)	−2586 (6)	952 (3)	17
C(17)	992 (4)	−2151 (6)	439 (2)	19
C(18)	1277 (4)	−3853 (6)	936 (3)	21
C(19)	2056 (4)	−2166 (6)	1139 (2)	15
O(20)	2416 (2)	660 (4)	1286 (1)	11
C(21)	3160 (4)	153 (6)	1391 (2)	12
C(22)	3395 (3)	−215 (5)	1856 (2)	12
C(23)	4095 (4)	−785 (6)	1937 (3)	19
C(24)	4543 (4)	−958 (6)	1574 (3)	20
C(25)	4304 (4)	−539 (6)	1126 (3)	20
C(26)	3615 (4)	49 (5)	1016 (2)	12
C(27)	2942 (4)	0 (6)	2281 (3)	19
C(28)	2842 (4)	1268 (6)	2349 (2)	18
C(29)	2186 (4)	−677 (6)	2219 (3)	20
C(30)	3396 (5)	−404 (7)	2754 (3)	27
C(31)	3409 (4)	548 (6)	515 (2)	16
C(32)	4083 (4)	457 (7)	218 (3)	23
C(33)	3216 (4)	1799 (7)	535 (3)	21
C(34)	2745 (4)	−154 (7)	242 (2)	20
atom	10^3x	10^3y	10^3z	$10B_{iso}$
H(1)	−108 (5)	−134 (6)	185 (3)	28 (17)
H(2)	−59 (4)	−320 (7)	198 (3)	32 (18)
H(3)	38 (4)	−365 (6)	155 (2)	15 (15)
H(4)	−38 (4)	73 (7)	67 (3)	28 (17)
H(5)	−85 (5)	173 (8)	83 (3)	43 (20)
H(6)	−10 (4)	165 (7)	107 (3)	24 (16)
H(7)	−58 (4)	127 (6)	193 (3)	18 (15)
H(8)	−132 (4)	149 (7)	165 (3)	21 (16)
H(9)	−134 (5)	44 (8)	191 (3)	43 (21)
H(10)	−200 (4)	43 (7)	88 (3)	23 (16)
H(11)	−153 (6)	−55 (9)	79 (4)	56 (25)
H(12)	−190 (5)	−73 (8)	124 (3)	46 (22)
H(13)	133 (5)	−248 (7)	23 (3)	31 (18)
H(14)	50 (5)	−243 (8)	29 (3)	45 (22)
H(15)	102 (4)	−121 (6)	41 (2)	11 (13)
H(16)	78 (3)	−420 (5)	80 (2)	0 (11)
H(17)	168 (4)	−413 (5)	70 (2)	8 (13)
H(18)	144 (4)	−415 (6)	114 (2)	20 (14)
H(19)	239 (4)	−243 (6)	93 (3)	20 (15)
H(20)	206 (6)	−136 (10)	115 (4)	62 (26)
H(21)	224 (4)	−249 (6)	146 (2)	12 (14)
H(22)	426 (4)	−108 (6)	225 (3)	24 (16)
H(23)	492 (4)	−142 (7)	164 (3)	26 (17)
H(24)	467 (3)	−63 (5)	88 (2)	7 (12)
H(25)	329 (4)	167 (7)	246 (2)	24 (15)
H(26)	262 (4)	165 (6)	208 (2)	14 (13)
H(27)	251 (4)	139 (5)	256 (2)	10 (14)
H(28)	186 (5)	−62 (8)	192 (4)	52 (24)
H(29)	230 (4)	−143 (7)	226 (3)	21 (15)
H(30)	193 (4)	−49 (6)	247 (2)	12 (14)
H(31)	345 (4)	−123 (6)	275 (2)	11 (13)
H(32)	393 (5)	−4 (7)	283 (3)	34 (19)
H(33)	318 (5)	−31 (8)	298 (3)	40 (22)
H(34)	424 (4)	−39 (6)	16 (2)	19 (15)
H(35)	394 (4)	80 (6)	−7 (3)	19 (15)
H(36)	454 (5)	93 (7)	37 (3)	31 (18)
H(37)	363 (4)	217 (6)	70 (3)	19 (15)
H(38)	311 (4)	216 (6)	23 (3)	18 (15)
H(39)	279 (3)	200 (5)	72 (2)	4 (12)
H(40)	259 (3)	17 (5)	−7 (2)	6 (12)
H(41)	286 (4)	−95 (6)	21 (2)	13 (14)
H(42)	233 (4)	−19 (6)	40 (2)	17 (15)

Solid-State Structure of $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ (IV). The solid-state structure of IV was determined for comparison with that of $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Me_3$. The latter was shown to adopt an approximately trigonal-bipyramidal geometry about tantalum with axial aryloxide ligands.[8] The equatorial methyl groups were found to be distorted by the bulky *tert*-butyl groups, causing an elongation of one Ta–CH_3 bond by 0.11 Å over that of the other two Ta–CH_3 bonds. Mild thermolysis of this compound leads to the metalation of the *tert*-butyl groups and loss of methane.[8]

In contrast, the solid-state structure of IV turned out to be completely different. An ORTEP view of the molecule is given in Figure 1 along with the numbering scheme used, while Table I contains the crystallographic data. Tables II and III contain the fractional coordinates and thermal parameters and some important bond distances and bond angles respectively. From Figure 1 it can be seen that the molecule adopts a square-based-pyramidal geometry about the tantalum atom with one aryloxide ligand occupying the axial position and the other occupying one of the basal sites.

From the number of structures so far determined for mononuclear, five-coordinate Ta(V) and Nb(V) compounds it is evident that both the trigonal-bipyramidal and square-pyramidal geometries are common (Table IV). A problem normally found in trying to rationalize the observed structure is the interplay of steric and electronic forces. The majority of structure have involved dialkylamido ligands, and one of the typical features of such groups is their ability to undergo strong nitrogen-p to metal-d π-bonding. Hence the arrangement of such bulky groups about the metal cannot be predicted on steric grounds. In the new compound (IV) one would expect on steric grounds that the bulky aryloxide groups would maximize their distance by occupying the axial sites of a tbp structure as is actually seen in $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Me_3$.[8] The adoption of the square-pyramidal geometry, however, maximizes the ability for oxygen to metal π-bonding. This can be seen from the very short Ta–O distances of 1.836 (4) Å (axial) and 1.872 (5) Å (basal) compared to 1.930 (6) Å

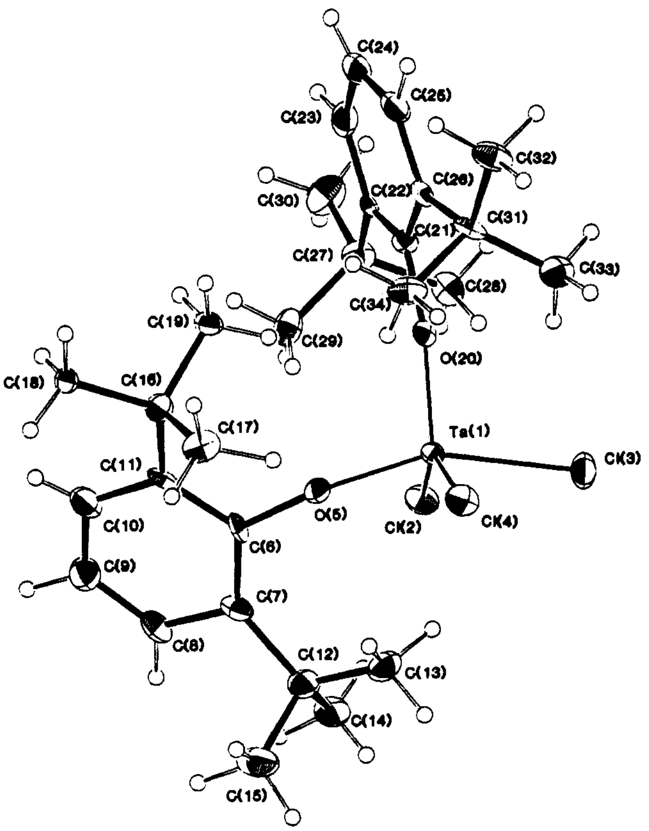

Figure 1. ORTEP view of $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$.

Table III. Important Bond Distances (Å) and Angles (deg) for $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$

Ta(1)-Cl(2)	2.339 (2)	Ta(1)-O(5)	1.872 (5)
Ta(1)-Cl(3)	2.358 (2)	Ta(1)-O(20)	1.836 (4)
Ta(1)-Cl(4)	2.335 (2)		
Cl(2)-Ta-Cl(3)	84.0 (1)	Cl(3)-Ta-O(20)	100.0 (1)
Cl(2)-Ta-Cl(4)	143.8 (1)	Cl(4)-Ta-O(5)	88.6 (1)
Cl(2)-Ta-O(5)	87.5 (1)	Cl(4)-Ta-O(20)	110.1 (1)
Cl(2)-Ta-O(20)	105.8 (1)	O(5)-Ta-O(20)	104.2 (2)
Cl(3)-Ta-Cl(4)	85.1 (1)	Ta-O(5)-C(6)	157.3 (4)
Cl(3)-Ta-O(5)	155.8 (1)	Ta-O(20)-C(21)	171.6 (4)

Table IV

compd	structure	ref
$M(NMe_2)_5$[a]	sp	15
$M(NC_5H_{10})_5$[a]	sp	15
$Ta(NEt_2)_5$	tbp	16
$Ta(NMe_2)_4\text{-}t\text{-}Bu$[b]	sp	17
$Ta(NMe_2)_3(p\text{-tolyl})Br$[c]	tbp	17
$Ta(NSi_2Me_6)_2Cl_3$[d]	tbp	18
$Ta(OAr')_2Me_3$[e]	tbp	8
$Ta(OAr')(OC_6H_3\text{-}t\text{-}BuCMe_2CH_2)Ph_2$[f]	tbp	8
$Ta(OAr')_2Cl_3$	sp	g

[a] M = Nb, Ta; compounds are isostructural. [b] Axial *t*-Bu group. [c] Axial Br; equatorial tolyl group. [d] Both amido ligands equatorial. [e] Axial OAr'; OAr' = $OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6$. [f] Axial oxygen atoms. [g] This work.

in the trimethyl compound. Further indication of strong π-bonding is the large Ta-O-Ar angles of 171.6 and 157.3°. Interestingly, in the very related compound $Ta(NSi_2Me_6)_2Cl_3$ containing the bulky silylamido ligand, a tbp arrangement of the TaN_2Cl_3 skeleton is observed with the amido ligands both in equatorial sites. Clearly, the energy difference between these two idealized geometries is small. The distance to the chlorine atoms are normal, although that to Cl(3) is slightly longer (by 0.02 Å) than those to Cl(2) and Cl(4). This can be explained by the presence of the approximately trans aryloxide ligand.

The orientation of the aryl rings on the aryloxide ligands is worthy of note. The axial aryloxide has an almost linear Ta-O-Ar angle. Hence, the ligand can be considered as a propeller occupying a wedge of the coordination sphere. The plane of this propellar is approximately parallel to the Cl(2)-Ta-Cl(4) plane. Hence, the bulky *tert*-butyl groups are placed over these two chlorine atoms. This steric influence is felt by the chlorine atoms as the O(20)-Ta-Cl(2) and O(20)-Ta-Cl(4) angles are 105.8 and 110.1°, significantly larger than the 0(20)-Ta-Cl(3) angle of 100.0°. The other bulky aryloxide "wedge" then fits into this geometry with the *tert*-butyl groups arranged approximately parallel with the axial Ta-O axis. The two cis aryloxides therefore tend to mesh into each other with their aryl planes roughly perpendicular. In this orientation repulsions between the two bulky groups is obviously not great as the O(20)-Ta-O(5) angle of 104.2° is not very large. This orientation of the aryloxide ligands results in one of the *tert*-butyl groups of the basal aryloxide occupying the "open" site trans to the axial Ta-O bond. The configuration of this *tert*-butyl group is such that one of the methyl groups is pushed into this space with one of its CH bonds pointing toward the metal atom. The distance to this hydrogen, H(6), was refined down to 2.67 Å. There is now a growing literature of examples of compounds in which three-center, two-electron bonds are present between CH bonds and electron-deficient metal centers. Such situations are extremely important for our understanding of CH bond activation by transition metals.[12] In particular, a number of examples have recently been reported in which these CH bonds interact with transition metals with a d^0 electron configuration.[13] In the present case, although the Ta-HC distance is well below the sum of the van der Waals radii of Ta and H, the situation is almost certainly not bonding. However, the close proximity of one of these CH bonds to the metal and also other substituents (leaving groups) at the metal in the ground state certainly indicates a pathway whereby this bond may be activated to cyclometalation.[8]

In the ^1H NMR spectrum, IV shows only one type of aryloxide *tert*-butyl group at room temp. This signal remains sharp even down to −70 °C (90 MHz) so that either a more symmetric structure is adopted in solution, or else the molecule is fluxional on the ^1H NMR time scale. In the infrared spectrum two bands at 358 cm^{-1} (with some structure) and 308 cm^{-1} can be tentatively assigned to Ta-Cl stretches. Other bands at 463 and 540 cm^{-1} of approximately equal intensity may be due to the two Ta-O vibrations expected.

Because the solid-state structure of IV is not a perfect square-based pyramid, it may also be described as a distorted trigonal bipyramid. This involves considering one of the aryloxides, O(5), as being an axial ligand along with Cl(3). Repulsions between these two groups and the bulky equatorial aryloxide causes a bending of the axial ligands, causing the Cl(3)-Ta-O(5) angle to close up to 155.8°. The bulky *tert*-butyl group from the axial aryloxide is then forced between Cl(2) and Cl(4), causing the Cl(2)-Ta-Cl(4) angle to open up to 143.8°. Clearly this highlights the problems with using idealized geometries about metal atoms containing bulky, nonspherical ligands.

Attempted Cyclometalation of $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ (IV). In contrast to the alkyl derivatives of IV,[8] the parent halide does not undergo thermal loss of HCl and cyclometalation under conditions so far employed. Hence heating IV to 170 °C for extended periods under vacuum only causes

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sublimation of the unchanged halide. Clearly, in contrast to later-transition-metal cyclometalation reactions, loss of HCl is a very unfavorable process for Ta(V). Work by Nugent and co-workers has shown that CH bond activation can occur at d^0-metal centers with alkoxide and amide leaving groups, although extremely high temperatures are needed.[14]

Experimental Section

All reactions and manipulations were carried out under N_2 by using Schlenk techniques. Solvents were dried by distillation over Na/benzophenone under N_2. $TaCl_5$ was purchased in resublimed form from Alfa. All phenols were dried over 4-Å molecular sieves. Lithium aryloxides were prepared from the corresponding phenol and *n*-butyllithium in hydrocarbon solvents.

$Ta(OC_6H_3Me_2\text{-}2,6)_5$ (I). The compound was easily prepared in good yield by the reaction of Li $(OC_6H_3Me_2\text{-}2,6)$ with $TaCl_5$ (6/1 ratio) in benzene over 2 h. Evaporation followed by extraction with pentane gave the pure product as a white, crystalline solid. Anal. Calcd for $TaC_{40}H_{45}O_5$: C, 61.07; H, 5.77. Found: C, 60.92; H, 5.57.

$Ta(OC_6H_3Me\text{-}t\text{-}Bu\text{-}2,6)_3Cl_2$ (II). To Li $(OC_6H_3Me\text{-}t\text{-}Bu\text{-}2,6)$ (8.25 g) suspended in benzene (300 mL) was added $TaCl_5$ (6 g). The reaction mixture was stirred overnight. The resulting suspension was then filtered to give a clear yellow filtrate. Removal of solvent and addition of hexane gave the product as a pale yellow solid, yield 9.8 g (78%). Anal. Calcd for $TaC_{33}H_{45}O_3Cl_2$: C, 53.45; H, 6.11; Cl, 9.56. Found: C, 52.90; H, 6.30; Cl, 9.32. ^1H NMR (C_6D_6, 30 °C): δ 1.42 (s, *t*-Bu), 2.50 (s, CH_3), 6.7–7.0 (m, OC_6H_3). IR spectrum (Nujol mull) between 650 and 200 cm^{-1}; 555 (s), 500 (m), 435 (s, br), 380 (w), 350 (vs, br), 318 (m), 255 (w).

$Ta(OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)_2Cl_3$ (III). A similar procedure using an excess of $Li(OC_6H_3\text{-}i\text{-}Pr_2\text{-}2,6)$ gave III as a yellow powder in yields of approximately 80%. Anal. Calcd for $TaC_{24}H_{34}O_2Cl_3$: C, 44.92; H, 5.34; Cl, 16.57. Found: C, 45.18; H, 5.52; Cl, 16.38. ^1H NMR (C_6D_5CD, 30 °C): δ 1.27 (d, CMe_2), 3.58 (septet, $CHMe_2$), 6.8–7.0 (m, OC_6H_3). IR (Nujol mull) 650–200-cm^{-1} region: 650 (w), 605 (w), 595 (m), 540 (m), 430 (s), 320 (vs, br).

$Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ (IV). A similar procedure using $Li(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)$ (excess) gave an orange suspension after stirring for 24 h. Filtration, removal of solvent, and addition of hexane gave the product as an orange solid in 30–40% yield. Recrystallization from toluene at −15 °C gave the product as large orange chunks. Anal. Calcd for $TaC_{28}H_{42}O_2Cl_3$: C, 48.19; H, 6.07; Cl, 15.24. Found: C, 48.82; H, 6.13; Cl, 14.98. ^1H NMR (C_6D_6, 30 °C): δ1.51 (s, *t*-Bu), 6.6–7.0 (m, OC_6H_3). IR (Nujol mull) 650–200-cm^{-1} region: 570 (w, sh), 540 (m), 510 (w), 463 (m), 358 (vs, br), 308 (m).

Thermolysis of $Ta(OC_6H_3\text{-}t\text{-}Bu_2\text{-}2,6)_2Cl_3$ (IV). A sample of IV was heated in an evacuated tube for 6–8 h in an oil bath at 170 °C. The initially orange oil began to melt to a red viscous liquid, and red crystals were slowly deposited on the cooler parts of the flask. Analysis of the sample by ^1H NMR showed only IV. Heating the sample while exposed to vacuum caused the compound to be sublimed unchanged.

Structure Determination of IV. General procedures have been described previously.[19] The position of the tantalum atom was determined from a three-dimensional Patterson map, and all remaining non-hydrogen atoms were located from a Fourier map phased on the Ta position. Hydrogen atoms were located in a subsequent difference Fourier map after several cycles of refinement and were included in all subsequent cycles. Automated ψ scans of several reflections indicated no absorption correction was necessary. A final difference Fourier map contained three peaks of intensity 0.9–1.1 e/Å^3 within 1.0 Å of the tantalum atom. All remaining peaks were less than 0.5 e/Å^3.

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Supplementary Material Available: Full listings of bond distances and angles, anisotropic temperature factors, and observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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catena-Dichloro(diphenylethanedione dioxime)copper(II), a New One-Dimensional $S = {}^1/_2$ Heisenberg Chain with a Novel Zigzag Structure

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The crystal and molecular structure of the compound *catena*-dichloro(diphenylethanedione dioxime)copper(II) has been determined from single-crystal, three-dimensional X-ray diffraction data collected at room temperature. The compound $[Cu(C_{14}H_{12}N_2O_2)Cl_2]$ crystallizes as green needles in the orthorhombic space group *Pbcn* with $Z = 4$ and unit cell dimensions $a = 13.382$ (2), $b = 19.925$ (4), and $c = 6.901$ (1) Å with $D_c = 1.35$ g cm^{-3}. The structure was refined by full-matrix least-squares techniques to a conventional *R* value of 0.049. The structure may be regarded as a chain of stacked planar dichloro(diphenylethanedione dioxime)copper(II) units, with the Cu^{II} sites equidistantly arranged in zigzagged infinite chains propagating along the *c* axis and with a relatively short Cu–Cu separation of 3.649 Å. Neighboring monomeric units are linked to each other by two chloro bridges. The bridging angle Cu–Cl–Cu′ is 89.3°. Magnetic susceptibility data collected in the temperature range 2.18–18.14 K may be fit by the $S = {}^1/_2$ Heisenberg antiferromagnetic linear-chain model with the best-fit magnetic parameters J(intrachain) = −0.85 (1) cm^{-1} and $g = 2.15$ (1).

Introduction

Complexes of copper(II) chloride or copper(II) bromide with α,β-dione dioximes (α,β-H{dodo}) as chelating ligands usually crystallize in discrete dimers[2] in which monomeric units, $Cu(\alpha,\beta\text{-}H\{dodo\})X_2$, are linked together by double halide

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