

of electrons to Re forming a Rh→Re dative bond, regenerating coordinative saturation at Re.

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Supplementary Material Available: Tables containing crystal data and details of intensity collection, anisotropic thermal parameters, positional and thermal parameters for the hydrogen atoms, bond lengths and angles within the phenyl groups, and positional and isotropic thermal parameters for all atoms (10 pages); a listing of structure factors (28 pages). Ordering information is given on any current masthead page.

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Alkyl Group Effects on CO Insertion into Coordinatively Unsaturated Early-Transition-Metal Alkyls. Preparations and the First Structural Characterizations of Tantalum Enolate-*O* and Tantalum η^2 -Acyl Complexes

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Low-pressure carbonylation of the mono(peralkylcyclopentadienyl)tantalum(V) alkyls (η -C₅Me₄R)TaR'Cl₃ (R = Me, Et; R' = CH₂C₆H₄-*p*-Me, CH₂CMe₃) yields either the *O*-bound enolate or the η^2 -acyl as shown by IR/NMR spectroscopy and X-ray diffractometry. The *p*-tolyl enolate (η -C₅Me₅)Ta(OCH=CHC₆H₄-*p*-Me)Cl₃, derived directly from carbonylation of the tantalum 4-methylbenzyl precursor, is shown to possess a *cis* configuration in solution and in the solid state. Key structural features from a single-crystal X-ray diffraction study of the tetrahydrofuran-ligated enolate complex include a nearly planar enolate with a O(1)–C(1)–C(2)/phenyl least-squares plane dihedral angle of 7 (7)°, a short C(1)–C(2) distance of 1.30 (2) Å, a Ta–O(1) distance of 1.947 (9) Å, and a large Ta–O(1)–C(1) angle of 142.7 (8)°. The mechanism of formation of the enolate from carbonylation of the 4-methylbenzyl complex is discussed. The previously reported acyl (η -C₅Me₄R)Ta[C(O)CH₂CMe₃]Cl₃ has been reexamined and found to possess a symmetric, strongly distorted η^2 -acyl coordination by solution ¹H NMR spectroscopy and solid-state X-ray diffractometry. Key features from the molecular structure determination include a large Ta–C(1)–C(2) angle of 167 (1)°, a C(1)–O bond length of 1.27 (1) Å, a Ta–O bond distance of 2.108 (9) Å, a Ta–C(1) bond distance of 2.07 (1) Å, and a Δ [= *d*(Ta–O) – *d*(Ta–C)] value of 0.04 Å, which is the lowest reported for transition-metal η^2 -acyls. The molecular structures of (η -C₅Me₅)Ta(OCH=CHC₆H₄-*p*-Me)Cl₃ and (η -C₅Me₅)Ta[C(O)CH₂CMe₃]Cl₃ are the first structural determinations of a tantalum enolate and of a tantalum η^2 -acyl.

Introduction

The migratory CO insertion reaction is very prominent in organotransition-metal chemistry, homogeneous catalysis, and organometallic applications in organic synthesis for carbon–carbon bond formation.¹ CO insertion into transition-metal alkyls normally generates the η^1 - or η^2 -acyl derivatives, with the latter² most common with the early transition metals, lanthanides, and actinides (though late-transition-metal complexes with η^2 -acyls are also known³).

In some cases, transition-metal acyls have been converted into metal-bound enolates through thermolysis,⁴ catalyzed H migration,⁵ or acyl C_α deprotonation.⁶ Such rearrangements may be facile with transition-metal η^2 -acyls because of their substantial oxycarbenoid/carbenium⁷ character, and examples of intermolecular coupling of postulated η^2 -acyls to enediolates⁸ and enolates

(via coupling with an acetone ligand⁹ or directly from alkyl carbonylation¹⁰) are known. Main-group and transition-metal enolates are of major importance in organic synthesis for reactions such as aldol condensations and olefin synthesis,¹¹ and group 4 enolate complexes have been used in aldol chemistry to control stereochemistry.¹² Enolate complexes of the early transition metals have been prepared via direct addition of an enolate anion to a metal halide¹³ and reactions¹⁴ of metal alkylidenes with acyl halides. There is one report of direct cyclic enolate ligand synthesis, via carbonylation of a bis(cyclopentadienyl)zirconacyclopentane, which was suggested to proceed through an acyl complex.¹⁵

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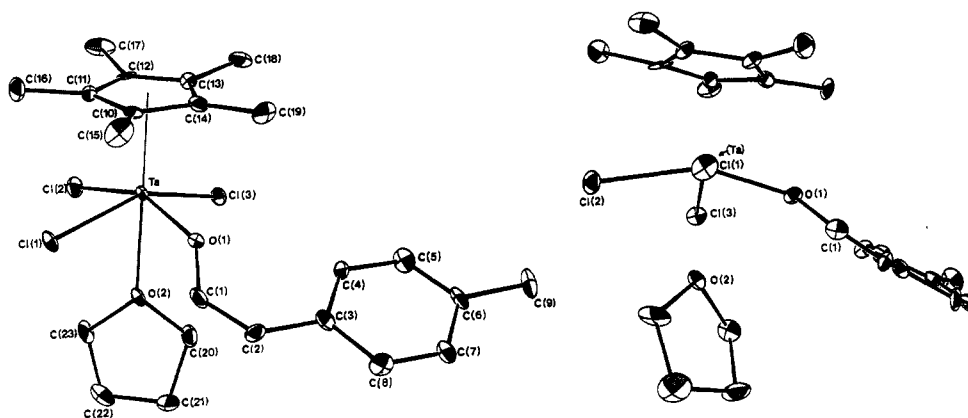


Figure 1. ORTEP diagrams for $(\eta\text{-C}_5\text{Me}_5)\text{TaCl}_3(\text{OCHCHC}_6\text{H}_4\text{-}p\text{-Me})(\text{OC}_4\text{H}_8)$ (**2a**) from two views (with hydrogen atoms omitted for clarity), the latter down the Ta–Cl(1) bond (Cl(1) concealing Ta; bond between thf ligand and Ta omitted for clarity) in order to demonstrate the approximate planarity of the enolate ligand.

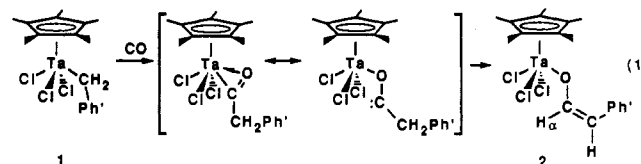
The bulk of early-transition-metal η^2 -acyls and enolates are bis(cyclopentadienyl) complexes. We were interested in developing the chemistry of these organometallic functional groups in more coordinatively unsaturated ligand environments, which could be more easily varied in order to tune acyl/enolate electronic properties. Therefore, we chose to examine mono(peralkylcyclopentadienyl)tantalum complexes with a single acyl ligand, in part because of our focus¹⁶ on group 5 mono(peralkylcyclopentadienyl) organometallic and organodimetallic¹⁷ chemistry.

The acyl complexes $(\text{C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{EMe}_3]\text{Cl}_3$ (E = Si, C) were first prepared by Rocklage and Schrock¹⁸ by carbonylation of the alkyl complexes $(\text{C}_5\text{Me}_5)\text{Ta}(\text{CH}_2\text{EMe}_3)\text{Cl}_3$. The results of Rocklage's ¹³C NMR spectroscopic studies on the isolated products left little doubt that the acyl ligands were coordinated in an η^2 -mode. Recently, the neopentyl compound has been reexamined by Tilley and co-workers, during their interesting studies of comparative CO insertion into Ta–SiR₃ and Ta–CH₂CMe₃ bonds,¹⁹ and by ourselves.²⁰ We became interested in learning the exact molecular structure of Rocklage's $(\text{C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3$, during our studies of its novel reduction chemistry,²¹ and in examining CO insertion into other coordinatively unsaturated tantalum alkyls. We report here the differences in carbonylation products from several mono(peralkylcyclopentadienyl)tantalum alkyls, additional spectroscopic and spectrometric data and the solid-state structure of $(\text{C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3$, and spectroscopic data and the molecular structure of a tantalum O-enolate from carbonylation of a tantalum 4-methylbenzyl complex. These structural determinations represent, to our knowledge, the first for tantalum η^2 -acyl and tantalum O-enolate complexes.

Results

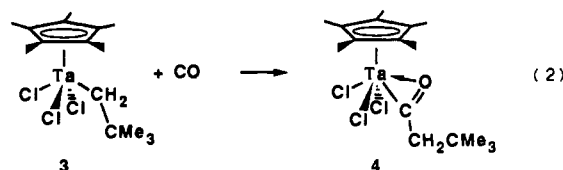
Synthetic and Spectroscopic Studies. The 4-methylbenzyl complexes $(\text{C}_5\text{Me}_5\text{R})\text{Ta}(\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Me})\text{Cl}_3$ (**1**) (R = Me, Cp*, Et), derivatives of the reported²² $(\text{C}_5\text{Me}_5\text{R})\text{Ta}(\text{CH}_2\text{Ph})\text{Cl}_3$, were

prepared in high yield (e.g., 88% yield, R = Me) by a modified procedure involving direct alkylation of $(\text{C}_5\text{Me}_5\text{R})\text{TaCl}_4$ with 0.5 equiv of $\text{Zn}(\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Me})_2$ in toluene. Compound **1** is readily carbonylated under mild conditions (35–100 psi, 25 °C) in tetrahydrofuran to the enolate complex $(\text{C}_5\text{Me}_5\text{R})\text{Ta}(\text{OCH}=\text{CHC}_6\text{H}_4\text{-}p\text{-Me})\text{Cl}_3$ (**2**, eq 1, Ph' = *p*-tolyl; tetrahydrofuran ligand



as found in structural study omitted for clarity) in 44% isolated yield (R = Me). Spectroscopic data, in particular the ¹H NMR olefinic ³J_{HH} value of 6.6 Hz, suggested that the enolate is O-bound and of Z configuration. The reaction of $(\text{C}_5\text{Me}_5)\text{Ta}(\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Me})\text{Cl}_3$ with ¹³CO yielded a product with the label incorporated into C_α of the resulting enolate. Tetrahydrofuran is not the source of the enolate's H_α, as ¹³C NMR spectra of the product from carbonylation of **1** with ¹³CO in tetrahydrofuran-*d*₈ showed only incorporation of hydrogen at H_α. The 4-methylbenzyl acyl $(\text{C}_5\text{Me}_5\text{R})\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{C}_6\text{H}_4\text{-}p\text{-Me}]\text{Cl}_3$ is a likely intermediate in the formation of the enolate, since ¹³C NMR spectra of the reaction mixture of ¹³CO and **1** exhibited an enriched resonance of δ 316.3 in the η^2 -acyl spectral region (vide infra). Etheral solvents are key to formation of the enolate, as carbonylation proceeded in ether but not in hexane or toluene. Enolate **2** is somewhat unstable in solution and as a solid, decomposing to unidentified products, which account for the lower isolated yield; enolate instability has been noted by others.^{10e} While thermal instability precluded elemental analysis, a high-resolution mass spectrum gave the exact mass as calculated for the (M – Cl)⁺ fragment ion.

Rocklage and Schrock, and Tilley and co-workers, have demonstrated that the carbonylation of the neopentyl complex leads to the acyl as the final product even in tetrahydrofuran. Our observations corroborate and expand on their spectroscopic data.^{18,19} $(\text{C}_5\text{Me}_5\text{R})\text{Ta}(\text{CH}_2\text{CMe}_3)\text{Cl}_3$ (**3**) is carbonylated (10–50 psi, hexane) to the acyl $(\text{C}_5\text{Me}_5\text{R})\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3$ (**4**) in 65% yield (eq 2). The IR spectrum of a solid sample in KBr



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Table I. Crystallographic Data for $(C_5Me_5)Ta(OCH=CHC_6H_4-p-Me)Cl_3(OC_4H_9)$

$TaC_{23}H_{32}Cl_3O_2$	fw 896
$a = 10.136 (6) \text{ \AA}$	space group $P\bar{1}$ (No. 2)
$b = 10.160 (3) \text{ \AA}$	$T = -100 \text{ }^\circ\text{C}$
$c = 11.733 (8) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$\alpha = 88.65 (4)^\circ$	$\rho_{\text{calc}} = 1.762 \text{ g cm}^{-3}$
$\beta = 81.27 (5)^\circ$	$\mu = 26.28 \text{ cm}^{-1}$
$\gamma = 82.14 (4)^\circ$	abs cor min, max (F_o) = 0.7172, 0.9997
$V = 1183.18 \text{ \AA}^3$	$R(F_o) = 0.059$
$Z = 2$	$R_w(F_o^2) = 0.082$

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(C_5Me_5)Ta(OCH=CHC_6H_4-p-Me)Cl_3(OC_4H_9)$

atom	x	y	z	$B^a \text{ \AA}^2$
Ta	0.22129 (5)	0.16445 (6)	0.23721 (5)	1.56 (1)
Cl(1)	0.0251 (4)	0.1996 (4)	0.3847 (3)	2.83 (8)
Cl(2)	0.0833 (4)	0.2956 (4)	0.1150 (4)	2.92 (8)
Cl(3)	0.3447 (3)	0.0653 (4)	0.0646 (3)	2.30 (7)
O(1)	0.2745 (9)	0.0061 (9)	0.3249 (8)	2.0 (2)
C(1)	0.225 (1)	-0.086 (2)	0.397 (1)	2.4 (3)
C(2)	0.282 (1)	-0.208 (1)	0.406 (1)	2.2 (3)
C(3)	0.407 (1)	-0.279 (2)	0.342 (1)	2.2 (3)
C(4)	0.486 (1)	-0.228 (1)	0.246 (1)	2.1 (3)
C(5)	0.605 (2)	-0.299 (2)	0.195 (1)	2.8 (3)
C(6)	0.653 (1)	-0.423 (2)	0.233 (1)	2.2 (3)
C(7)	0.571 (1)	-0.476 (2)	0.322 (1)	2.3 (3)
C(8)	0.453 (2)	-0.409 (2)	0.376 (1)	2.9 (3)
C(9)	0.786 (2)	-0.494 (2)	0.186 (2)	3.9 (4)
C(10)	0.313 (1)	0.271 (1)	0.384 (1)	2.0 (3)
C(11)	0.251 (1)	0.375 (1)	0.320 (1)	1.9 (3)
C(2)	0.327 (1)	0.375 (1)	0.205 (1)	2.4 (3)
C(13)	0.434 (1)	0.275 (1)	0.202 (1)	1.9 (2)*
C(14)	0.429 (1)	0.207 (1)	0.308 (1)	2.3 (3)
C(15)	0.280 (2)	0.238 (2)	0.508 (1)	3.8 (4)
C(16)	0.134 (2)	0.476 (2)	0.366 (2)	3.7 (4)
C(17)	0.306 (2)	0.482 (2)	0.118 (1)	3.9 (4)
C(18)	0.551 (2)	0.247 (2)	0.106 (2)	3.5 (4)
C(19)	0.529 (2)	0.099 (2)	0.345 (2)	3.9 (4)
O(2)	0.08368 (9)	0.012 (1)	0.1915 (8)	2.3 (2)
C(20)	0.129 (2)	-0.123 (2)	0.152 (1)	2.9 (3)
C(21)	0.012 (2)	-0.198 (2)	0.185 (2)	4.3 (4)
C(22)	-0.108 (2)	-0.091 (2)	0.180 (2)	5.9 (6)
C(23)	-0.060 (1)	0.033 (2)	0.190 (2)	4.8 (4)

*Starred B value for atom refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

exhibited a strong, broad absorption at 1472 cm^{-1} , which we assign to the acyl C-O stretch; this band shifted to 1440 cm^{-1} in ^{13}CO -derived **4**. A low-field ^{13}C NMR resonance at $\delta 315$ is consistent² with η^2 -coordination. A ^1H NMR spectrum of $(C_5Me_4Et)Ta[C(O)CH_2CMe_3]Cl_3$ at $25 \text{ }^\circ\text{C}$ showed two ring Me resonances and equivalent ring CH_2Me hydrogens consistent with a plane of symmetry passing through the C_5Me_4Et ligand. Therefore, the molecule either has a symmetric acyl orientation with respect to the C_5Me_4Et ring or is undergoing rapid acyl rotation.²³

In preliminary experiments, we have observed formation of η^2 -acetyl and a dinuclear monoacetyl species from carbonylation of a mono(peralkylcyclopentadienyl)tantalum methyl complex. The methyl compound $[(C_5Me_5)TaMeCl_3]_2$ reacts with CO to yield a mixture of the mononuclear acyl ($\delta 311$ in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, $\sim 1470 \text{ cm}^{-1}$ in the IR spectrum), a dinuclear monoacyl ($\delta 322.9$ in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum), also near 1470

Table III. Bond Distances (\AA) in $(C_5Me_5)Ta(OCH=CHC_6H_4-p-Me)Cl_3(OC_4H_9)^a$

Ta-Cl(1)	2.422 (3)	C(6)-C(9)	1.47 (2)
Ta-Cl(2)	2.408 (4)	C(7)-C(8)	1.36 (2)
Ta-Cl(3)	2.380 (3)	C(10)-C(11)	1.41 (2)
Ta-O(1)	1.947 (9)	C(10)-C(14)	1.45 (2)
Ta-C(10)	2.42 (2)	C(10)-C(15)	1.48 (2)
Ta-C(11)	2.45 (1)	C(11)-C(12)	1.45 (2)
Ta-C(12)	2.52 (1)	C(11)-C(16)	1.50 (2)
Ta-C(13)	2.53 (1)	C(12)-C(13)	1.38 (2)
Ta-C(14)	2.48 (2)	C(12)-C(17)	1.49 (2)
Ta-O(2)	2.34 (1)	C(13)-C(14)	1.41 (2)
O(1)-C(1)	1.34 (2)	C(13)-C(18)	1.50 (2)
C(1)-C(2)	1.30 (2)	C(14)-C(19)	1.49 (2)
C(2)-C(3)	1.47 (2)	O(2)-C(20)	1.45 (2)
C(3)-C(4)	1.41 (2)	O(2)-C(23)	1.44 (2)
C(3)-C(8)	1.41 (2)	C(20)-C(21)	1.49 (2)
C(4)-C(5)	1.38 (2)	C(21)-C(22)	1.52 (3)
C(5)-C(6)	1.38 (2)	C(22)-C(23)	1.43 (3)
C(6)-C(7)	1.37 (2)		

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Table IV. Bond Angles (deg) in $(C_5Me_5)Ta(OCH=CHC_6H_4-p-Me)Cl_3(OC_4H_9)^a$

Cl(1)-Ta-Cl(2)	85.5 (1)	C(11)-Ta-O(2)	151.2 (4)
Cl(1)-Ta-Cl(3)	153.0 (2)	C(12)-Ta-C(13)	31.8 (4)
Cl(1)-Ta-O(1)	85.5 (2)	C(12)-Ta-C(14)	54.9 (5)
Cl(1)-Ta-C(10)	79.7 (3)	C(12)-Ta-O(2)	153.0 (4)
Cl(1)-Ta-C(11)	78.7 (4)	C(13)-Ta-C(14)	32.8 (4)
Cl(1)-Ta-C(12)	109.9 (3)	C(13)-Ta-O(2)	152.4 (4)
Cl(1)-Ta-C(13)	131.5 (4)	C(14)-Ta-O(2)	148.9 (4)
Cl(1)-Ta-C(14)	112.3 (4)	O(1)-C(1)-C(2)	125 (1)
Cl(1)-Ta-O(2)	76.0 (2)	C(1)-C(2)-C(3)	131 (1)
Cl(2)-Ta-Cl(3)	86.4 (1)	C(2)-C(3)-C(4)	125 (1)
Cl(2)-Ta-O(1)	154.1 (3)	C(2)-C(3)-C(3)	119 (1)
Cl(2)-Ta-C(10)	119.9 (4)	C(4)-C(3)-C(8)	115 (1)
Cl(2)-Ta-C(11)	86.4 (4)	O(2)-C(23)-C(22)	110 (1)
Cl(2)-Ta-C(12)	76.1 (4)	C(3)-C(4)-C(5)	122 (1)
Cl(2)-Ta-C(13)	101.1 (4)	C(4)-C(5)-C(6)	122 (1)
Cl(2)-Ta-C(14)	130.8 (4)	C(5)-C(6)-C(7)	116 (1)
Cl(2)-Ta-O(2)	78.2 (3)	C(5)-C(6)-C(9)	122 (1)
Cl(3)-Ta-O(1)	90.7 (3)	C(7)-C(6)-C(9)	122 (1)
Cl(3)-Ta-C(10)	126.3 (4)	C(6)-C(7)-C(8)	124 (1)
Cl(3)-Ta-C(11)	126.5 (3)	C(3)-C(8)-C(7)	121 (1)
Cl(3)-Ta-C(12)	93.1 (4)	C(11)-C(10)-C(14)	107 (1)
Cl(3)-Ta-C(13)	75.4 (3)	C(11)-C(10)-C(15)	129 (1)
Cl(3)-Ta-C(14)	92.3 (3)	C(14)-C(10)-C(15)	124 (1)
Cl(3)-Ta-O(2)	77.1 (2)	C(10)-C(11)-C(12)	108 (1)
O(1)-Ta-C(10)	82.2 (4)	C(10)-C(11)-C(16)	126 (1)
C(21)-C(22)-C(23)	107 (2)	C(12)-C(11)-C(16)	125 (1)
O(1)-Ta-C(11)	115.5 (4)	C(11)-C(12)-C(13)	107 (1)
O(1)-Ta-C(12)	129.9 (5)	C(11)-C(12)-C(17)	124 (1)
O(1)-Ta-C(13)	103.1 (4)	C(13)-C(12)-C(17)	128 (1)
O(1)-Ta-C(14)	75.0 (4)	C(12)-C(13)-C(14)	111 (1)
O(1)-Ta-O(2)	76.0 (4)	C(12)-C(13)-C(18)	127 (1)
C(10)-Ta-C(11)	33.7 (5)	C(14)-C(13)-C(18)	122 (1)
C(10)-Ta-C(12)	56.1 (5)	C(10)-C(14)-C(13)	107 (1)
C(10)-Ta-C(13)	55.2 (4)	C(10)-C(14)-C(19)	125 (1)
C(10)-Ta-C(14)	34.4 (4)	C(13)-C(14)-C(19)	128 (1)
C(10)-Ta-O(2)	148.3 (4)	C(20)-O(2)-C(23)	105 (1)
C(11)-Ta-C(12)	34.0 (4)	O(2)-C(20)-C(21)	107 (1)
C(11)-Ta-C(13)	54.4 (4)	C(20)-C(21)-C(22)	102 (1)
C(11)-Ta-C(14)	55.8 (4)		

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

cm^{-1} in the IR spectrum), and possibly an enediolate species (1655 cm^{-1}). We do not know at present the structures of these species or whether the acetyl is a direct precursor to either the dinuclear acetyl or the enediolate.

Structural Determinations. Single-crystal X-ray diffraction on **2a** ($R = \text{Me}$) confirmed the O-bound enolate formulation and the presence of a coordinated thf (Figure 1). Tables I-IV list data collection parameters, fractional coordinates for non-hydrogen atoms, bond distances, and bond angles, respectively, from the structural determination on **2a**. The enolate is oriented roughly

(23) ^1H and ^{13}C NMR resonances associated with the acyl and cyclopentadienyl groups of $(C_5Me_4Et)Ta[C(O)CH_2CMe_3]Cl_3$ exhibit temperature-dependent line broadening and chemical shift variation. Below 230 K , two equilibrating acyl species, in a ratio of 94:1, are observed by ^{13}C NMR spectroscopy at $\delta 315.9$ and 284.0 , respectively, indicating the existence of an equilibrium between different acyl species and not tantalum quadrupolar broadening as the origin of the line broadening. Further spectral and simulation studies of this equilibrium are in progress.

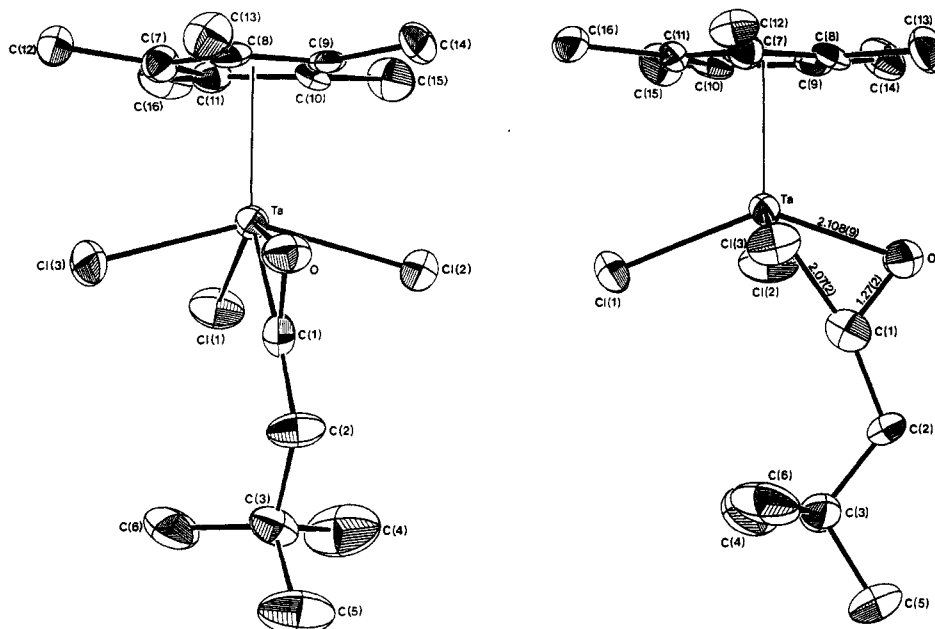


Figure 2. ORTEP diagrams for $(\eta\text{-C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3$ (**4a**) (with hydrogen atoms omitted for clarity), the first view demonstrating the acyl orientation approximately perpendicular to the plane defined by the chlorine atoms. Key bond distances (\AA) and bond angles (deg; CNT \equiv centroid of Cp* ligand, ACYL \equiv midpoint of C(1)–O bond) not specified in text or tables: Ta–CNT, 2.143; CNT–Ta–O, 112.9 (4); CNT–Ta–Cl(1), 108.5 (1); CNT–Ta–Cl(2), 104.5 (1); CNT–Ta–Cl(3), 105.4 (1); CNT–Ta–ACYL, 130.4 (7).

Table V. Crystallographic Data for $(\text{C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3$

TaCl ₃ OC ₁₆ H ₂₆	fw 521.69
$a = 11.404$ (8) \AA	space group $P2_12_12_1$ (No. 19)
$b = 12.006$ (3) \AA	$\rho_{\text{calcd}} = 1.801$ g cm ⁻³
$c = 14.018$ (3) \AA	$\mu = 60.67$ cm ⁻¹
$V = 1923.374$ (4) \AA^3	abs cor min, max (F_o) = 0.7903, 0.996
$Z = 4$	$R(F_o) = 0.037$
$T = 22$ °C	$R_w(P_o^2) = 0.046$
$\lambda = 0.71073$ \AA	

Table VI. Positional and Thermal Parameters and Their Estimated Standard Deviations for $(\text{C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3$

atom	x	y	z	$B, \text{\AA}^2$
Ta	0.76510 (3)	0.24651 (2)	0.31486 (2)	3.344 (8)
Cl(1)	0.7504 (3)	0.0813 (2)	0.2256 (2)	6.08 (6)
Cl(2)	0.6935 (3)	0.3404 (3)	0.1735 (2)	7.11 (7)
Cl(3)	0.9221 (2)	0.1594 (3)	0.4008 (2)	6.30 (7)
O	0.8751 (7)	0.3872 (6)	0.3239 (6)	6.2 (2)
C(1)	0.910 (1)	0.3249 (9)	0.2560 (8)	5.3 (3)
C(2)	1.013 (1)	0.3594 (9)	0.1979 (9)	6.0 (3)
C(3)	1.064 (1)	0.2776 (9)	0.1261 (9)	5.7 (3)
C(4)	0.966 (1)	0.252 (1)	0.052 (1)	11.6 (6)
C(5)	1.166 (1)	0.328 (1)	0.076 (1)	10.8 (5)
C(6)	1.094 (1)	0.171 (1)	0.171 (1)	11.4 (4)
C(7)	0.6723 (9)	0.1951 (8)	0.4687 (7)	4.5 (2)
C(8)	0.6825 (9)	0.3125 (8)	0.4620 (6)	4.0 (2)
C(9)	0.6059 (8)	0.3492 (7)	0.3858 (6)	3.7 (2)
C(10)	0.5523 (8)	0.2497 (8)	0.3469 (7)	4.3 (2)
C(11)	0.5937 (8)	0.1584 (6)	0.4009 (6)	3.6 (2)
C(12)	0.7193 (9)	0.1275 (9)	0.5475 (7)	5.3 (2)
C(13)	0.752 (1)	0.3878 (9)	0.5251 (8)	6.0 (3)
C(14)	0.579 (1)	0.4661 (8)	0.3635 (8)	5.6 (3)
C(15)	0.4608 (9)	0.2464 (9)	0.2731 (8)	5.8 (3)
C(16)	0.550 (1)	0.0391 (8)	0.390 (1)	6.3 (3)

^a B values for anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \alpha)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)$.

parallel (24°) to the Cp* ligand and, as shown in Figure 1 in a view down Ta–Cl(1), is nearly planar with a O(1)–C(1)–C(2)/phenyl least-squares plane dihedral angle of 7 (7)°. This orientation presumably minimizes intramolecular steric repulsions between the enolate and C₅Me₅/thf ligands (e.g., C(1)⋯H(20a) = 2.76 \AA), while the planarity maximizes delocalization. The

Table VII. Bond Distances (\AA) in $(\text{C}_5\text{Me}_5)\text{Ta}[\text{C}(\text{O})\text{CH}_2\text{CMe}_3]\text{Cl}_3^a$

Ta–Cl(1)	2.352 (3)	C(3)–C(5)	1.49 (2)
Ta–Cl(2)	2.423 (4)	C(3)–C(6)	1.47 (2)
Ta–Cl(3)	2.400 (4)	C(4)–C(3)	1.55 (3)
Ta–O	2.108 (9)	C(5)–C(3)	1.49 (2)
Ta–C(1)	2.07 (2)	C(6)–C(3)	1.47 (2)
Ta–C(7)	2.48 (1)	C(7)–C(8)	1.42 (2)
Ta–C(8)	2.40 (1)	C(7)–C(11)	1.38 (2)
Ta–C(9)	2.41 (1)	C(7)–C(12)	1.47 (2)
Ta–C(10)	2.47 (1)	C(3)–C(7)	1.42 (2)
Ta–C(11)	2.53 (1)	C(8)–C(9)	1.45 (2)
O–Ta	2.108 (9)	C(8)–C(13)	1.49 (2)
O–C(1)	1.27 (2)	C(6)–H(6B)	0.99 (3)
C(1)–Ta	2.07 (2)	C(6)–C(6C)	0.93 (3)
C(1)–O	1.27 (2)	C(9)–C(3)	1.45 (2)
C(1)–C(2)	1.49 (2)	C(9)–C(10)	1.45 (2)
C(2)–H(2A)	0.92 (2)	C(9)–C(14)	1.47 (2)
C(2)–H(2B)	0.99 (2)	C(10)–C(9)	1.45 (2)
C(4)–H(4A)	0.94 (3)	C(10)–C(11)	1.41 (2)
C(4)–H(4B)	0.95 (2)	C(10)–C(15)	1.47 (2)
C(4)–H(4C)	0.96 (3)	C(11)–C(7)	1.38 (2)
C(5)–H(5A)	0.92 (2)	C(11)–C(10)	1.41 (2)
C(5)–H(5B)	0.98 (3)	C(11)–C(16)	1.53 (2)
C(5)–H(5C)	0.95 (3)	C(12)–C(7)	1.47 (2)
C(6)–H(6A)	0.95 (2)	C(13)–C(8)	1.49 (2)
C(2)–C(1)	1.49 (2)	C(14)–C(9)	1.47 (2)
C(2)–C(3)	1.52 (2)	C(15)–C(10)	1.47 (2)
C(3)–C(2)	1.52 (2)	C(16)–C(11)	1.53 (2)
C(3)–C(4)	1.55 (3)		

^aNumbers in parentheses are estimated standard deviations in the least significant digits.

Ta–O(1) distance of 1.947 (9) \AA is in the range for Ta–O single bonds as found in aryloxy/alkoxy complexes,²⁴ and the Ta–O(1)–C(1) angle of 142.7 (8)° suggests partial O(1) π -donation²⁵ to Ta. The C(1)–C(2) distance of 1.30 (2) \AA is rather short, as also noted in a Ti enolate structure,²⁶ and the C(1)–O(1) bond (1.34 (2) \AA) in **2a** is shorter than that in alcohols or ethers or that

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Table VIII. Bond Angles (deg) in $(C_5Me_5)Ta[C(O)CH_2CMe_3]Cl_3^a$

Cl(1)-Ta-Cl(2)	86.1 (1)	C(10)-Ta-C(11)	32.8 (4)
Cl(1)-Ta-Cl(3)	87.3 (1)	Ta-O-C(1)	70.8 (9)
Cl(1)-Ta-O	138.6 (2)	Ta-C(1)-O	73.7 (9)
Cl(1)-Ta-C(1)	103.2 (4)	Ta-C(1)-C(2)	167 (1)
Cl(2)-Ta-Cl(3)	150.0 (2)	O-C(1)-C(2)	120 (1)
Cl(2)-Ta-O	83.0 (4)	C(1)-C(2)-C(3)	119 (1)
Cl(2)-Ta-C(1)	74.4 (4)	C(2)-C(3)-C(4)	107 (1)
Cl(3)-Ta-O	82.8 (4)	C(2)-C(3)-C(5)	111 (1)
Cl(3)-Ta-C(1)	78.6 (5)	C(2)-C(3)-C(6)	112 (1)
O-Ta-C(1)	35.5 (4)	C(4)-C(3)-C(5)	109 (2)
C(7)-Ta-C(8)	33.7 (4)	C(4)-C(3)-C(6)	106 (2)
C(7)-Ta-C(9)	56.4 (5)	C(5)-C(3)-C(6)	112 (2)
C(7)-Ta-C(10)	55.0 (4)	C(8)-C(7)-C(11)	109 (1)
C(7)-Ta-C(11)	31.9 (5)	H(6B)-C(6)-H(6C)	108 (2)
C(8)-Ta-C(9)	35.0 (5)	C(8)-C(7)-C(12)	125 (1)
C(8)-Ta-C(10)	56.8 (4)	C(11)-O(7)-C(12)	125 (1)
H(2A)-C(2)-H(2B)	109 (1)	C(7)-C(8)-C(9)	108 (1)
H(4A)-C(4)-H(4B)	110 (3)	C(7)-C(8)-C(13)	127 (1)
H(4A)-C(4)-H(4C)	109 (2)	C(9)-C(8)-C(13)	125 (1)
H(4B)-C(4)-H(4C)	108 (2)	C(8)-C(9)-C(10)	106 (1)
H(5A)-C(5)-H(5B)	109 (2)	C(8)-C(9)-C(14)	125 (1)
H(5A)-C(5)-H(5C)	112 (2)	C(10)-C(9)-C(14)	128 (1)
H(5B)-C(5)-H(5C)	107 (2)	C(9)-C(10)-C(11)	107 (1)
H(6A)-C(6)-H(6B)	107 (2)	C(9)-C(10)-C(5)	126 (1)
H(6A)-C(6)-H(6C)	111 (3)	C(11)-C(10)-C(15)	126 (1)
C(3)-Ta-C(11)	54.9 (4)	C(7)-C(11)-C(10)	110 (1)
C(9)-Ta-C(10)	34.5 (4)	C(7)-C(11)-C(16)	126 (1)
C(9)-Ta-O(11)	55.5 (4)	C(10)-C(11)-C(16)	124 (1)

^a Numbers in parentheses are estimated standard deviations in the least significantly digits.

calculated (1.43 Å) from covalent radii.²⁷

The η^2 -nature of the neopentyl acyl coordination, as suggested by published ¹³C NMR data and our IR data, was substantiated by single-crystal X-ray diffraction on **4a** (R = Me; Figure 2). Tables V–VIII list data collection parameters, fractional coordinates for non-hydrogen atoms, bond distances, and bond angles, respectively, from the structural determination on **4a**. The acyl is perpendicular to the plane formed by the chlorines, with the neopentyl group oriented away from the C_5Me_5 ring. The Ta–O (2.108 (9) Å) and Ta–C(1) (2.07 (1) Å) bond lengths are similar, and the Ta–C(1) distance is in the range between Ta–C single and double bonds;²⁸ the large Ta–C(1)–C(2) angle of 167 (1)° is also suggestive of partial Ta–C(1) multiple bonding. The value of $\Delta [d(M-O) - d(M-Cl)]$, which has been used to characterize the degree of η^2 -interaction,^{2,29} of 0.04 Å for **4** is the lowest of reported transition-metal η^2 -acyls and is comparable to values for actinide acyls.² The C(1)–O bond length of 1.27 (1) Å is shorter than expected for a single bond, though in the 1.15–1.30-Å range of other η^2 -acyls,² and the angle summation about C(1) of 360° indicates a trigonal-planar acyl carbon.

Discussion

The reason or reasons for the variation in reaction course for carbonylation of the 4-methylbenzyl and neopentyl complexes are not known at present and will not become clear until other alkyls have been examined. Tetrahydrofuran plays a key role in the 1,2-hydrogen shift leading to the O-bound enolate in the 4-methylbenzyl case, as the carbonylation does not proceed in nonethereal solvents; pyridine has been shown¹⁹ to assist in enolization of the neopentyl compound at elevated temperatures. The *p*-tolyl group may assist in the 1,2-hydrogen shift by stabilizing an intermediate in the isomerization to the enolate, although group **4** iminoacyls derived from RNC insertion into metal–benzyl compounds do not undergo ready isomerization to vinylamides.³⁰

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If a carbenium species is involved in the carbonylation of **1** to **2**, then intramolecular 1,2-hydrogen migration must be faster than intermolecular coupling to dinuclear enediolates.

Conclusions

Carbonylation of mono(peralkylcyclopentadienyl)tantalum alkyls has been shown to lead to at least two possible outcomes—either O-bound enolates or η^2 -acyls (in the neopentyl case, shown by Rocklage and independently by Tilley and co-workers), which are more resistant to a 1,2-hydrogen shift. The 4-methylphenyl enolate is exclusively *cis*, as shown in solution by IR and ¹H NMR spectroscopy and in the solid-state by X-ray diffraction. The X-ray structure is the first obtained on a tantalum enolate species. The solid-state structure of the neopentyl acyl **4** represents a new structural class of early-transition-metal η^2 -acyl, distinct from the common bis(cyclopentadienyl) early-transition-metal acyls, and shows that substantial distortion of an acyl is possible in transition-metal chemistry.

We believe that the mono(peralkylcyclopentadienyl) environment will allow a greater range of electronic variations (for example, by use of stronger or weaker π -donor ligands in place of the halides) and synthetically useful reactivity studies as compared to bis(cyclopentadienyl) complexes. Comparative structures and reactivities of acyl and enolate ligands in high-valent and midvalent compounds of the same metal can also be more readily examined in mono(peralkylcyclopentadienyl) environments, and such studies are in progress.²¹

Experimental Section

General Procedures. Compounds were manipulated under a prepurified dinitrogen/helium or argon atmosphere in a Vacuum Atmospheres glovebox (under continuous atmosphere recirculation and purification; helium present to aid in gas stream cooling) or on a Schlenk line of local design. Reagent grade benzene, toluene, diethyl ether, and tetrahydrofuran were thoroughly degassed with a stream of prepurified dinitrogen and distilled under dinitrogen in greaseless stills from sodium benzophenone ketyl. Hexane was washed several times with 5% nitric/sulfuric acid followed by water, dried over CaCl₂, and then distilled from sodium/potassium benzophenone ketyl solubilized by tetraglyme. Methylene chloride was rigorously degassed and then distilled from granular P₂O₅.

Tantalum pentachloride (Cerac, Inc; Pressure Chemical Co.) and neopentanol (Fluka Chemical) were used as received. Perdeuterio-benzene (Aldrich) was stored over freshly cut sodium prior to use. Chlorotributyltin (Aldrich) and *p*-methylbenzyl chloride (Lancaster Synthesis Ltd.) were fractionally distilled in vacuo prior to use. *cis/trans*-2-Butene (Matheson), carbon monoxide (Air Products, UHP grade), and 99% ¹³C ¹³CO under pressure in a lecture bottle (Amersham; Isotec) were used as received.

2-Bromo-2-butene,³¹ pentamethylcyclopentadiene,³² tetramethylcyclopentadiene,³³ (peralkylcyclopentadienyl)lithium,³³ (peralkylcyclopentadienyl)tributyltin,³⁴ Me₃CCH₂Cl,³⁵ LiCH₂CMe₃,³⁶ and Zn(CH₂CMe₃)₂³⁶ were prepared by literature procedures. 2,3-Dibromobutane was prepared by passing gaseous *cis/trans*-2-butene directly into water-cooled bromine until decolorization was noted. Zn(CH₂C₆H₄-*p*-Me)₂ was prepared from ZnCl₂(1,4-dioxane)³⁷ and *p*-MeC₆H₄CH₂MgCl by using the literature procedure for Zn(CH₂Ph)₂.³⁸ (C₅Me₄R)TaCl₄ (R = Me, Et) were prepared in 90–95% yields in a modification of the procedure^{34c} from TaCl₅ and Sn(CH₂CH₂CH₂CH₃)₃(C₅Me₄R) at room temperature by use of CH₂Cl₂ as solvent and low-temperature crystal-

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lization; recrystallization was unnecessary. $(C_5Me_4R)Ta(CH_2C_6H_4-p-Me)Cl_3$ was made, in a variation of the published procedure,²² by alkylation of $(C_5Me_4R)TaCl_4$ with $Zn(CH_2C_6H_4-p-Me)_2$ in ether in 77% yield rather than via addition of LiC_5Me_4R to $Ta(CH_2C_6H_4-p-Me)Cl_4$. $(C_5Me_4R)Ta(CH_2CMe_3)Cl_3$ was made in 89% yield, in a variation of the literature methods,^{19,39} by alkylation of $(C_5Me_4R)TaCl_4$ in ether with $Zn(CH_2CMe_3)_2$.

All NMR spectra were obtained in the internal deuterium-locked mode, and all chemical shifts are reported in ppm with positive chemical shifts representing resonances at lower field strength than that of the standard. Proton NMR spectra were obtained on either a Jeol FX-90Q (89.55-MHz proton observe frequency), Bruker WM-360 (360 MHz), or Bruker MSL-300 (300 MHz) NMR spectrometer; spectra are internally referenced to the residual protio solvent (e.g., C_6D_6 , $\delta = 7.15$) impurity. $\{^1H\}^{13}C$ and gated $\{^1H\}^{13}C$ NMR spectra were obtained on the Bruker WM-360 NMR or MSL-300 spectrometer by using the solvent ^{13}C resonance (e.g., C_6D_6 , $\delta \approx 128.0$) as internal reference. Mass spectra were obtained in the electron-impact mode on a VG Instruments ZAB-HF magnetic sector spectrometer or on a VG Instruments TRIO 1 quadrupole spectrometer; samples were introduced into the spectrometer direct inlet under argon purge via a sample holder of local design.⁴⁰ Infrared spectra were obtained as KBr pellets on a Mattson Cygnus 25 FT-IR spectrophotometer.

Single-crystal X-ray diffraction was performed on an Enraf-Nonius CAD-4 diffractometer interfaced to a Micro VAX II minicomputer with Tektronix 4106A color graphics terminals and Telaris laser printer; data were processed with the Enraf-Nonius SDP software package. Crystals for X-ray diffraction were grown in either cosolvent mixtures or layered cosolvent/solution mixtures in 5-mm-o.d. glass tubes; crystals were inspected under an inert atmosphere by using a stereomicroscope mounted on the glovebox window and placed in appropriately sized glass capillaries, internally coated with a thin film of Apiezon grease, which were then stoppered with a rubber septum and flame sealed with a microtorch. Data were collected at 22 °C (unless otherwise indicated) by using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite-crystal monochromator in the incident beam. An empirical absorption correction based on φ scans of six–nine reflections at $\chi = 90^\circ$ was applied to all data sets. Preliminary positions for the heavy atoms (i.e., metal atoms) were determined from a three-dimensional Patterson function or by using the MULTAN package of programs. Atomic positions were refined by full-matrix least-squares calculations. Subsequent difference Fourier maps followed by least-squares refinement located all non-hydrogen atoms and, in many cases, a substantial number of the hydrogen atoms. The remaining hydrogen atoms were calculated by the HYDRO program (using found hydrogen atoms with reasonable distances and angles as input in the HYDRO calculation) after anisotropic convergence of all non-hydrogen atoms, and hydrogen atom positions and isotropic temperature factors were fixed in the final refinements.

Gas reactions with organometallic complexes in solution were performed at 30–100 psig in Fischer–Porter glass reactors of local design⁴¹ with sampling port or with provision to add reagents under pressure. A low-temperature (–35 °C) refrigerator in the glovebox was used for compound recrystallizations.

Preparation of $(C_5Me_5)Ta(OCHCHC_6H_4-p-Me)Cl_3(thf)$. $(C_5Me_5)Ta(CH_2C_6H_4-p-Me)Cl_3$ (2.15 g, 4.1 mmol) was dissolved in 35 mL of thf, and the mixture was pressurized with 50-psi carbon monoxide at 0 °C for 8 h. The red solution was concentrated in vacuo to 10 mL and cooled, yielding 0.47 g of red prisms. A second crop of 0.67 g was later collected (44% total yield). The compound is unstable in solution, decomposing to a yellow solid within days even at –30 °C. The solid enolate is also unstable, decomposing within days at room temperature, but is indefinitely stable at –30 °C. The occluded thf can be removed by recrystallization from toluene, but the resulting red solid is not crystalline and is less stable than the thf adduct. Mass spectrum (30 eV, direct inlet): m/e 554, $^{35}Cl^{35}Cl^{35}Cl$ isotopomer of Cl_3 isotope pattern. High-resolution mass spectrum (EI): found, m/e 519.068 817, $(M - Cl)^+$; calcd for $^{181}Ta^{35}Cl_2^{16}O^{12}C_{19}H_{24}$, m/e 519.068 817; no parent ion observed. Thermal instability precluded elemental analysis. IR (Nujol mull): 1615 cm^{-1} , $\nu_{C=C}$. 1H NMR (δ , C_6D_6 , 360 MHz, 25 °C): 2.06

(s, C_5Me_5), 2.14 (s, tolyl Me), 5.31 (d, H_β , $^3J_{HH} = 6.6$ Hz), 6.99 (d, H_α , $^3J_{HH} = 6.6$ Hz), 7.07–7.57 (m, phenyl). ^{13}C [gated 1H] NMR (δ , thf- d_6 , 90.56 MHz, 25 °C): 108.5 (d, $OC_a=C_\beta$, $^1J_{CH} = 151$ Hz), 150.6 (d, OC_α , $^1J_{CH} = 181$ Hz).

The C_5Me_4Et analogue was prepared by pressurizing a solution of $(C_5Me_4Et)Ta(CH_2C_6H_4-p-Me)Cl_3$ (0.26 g, 0.5 mmol) in thf with 50-psi CO at 25 °C for 4 h. The cherry red solution was concentrated to 4 mL and cooled. Two crops of 0.13 g total weight were collected (ca. 30% yield). $(C_5Me_4Et)Ta(OCHCHC_6H_4-p-Me)Cl_3(thf)$ is much more soluble than the C_5Me_5 analogue, which hinders isolation. 1H NMR (δ , C_6D_6 , 90 MHz, 25 °C): 0.57 (t, 3, $C_5Me_4CH_2CH_3$, $^3J_{HH} = 8$ Hz), 2.03, 2.12 (s, 12, $C_5Me_4CH_2Me$), 2.24 (s, 3, tolyl Me), 2.56 (q, 2, $C_5Me_4CH_2Me$, $^3J_{HH} = 8$ Hz), 5.31 (d, 1, H_β , $^3J_{HH} = 7$ Hz), 7.00 (d, 1, H_α , $^3J_{HH} = 7$ Hz), 7.07–7.57 (m, 4, phenyl).

Preparation of $(C_5Me_5)Ta[\eta^2-C(O)CH_2CMe_3]Cl_3$. $(C_5Me_5)Ta(CH_2CMe_3)Cl_3$ (1.40 g, 2.8 mmol) was dissolved in 100 mL of hexanes, and the solution was pressurized with 50-psi carbon monoxide for 1 h. The solution was filtered and cooled; 0.89 g of orange rectangular prisms were collected. After the solution was concentrated in vacuo a second crop of 0.10 g was collected (67% yield). 1H NMR (δ , 25 °C, C_6D_6): 1.22 (s, 9, CMe_3), 2.13 (s, 15, C_5Me_5), 3.22 (s, 2, CH_2); $^2J_{CH} = 6.0$ Hz for the CH_2 resonance in $(C_5Me_5)Ta[^{13}C(O)CH_2CMe_3]Cl_3$. ^{13}C NMR (δ , 25 °C, C_6D_6 , 1H): 11.8 (C_5Me_5), 30.1 (CMe_3), 31.3 (CMe_3), 54.9 (CH_2), 130.7 (C_5Me_5), 315.4 (acyl C_α). The above data are similar to those reported by Tilley and co-workers.¹⁹ Additional IR data (KBr pellet, cm^{-1}): ~1472 (s, br); 1440 for ^{13}C -labeled **4a**. Mass spectra consistently showed the absence of the parent ion; the highest ion, at m/e 584, was assigned to $(C_5Me_5)TaCl_2[C(O)CH_2CMe_3]_2^+$.

The C_5Me_4Et analogue was prepared analogously: carbonylation of $(C_5Me_4Et)Ta(CH_2CMe_3)Cl_3$ (0.5 g, 0.98 mmol) yielded 0.30 g of orange product (56% yield). $(C_5Me_4Et)Ta[\eta^2-C(O)CH_2CMe_3]Cl_3$ is more soluble than the C_5Me_5 analogue. 1H NMR (δ , 25 °C, C_6D_6): 0.78 (t, 3, $C_5Me_4CH_2CH_3$, $^3J_{HH} = 7.6$ Hz), 1.23 (s, 9, CH_2CMe_3), 2.14, 2.22 (s, 12, $C_5Me_4CH_2Me$), 2.64 (q, 2, $C_5Me_4CH_2Me$, $^3J_{HH} = 7.6$ Hz), 3.23 (s, 2, CH_2CMe_3).

X-ray Structural Determination of **2a.** Intensity data for the half-sphere was collected at –100 °C, with 3462 unique reflections collected ($2^\circ \leq 2\theta \leq 48^\circ$; $\pm h, \pm k, -l$) via an ω -2 θ scan mode and 2948 observed with $I \geq 3\sigma(I)$. The data were corrected for Lorentz, polarization, and absorption (empirical absorption method; 0.7172 minimum, 0.997 maximum) effects, and the structure was solved with a combination of direct (DIRDIF) and difference methods (including DIRDIF) using the Enraf-Nonius SDP-VAX program package. Anisotropic least-squares refinement on all atoms except Cp* ring carbon C(13) (isotropic) and the hydrogens (calculated and placed in fixed positions) gave final agreement factors of $R = 0.059$ and $R_w = 0.082$.

X-ray Structural Determination of **4a.** Intensity data (two octants, $2^\circ \leq 2\theta \leq 40^\circ$; four octants, $40^\circ \leq 2\theta \leq 50^\circ$) was collected, with 1917 independent reflections after averaging and 1598 observed with $I \geq 3\sigma(I)$. The data were corrected for Lorentz, polarization, and absorption (empirical absorption method) effects, and the structure was solved with a combination of direct (MULTAN) and difference methods using the Enraf-Nonius SDP-VAX program package. Anisotropic least-squares refinement on all atoms except hydrogens (one found per carbon except C(2)); others calculated, all placed in fixed positions) gave final agreement factors of $R = 0.037$ and $R_w = 0.046$.

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Supplementary Material Available: Tables of crystal data, hydrogen fractional coordinates and thermal parameters, anisotropic thermal parameters (B 's and U 's), and bond lengths and bond angles including hydrogen atoms for **2b** and **3a** (13 pages); listings of observed and calculated structure factors for **2b** and **3a** (21 pages). Ordering information is given on any current masthead page.

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