Synthesis and Structural Characterization of a Meerwein–Ponndorf–Verley/Oppenauer Redox Intermediate at a Tantalum(V) Center

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The alkyne adducts $(DIPP)_3Ta(PhC{\equiv}CPh)$ (**1**) and $(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$ (**2**, DIPP = 2,6-diisopropylphenoxide) are precursors to the metallacyclic products $(DIPP)_3\overline{Ta(CPh{=}CPhCPh(Me)O)}$ (**3**) and $(DIPP)_3\overline{Ta(C(SiMe_3){=}CMeCPh_2O)}$ (**4**) from their reactions with 1 equiv of acetophenone and benzophenone, respectively. $(DIPP)_3Ta(PhC{\equiv}CPh)$ (**1**) also reacts with 1 equiv of benzaldehyde to form the related metallacyclic compound $(DIPP)_3\overline{Ta(CPh{=}CPhCH(Ph)O)}$ (**5**) in high yield. Excess benzaldehyde reacts with **1** and **2** to form the benzyl alkoxide complexes $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CR{=}CR'CPh{=}O)$ (**6**, R = R′ = Ph; **7**, R = Me_3Si, R′ = Me) with a dative bonding interaction between the ring oxygen and the tantalum(V) center. Deuterium-labeling experiments and reactivity studies of this reaction have implicated the oxophilic complex **5** as an intermediate that is capable of transferring a hydride to a weakly coordinated (probably η^1, O-bound), second molecule of an aldehyde or ketone. Thus, $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (**6**), $(DIPP)_3(CH_3CH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (**8**), and $(DIPP)_3(CH_3CH_2(CH_3)CHO)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (**9**) are formed from the reaction of **5** with benzaldehyde, acetaldehyde, and 2-butanone, respectively. The hydride-transfer step of this reaction is equivalent to the Meerwein–Ponndorf–Verley/Oppenauer reactions in which a secondary alkoxide ligand transfers a hydride to the carbonyl of a coordinated aldehyde or ketone. Support that the reaction **5** → **6** proceeds through an η^1-benzaldehyde intermediate is provided in the isolation of $(DIPP)_3(\eta^1\text{-}EtCN)\overline{Ta(CPh{=}CPhCH(Ph)O)}$ (**11**) from the reaction of $(DIPP)_3\overline{Ta(CPh{=}CPhCH(Ph)O)}$ (**5**) with propionitrile. An X-ray structural study of **6** reveals that it belongs to the space group $P\bar{1}$ (No. 2) with triclinic cell parameters a = 11.552 (1) Å, b = 13.479 (1) Å, c = 20.246 (2) Å, α = 90.82 (1)°, β = 99.44 (1)°, γ = 114.82 (1)°, and V = 2810.5 Å^3 for Z = 2. Final agreement factors for 8791 reflections with $F_o^2 > 3.0\sigma(F_o^2)$ were 0.022 (unweighted) and 0.028 (weighted). The Ta—O(CH_2Ph) bond length of 1.865 (2) Å, the Ta–O(metallacycle) distance of 2.182 (2) Å, the C=O bond length within the ring (1.265 (3) Å), and the O–C(H_2)–C_{ipso} angle of the alkoxide (113.2 (3)°) are all consistent with the formulation of **6** as $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ with a dative bonding interaction between the ring oxygen and the metal.

Introduction

Even after the advent of hydride reducing agents, the Meerwein–Ponndorf–Verley (MPV) reduction has remained a useful synthetic strategy in many applications.[1,2] The current mechanistic view of this reduction and of its microscopic reverse, the Oppenauer oxidation,[3,4] is as follows:[5] (i) coordination of a ketone to an alkoxide catalyst, typically $Al(O\text{-}i\text{-}Pr)_3$ (ii) hydride transfer from an alkoxide ligand to the ketone through a cyclic transition state to produce a new ketone and a new alkoxide ligand (eq 1), and (iii) dissociation of the new ketone and alcoholysis of the mixed alkoxide metal complex to regenerate the catalyst and release the alcohol.[6] Early work by Meerwein demonstrated[7] the utility of certain transition metals, including zirconium and iron, in this catalytic reaction, and indeed, d-orbital participation in the aluminum-catalyzed reaction has been implicated.[5c,8]

(1)

During the course of our studies on coordinated alkyne cyclooligomers,[9] we observed that an alkyne ligand bound to a tantalum(III) metal center exhibits properties more like those of a tantalum(V) metallacyclopropene complex;[10] i.e., the alkyne exhibits features resembling those of a dianion. Herein we report an unusual manifestation of this dianionic behavior, viz. that these compounds can participate in a type of "Cannizzaro reaction"[11-13] in which the

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(1) (a) Meerwein, H.; Schmidt, R. *Justus Liebigs Ann. Chem.* **1925**, *444*, 221. (b) Ponndorf, W. *Angew Chem.* **1926**, *39*, 138. (c) Verley, A. *Bull. Soc. Chim. Fr.* **1925**, *37*, 537. (d) Verley, A. *Ibid.* **1925**, *37*, 871. (e) For a review of the Meerwein–Ponndorf–Verley reduction, see: Wilds, A. L. *Org. React.* **1944**, *2*, 178.

(2) For examples of Meerwein–Ponndorf–Verley reductions, see: (a) Hach, V. *J. Org. Chem.* **1973**, *38*, 293. (b) Botta, M.; De Angelis, F.; Gambacorta, A.; Labbiento, L.; Nicoletti, R. *Ibid.* **1985**, *50*, 1916. (c) Hutton, J. *Synth. Commun.* **1979**, *9*, 483.

(3) For a review of the Oppenauer oxidation, see: Djerassi, C. *Org. React.* **1951**, *6*, 207.

(4) For examples of Oppenauer oxidations, see: (a) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960**, *82*, 1240. (b) Terao, S.; Shiraishi, M.; Kato, K. *Synthesis* **1979**, 467. (c) Ringold, H. J.; Löken, B.; Rosenkranz, G.; Sondheimer, F. *J. Am. Chem. Soc.* **1956**, *78*, 816.

(5) (a) For mechanistic details of the Meerwein–Ponndorf–Verley reduction, see refs 5b–e. (b) Warnhoff, E. W.; Reynolds-Warnhoff, P.; Wong, M. Y. H. *J. Am. Chem. Soc.* **1980**, *102*, 5956. (c) Shiner, V. J., Jr.; Whittaker, D. *Ibid.* **1963**, *85*, 2337. (d) Moulton, W. N.; Van Atta, R. E.; Ruch, R. R. *J. Org. Chem.* **1961**, *26*, 290. (e) Williams, E. D.; Krieger, K. A.; Day, A. R. *J. Am. Chem. Soc.* **1953**, *75*, 2404.

(6) There is evidence that, in some cases, single-electron-transfer pathways may be in operation in the $Al(O\text{-}i\text{-}Pr)_3$-catalyzed Meerwein–Ponndorf–Verley reaction; see: Ashby, E. C.; Goel, A. B.; Argyropoulos, J. N. *Tetrahedron Lett.* **1982**, 2273.

(7) Meerwein, H.; von Bock, B.; Kirschnick, B.; Lenz, W.; Migge, A. *J. Prakt. Chem.* **1936**, *147*, 211.

(8) Shiner, V. J., Jr.; Whittaker, D. *J. Am. Chem. Soc.* **1969**, *91*, 394.

(9) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.

(10) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.

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formal anion of the alkyne replaces OH^- as the base and induces the disproportionation of aldehydes within the coordination sphere of the metal. The last step of this reaction, the hydride transfer from an alkoxide ligand to a coordinated aldehyde, is formally equivalent to the Meerwein–Ponndorf–Verley/Oppenauer reaction. In our case, because the newly formed ketone is a part of a metallacyclic chelate, the ligand remains η^1 (oxygen) bound to the metal, which has permitted the complete characterization, including an X-ray structural study, of this purported MPV/Oppenauer-type reaction intermediate.

Results

When $Ta(DIPP)_3Cl_2{\cdot}OEt_2$ (DIPP = 2,6-diisopropylphenoxide) is reduced with 2 equiv of Na/Hg, in the presence of $PhC{\equiv}CPh$ or $Me_3SiC{\equiv}CMe$, the alkyne adducts $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1) and $(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$ (2) can be isolated in high yield.[10] The $^{13}C_{alkyne}$ resonances at δ 216.2 for 1 ($CDCl_3$) and at δ 226.0 and 224.4 for 2 (C_6D_6) suggest a formal four-electron interaction involving both acetylene $\pi_\parallel$ and $\pi_\perp$ bonding orbitals with the metal.[14,15] Furthermore, compound 1 can be hydrolyzed (H_2O/acetone, 1:9 v/v) to provide a quantitative yield of *cis*-PhCH=CHPh (^1H NMR spectroscopy), thereby suggesting the formulation of the acetylene ligand as substantially reduced.[16] On the basis of the successful cross-coupling reactions of 1 with terminal alkynes,[10,17] we turned to heteroatom substrates, including aldehydes and ketones, in an effort to extend the potential utility of these reactions.

Scheme I

DIPP = 2,6 - diisopropylphenoxide

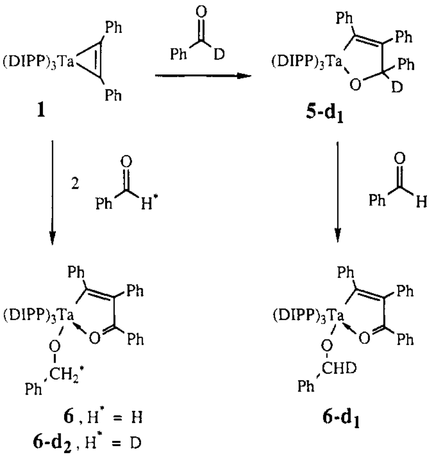
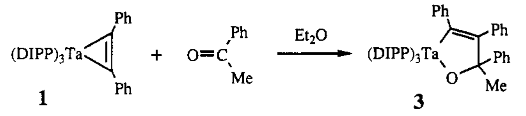


Table I. Details of the X-ray Diffraction Study for $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (6)

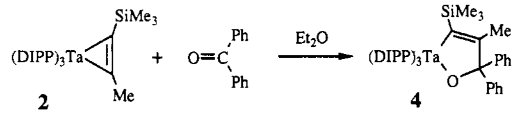
mol formula	$C_{64}H_{73}TaO_5$
mol wt	1103.24
space group	$P\bar{1}$ (No. 2)
unit cell vol, Å^3	2810.5
a, Å	11.552 (1)
b, Å	13.479 (1)
c, Å	20.246 (2)
α, deg	90.82 (1)
β, deg	99.44 (1)
γ, deg	114.82 (1)
Z	2
calcd dens, g cm^{-3}	1.30
cryst dimens, mm	0.42 × 0.33 × 0.33
data collecn temp, °C	23 ± 1
Mo Kα radiation, λ, Å	0.71073
monochromator	graphite
abs coeff, cm^{-1}	19.8
2θ range, deg	2–50
total no. of rflns measd	11527, 9942 unique
no. of rflns measd with $I > 3\sigma(I)$	8791
scan type	θ–2θ
scan speed, deg min^{-1}	2–8
no. of params refined	631
R	0.022
R_w	0.028

Table II. Selected Bond Distances (Å) in $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (6)

Ta–O(10)	1.918 (2)	Ta–C(60)	2.287 (3)
Ta–O(20)	1.915 (2)	C(60)–C(70)	1.354 (4)
Ta–O(30)	1.921 (2)	C(70)–C(80)	1.467 (4)
Ta–O(40)	1.865 (2)	C(80)–O(50)	1.265 (3)
Ta–O(50)	2.181 (2)	O(40)–C(41)	1.418 (4)



(2)



(3)

The reaction of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1) with acetophenone (Et_2O solution, room temperature) results in a pale yellow solution from which the metallacycle 3 can be isolated in high yield (eq 2). The acetylene adduct 2, $(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$, reacts similarly with ketones as seen in its reaction with benzophenone to form the metallacycle 4 (eq 3). The regioselectivity presented in eq 3 for compound 4 is based upon the products obtained upon its hydrolysis (H_2O/acetone, 1:9 v/v), which provides (*E*)-$Me_3SiCH{=}C(Me)CPh_2OH$, rather than (*Z*)-$MeCH{=}C(SiMe_3)CPh_2OH$, expected for the opposite regioisomer.[18] These reactions most likely proceed by an initial coordination of the ketone via an oxygen lone pair, consistent with the oxophilic nature of the tantalum center. Related couplings with zirconocene alkyne, cycloalkyne, and benzyne reagents have been reported recently.[19]

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(11) For a review of the Cannizzaro reaction, see: Geissman, T. A. *Org. React.* **1944**, *2*, 94.

(12) For synthetic applications of the Cannizzaro reaction, particularly intramolecular reactions, see: (a) Hendrickson, J. B.; Bogard, T. L.; Fisch, M. E. *J. Am. Chem. Soc.* **1970**, *92*, 5538. (b) McDonald, R. S.; Sibley, C. E. *Can. J. Chem.* **1981**, *59*, 1061.

(13) For a concise discussion of the Meerwein–Ponndorf–Verley reaction and its relation to Cannizzaro chemistry, see: Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978; pp 250–263.

(14) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288.

(15) For examples of four-electron-donor alkynes, see: (a) Theopold, K. H.; Holmes, S. J.; Schrock, R. R. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 1010. (b) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1980**, *19*, 2352. (c) Smith, G.; Schrock, R. R.; Churchill, M. R.; Youngs, W. J. *Ibid.* **1981**, *20*, 387. (d) Chao, Y.-W.; Wexler, P. A.; Wigley, D. E. *Ibid.* **1989**, *28*, 3860.

(16) (a) A recently completed structural study of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1) reveals that the alkyne C–C bond length is 1.346 (5) Å and the Ta–C(alkyne) bond lengths are 2.070 (3) and 2.076 (3) Å. Full structural results and reactivity studies will be reported.[16b] (b) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. Manuscript in preparation.

(17) (a) Terminal alkynes often protonate group 4 amido and related compounds to produce acetylide (alkynyl) complexes; for example, see ref 17b. A $HC{\equiv}CH$ adduct of Ti is known[17c] and a group 4 metallocene system has recently been developed that permits the coupling of terminal alkynes with coordinated alkynes.[17d] (b) Jenkins, A. D.; Lappert, M. F.; Srivastava, R. C. *J. Organomet. Chem.* **1970**, *23*, 165. (c) Alt, H. G.; Engelhardt, H. E.; Rausch, M. D.; Kool, L. B. *J. Am. Chem. Soc.* **1985**, *107*, 3717. (d) Buchwald, S. L.; Nielsen, R. B. *Ibid.* **1989**, *111*, 2870.

(18) The ^1H NMR signal of the olefin (*Z*)-$MeC\mathit{H}{=}C(SiMe_3)CPh_2OH$ would be expected to couple to the protons of the geminal methyl group. We assign the hydrolysis product as (*E*)-$Me_3SiCH{=}C(Me)CPh_2OH$ since no such coupling is observed. We also have proposed the regioselectivity of compound 7 on the basis of this observation.

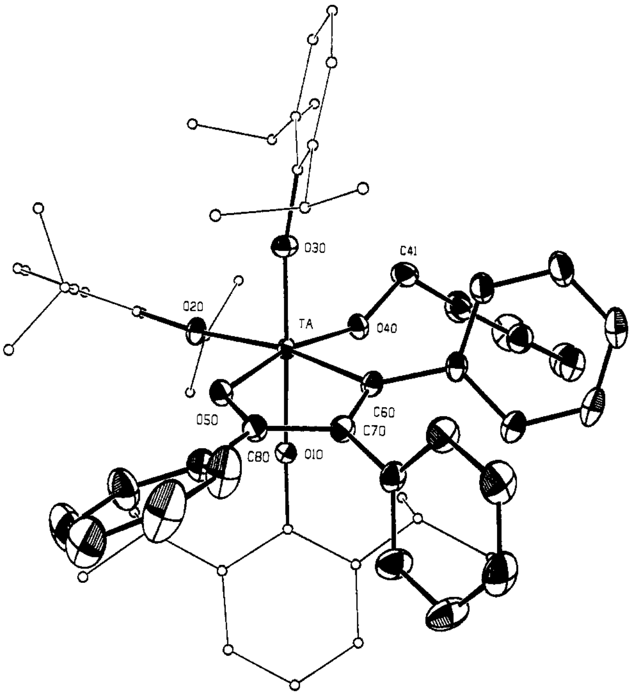

Figure 1. ORTEP drawing of (DIPP)$_3$(PhCH$_2$O)Ta(η^2-CPh=CPhCPh=O) (**6**) with the DIPP ligands reduced for clarity (DIPP = O-2,6-C$_6$H$_3$-*i*-Pr$_2$).

Table III. Selected Bond Angles (deg) in (DIPP)$_3$(PhCH$_2$O)Ta(η^2-CPh=CPhCPh=O) (6)

Ta-O(10)-C(11)	158.6 (2)	O(50)-Ta-C(60)	71.07 (8)
Ta-O(20)-C(21)	173.3 (2)	O(50)-C(80)-C(81)	117.0 (3)
Ta-O(30)-C(31)	167.6 (2)	C(70)-C(80)-C(81)	124.9 (3)
Ta-O(40)-C(41)	147.8 (2)	O(10)-Ta-O(30)	172.11 (8)
O(40)-C(41)-C(42)	113.2 (3)	O(30)-Ta-O(40)	94.52 (9)
Ta-C(60)-C(70)	115.5 (2)	O(20)-Ta-O(30)	90.59 (8)
C(60)-C(70)-C(80)	113.1 (2)	O(30)-Ta-O(50)	89.41 (8)
C(70)-C(80)-O(50)	118.0 (2)	O(30)-Ta-C(60)	88.23 (9)
Ta-O(50)-C(80)	120.5 (2)	O(20)-Ta-O(40)	106.90 (8)

When 1 equiv of benzaldehyde is added to a −40 °C solution of **1**, an immediate reaction occurs to provide a pale yellow complex (**5**), which exhibits properties closely resembling those of metallacycles **3** and **4**. Thus, the spectroscopic and analytical data for **5** are in accord with its formulation as the analogous metallacycle (DIPP)$_3$Ta(CPh=CPhCH(Ph)O) (Scheme I). However, when 2 equiv or more of benzaldehyde is added to solutions of **1**, a rapid solution color change from yellow to orange-red occurs and red crystals that are analyzed as "(DIPP)$_3$Ta(PhC≡CPh)(PhCHO)$_2$" (**6**) are isolated. The diagnostic spectroscopic features of **6** include a δ 5.19 singlet that is integrated for 2 H in the ^{1}H NMR spectrum and a δ 76.1 *triplet* in the off-resonance-decoupled ^{13}C NMR spectrum. In addition, no ν(C=O) mode is observed in the IR spectrum of **6** between 1800 and 1600 cm^{-1}, but a medium-to-strong-intensity band occurs at 1530 cm^{-1} that does not appear in compounds **3**–**5** and that cannot be attributed to either DIPP or PhC≡CPh ligands. All of these data implicate the *transfer* of a hydride from one aldehyde to the other. Since more than one structure consistent with this information could be formulated, a single-crystal X-ray diffraction study of compound **6** was undertaken.

The molecular structure of **6** is presented in Figure 1, with a view of the local coordination about the metal shown in Figure 2. A summary of the crystal data and the structural analysis is given in Table I, and selected bond distances and bond angles are provided in Tables II and III, respectively. In addition to the three DIPP ligands, the overall octahedral coordination geometry of **6** features a Ta-O(40)-C(41)-C(42)$_{\text{ipso}}$ linkage with a Ta-O(40) bond length of 1.865 (2) Å, reflecting the covalent bond of an *alkoxide* ligand. This assignment is confirmed by the acute O(40)-C(41)-C(42)$_{\text{ipso}}$ angle of 113.2 (3)°, indicating an sp^3 carbon hybridization. (The hydrogen atoms bonded to C(41) were not located, although all hydrogen atoms were included in fixed positions in the structure refinement.) Thus, one benzaldehyde molecule that was introduced has been reduced to a benzyl alkoxide ligand, Ta-O-CH$_2$Ph, as was observed in the ^{1}H NMR (δ 5.19, CH_2Ph) and ^{13}C NMR (δ 76.1, CH$_2$Ph) spectra.

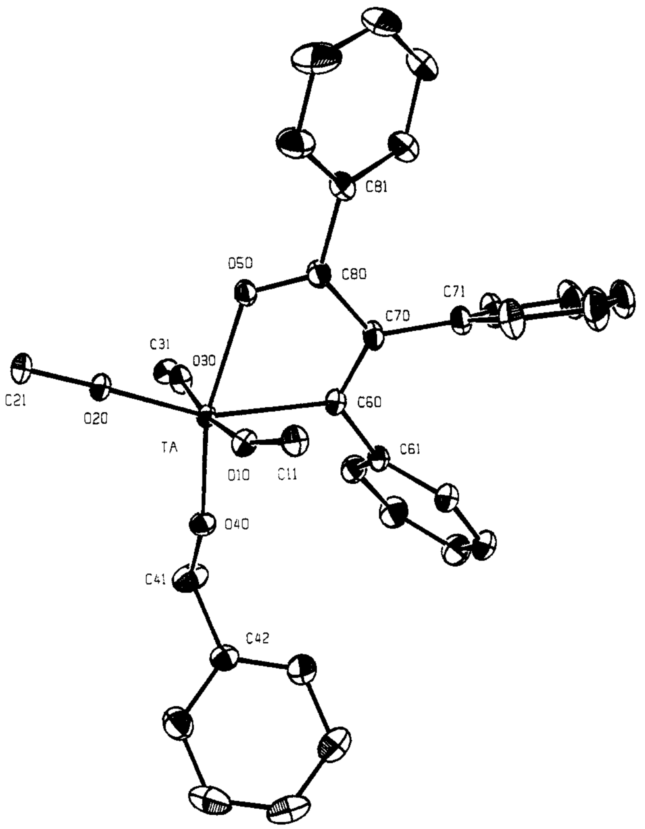

Figure 2. ORTEP drawing of the local coordination of (DIPP)$_3$(PhCH$_2$O)Ta(η^2-CPh=CPhCPh=O) (**6**; DIPP = O-2,6-C$_6$H$_3$-*i*-Pr$_2$), with the DIPP ligands omitted.

The nature of the metallacyclic ring is also revealed from Figures 1 and 2. The short C(80)–O(50) distance (1.265 (3) Å) and the almost perfect trigonal-planar geometry about C(80) (χ^2 for the C(80)–O(50)–C(70)–C(81) plane is 37.3), including the near-120° angles about this carbon, all require an sp^2 hybridization about C(80) and a double bond between C(80) and O(50). The Ta–O(50) bond (2.181 (2) Å) is distended relative to Ta–O covalent bonds (cf. the average Ta–O(DIPP) bond length of 1.918 Å) and falls in the range of coordinated *neutral* oxygen donors coordinated to tantalum centers.[20] All of these data require the formulation of **6** as the product resulting from a Meer-

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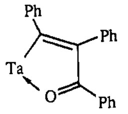
(19) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *Ibid.* **1986**, *108*, 7441. (c) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *Ibid.* **1987**, *109*, 2544.

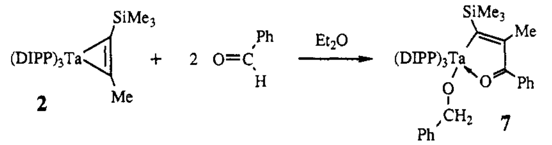
(20) Several tantalum compounds containing coordinated THF or dimethoxyethane have been structurally characterized. See, for example: (a) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050. (b) Churchill, M. R.; Wasserman, H. J. *Ibid.* **1982**, *21*, 218. (c) Churchill, M. R.; Wasserman, H. J. *Ibid.* **1982**, *21*, 223. (d) Gal, A. W.; van der Heijden, H. *J. Chem. Soc., Chem. Commun.* **1983**, 420. (e) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.

wein–Ponndorf–Verley/Oppenauer hydride-transfer reaction, viz. $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (Scheme I). The incorporation of the newly formed ketone into the metallacyclic chelate prevents its loss from the coordination sphere of the metal.

With the structural analysis of **6** in hand, we can assign the 1530-cm^{-1} IR band as the $\nu(C{=}O)$ mode of the metallacyclic ring, which reflects the strong dative interaction between O(50) and the oxophilic metal,[21] as represented by



The molecular structure of **6**, as well as our synthetic results, strongly suggests that C(80), after attack by C(70), is the origin of the transferred hydride. The $Me_3SiC{\equiv}CMe$ adduct **2**, $(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$, also reacts with 2 equiv or more of benzaldehyde to provide red-orange crystals of compound **7**, which, on the basis of its analysis and its spectroscopic properties similar to those of **6**, we also formulate as the benzyl alkoxide complex $(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}C(SiMe_3){=}CMeCPh{=}O)$ (eq 4).



(4)

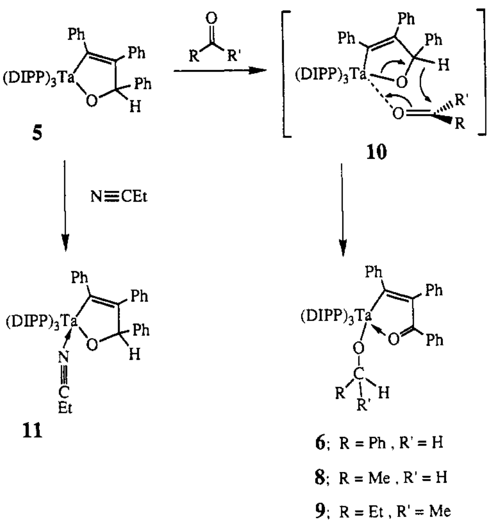
To implicate further a hydride transfer from C(80), as well as to eliminate exogenous sources of hydrogen, the reaction of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (**1**) with benzaldehyde-α-d (PhDC=O) was undertaken. Red crystals of compound **6**-d_2 were isolated from the reaction of **1** with 2 equiv of PhCD=O in a manner analogous to that used for **6** (Scheme I). Compound **6**-d_2 is formulated as $(DIPP)_3(PhCD_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ from its spectral data. Thus, the NMR spectra of **6**-d_2 are identical with those of **6** except that the δ 5.19 singlet in the ^1H NMR spectrum is absent (OCD_2Ph) and the δ 76.1 signal in the ^{13}C NMR spectrum (OCD_2Ph) is broadened into the base line and unobserved.

The final evidence for this hydride transfer is obtained from the reaction of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (**1**) with 1 equiv of benzaldehyde-α-d to produce $(DIPP)_3Ta(CPh{=}CPhCD(Ph)O)$ (**5**-d) in situ. An excess of unlabeled benzaldehyde is then added to this solution, which, after appropriate workup, provides red crystals of the product **6**-d (Scheme I). Compound **6**-d is assigned by its NMR spectra, which are identical with those of **6** except for a ^1H resonance that appears as a broad signal at δ 5.18 and is integrated for 1 H (OC*H*DPh) and a δ 75.7 triplet in the broad-band-decoupled $^{13}C\{^1H\}$ NMR spectrum (OCHDPh) resulting from coupling to one deuterium. These data establish **6**-d as the "crossed-Cannizzaro" type product $(DIPP)_3(PhCHDO)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$, resulting from a selective deuterium transfer that provides this complex as the only product. A summary of these reactions is presented in Scheme I.

Compound **5** reacts in other crossed-Cannizzaro modes as seen in its reaction with acetaldehyde or 2-butanone (Scheme II). Thus, $(DIPP)_3Ta(CPh{=}CPhCH(Ph)O)$ reacts with CH_3CHO and $CH_3CH_2COCH_3$ to provide red crystals of compounds **8** and **9**, respectively, in moderate yields. The spectroscopic and analytical data allow us to formulate unequivocally these crossed-Cannizzaro products as $(DIPP)_3(CH_3CH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (**8**) and $(DIPP)_3(CH_3CH_2(CH_3)CHO)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (**9**) (Scheme II).

Scheme II

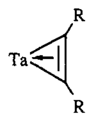
DIPP = 2,6 - diisopropylphenoxide



In the MPV/Oppenauer reactions, the coordinations of the ketone to be reduced and the new ketone formed after hydride transfer, both in an η^1 mode, have been implicated as in reaction 1.[22] In more fully establishing the intermediacy of proposed structure **10** (Scheme II) in the reactions that we observe, we note that compound **5** exhibits the Lewis acidic behavior required for the formation of such adducts. Thus, the reaction of $(DIPP)_3Ta(CPh{=}CPhCH(Ph)O)$ (**5**) with $EtC{\equiv}N$ (ca. 3 equiv) forms the η^1-propionitrile adduct $(DIPP)_3(\eta^1\text{-}EtCN)Ta(CPh{=}CPhCH(Ph)O)$ (**11**). This compound is not observed to undergo a hydrogen transfer to the nitrile; however, the facile formation of complex **11** clearly establishes the electrophilic nature of **5**.

Discussion

The reactivity of compounds **1** and **2** toward aldehydes indicates that an alkyne ligand may exhibit chemistry resulting from its formal anionic behavior when coordinated to d^2 early transition metals that exhibit low oxidation potentials. The observed Cannizzaro-type reaction is one manifestation of this behavior, in which C_{alkyne} of the "metallacyclopropene" acts formally as a base and attacks the carbonyl carbon. This reactivity, along with the spectroscopic data, indicates that the most significant valence bond representation for the coordinated alkyne is probably



Structural evidence for this formulation has been obtained

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[21] (a) Similar values for $\nu(C{=}O)$ are reported in acetophenone and benzophenone complexes of the tantalum(V) halides $TaX_5(O{=}CR_2)$.[21b] (b) Gill, M. S.; Ahuja, H. S.; Rao, G. S. *J. Less-Common Met.* **1970**, *21*, 447.

[22] This proposal originated with Meerwein.[7] An η^2-aldehyde intermediate is highly unlikely in the aluminum-catalyzed reaction and in compound **10** in this tantalum system, since in both cases the metal is a d^0 center.

in this compound and in other early-transition-metal–alkyne complexes.[15,16]

A possible electrocyclic mechanism for this disproportionation reaction is presented in Scheme II.[23] The first step, which is described above as the nucleophilic attack on the carbonyl,[24] is simply the reductive coupling of the aldehyde and coordinated acetylene. This step has been documented in other transition-metal–alkyne systems and is consistent with the observed ketone couplings to provide compounds **3** and **4**. The tantalum(V) center of **5** is still sufficiently electrophilic that it most likely induces a second molecule of benzaldehyde to coordinate through the oxygen in an η^1 fashion as postulated in structure **10** (Scheme II). From this η^1-OCRR′ compound, the observed hydride transfer is consistent with a six-electron electrocyclic process to provide compounds **6**–**9**.

The Lewis acidity and the "oxophilicity" of the tantalum center may in fact constitute significant driving forces in this hydride-transfer reaction. Since the η^1-OCRR′ intermediates postulated in **10** probably contain loosely bound aldehydes or ketones, and since the ketone end of the "chelates" in compounds **6**–**9** is no doubt more tightly bound to the metal than the η^1-OCRR′ ligand is in **10**, then the tantalum center can probably maximize strong interactions with oxygen donors by forming metallacyclic complexes **6**–**9**.

The new benzyl alkoxide ligand in **6** is situated trans to the new η^1-ketone of the metallacycle, although the first-formed product from the proposed six-membered transition state is predicted to be cis. (Strong evidence for a cyclic transition state has been obtained in the aluminum systems.[5b,d]) Therefore, the structure of **6** suggests that the molecule displays no "memory" of the reaction when crystallized from solution; i.e. the structure does not appear to be that of a kinetic product with the expected cis O(40) and O(50) ligands (Scheme II). Instead, isolated **6** appears to reflect the thermodynamic product in which these ligands have isomerized presumably to a more sterically feasible configuration. This presumed rearrangement places the bulky DIPP ligands in a *mer* configuration, rather than in the more crowded *fac* arrangement predicted in the kinetic product. What is not known is whether such an isomerization takes place from a 5-coordinate intermediate resulting from the dissociation of the η^1-ketone end of the metallacycle or from the 6-coordinate product.

Complexes **8** and **9** are the result of highly selective "mixed"- or "crossed"-Cannizzaro reactions in which a different aldehyde or ketone is involved in the disproportionation. The distinctive difference between the classical Cannizzaro reaction[25] and this organo-transition-metal version is that the simple or formal oxidation of the first 1 equiv of aldehyde is replaced by a new, irreversible carbon–carbon bond-forming process. Finally, we note that its reaction proceeds under conditions considerably different from those for the classical Cannizzaro one, which usually requires a concentrated (50% aqueous) base solution and days for the reaction to proceed to completion.[11,12]

This unique reactivity demonstrates the difference between alkoxide-supported early transition metals, which are still very electrophilic, and the bis(cyclopentadienyl)-supported alkyne complexes of the group 4 metals,[19] which, although they readily metallacyclize with ketones and aldehydes, are not reported to reduce a second molecule of these substrates to form an alkoxide. These reactions may be synthetically applicable for carbon–carbon bond formations in the synthesis of new carbonyl compounds, given the variety of unsaturated substrates that may coordinate to the d^2 "(π-donor)$_3$Ta" fragment,[23c,d,26] and may thereby complement the utility of base-catalyzed condensations[27] in this regard.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere either by standard Schlenk techniques[28] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under N_2 by standard techniques[29] and transferred to the drybox without exposure to air. In all preparations, DIPP = 2,6-diisopropylphenoxide.

Starting Materials. Tantalum(V) chloride (resublimed) was purchased from Alfa and used as received. Diphenylacetylene, benzophenone, acetophenone, benzaldehyde, acetaldehyde, and 2-butanone were purchased from Aldrich, and 1-(trimethylsilyl)-1-propyne was obtained from Farchan Laboratories. Acetophenone, benzaldehyde, acetaldehyde, 2-butanone, and 1-(trimethylsilyl)-1-propyne were passed down a short (6–7-cm) column of activated alumina prior to use. Diphenylacetylene and benzophenone were used as received. Benzaldehyde-α-d was purchased from MSD Isotopes and used without further purification.

$Li(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)\cdot OEt_2$. The lithium phenoxide salt $Li(O\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2)$ (LiDIPP) was prepared by adding equimolar n-butyllithium to a pentane solution of $HO\text{-}2,6\text{-}C_6H_3\text{-}i\text{-}Pr_2$ at 0 °C and warming the reaction mixture to room temperature and stirring overnight. This solution was then stripped to dryness to provide ether-free LiDIPP. The highly crystalline monoetherate LiDIPP·OEt$_2$ was obtained by dissolving LiDIPP in diethyl ether, followed by ether removal to provide the etherate in an overall 90% isolated yield. ^{1}H NMR (C_6D_6): δ 7.12–6.77 (A_2B multiplet, 3 H, H_{aryl}), 3.48 (spt, 2 H, $CHMe_2$), 2.86 (q, 4 H, $O(CH_2CH_3)_2$), 1.29 (d, 12 H, $CHMe_2$), 0.68 (t, 6 H, $O(CH_2CH_3)_2$).

$Ta(DIPP)_3Cl_2\cdot OEt_2$. To a solution of 12.01 g (33.53 mmol) of $TaCl_5$ in 250 mL of benzene and 40 mL of diethyl ether was added 25.85 g (100.1 mmol) of solid LiDIPP·OEt$_2$. The mixture was stirred at room temperature for 24 h, over which time a white

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[23] (a) We have specifically not indicated an axial or equatorial site preference for the alkoxide vs vinyl portions of the metallacyclic ring in the presumed trigonal-bipyramidal structure **5**,[23b] since the complications of the chelate ring as well as the steric influence of the bulky alkoxide ligands can dramatically affect such questions. On the basis of related structures, it is assumed that the metallacyclic structure constrains the α-atoms of the ring to occupy one axial and one equatorial site of a TBP.[10,23c,d] We note two related structures of the general formula Ta(π-donor)$_4$R have been reported $Ta(O\text{-}2,6\text{-}C_6H_3Me_2)_4(CH_3)$[23e] and $Ta(NMe_2)_4(CMe_3)$,[23f] both of which display an approximate *square-pyramidal* geometry with the alkyl group in the apical position. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; pp 310–338. (c) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1986**, 1203. (d) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Kobriger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffey, B. D.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 6068 (e) Chamberlain, L. R.; Rothwell, I. P.; Folting, K.; Huffman, J. C. *J. Chem. Soc., Dalton Trans.* **1987**, 155. (f) Chisholm, M. H.; Tan, L.-S.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 4879.

[24] (a) Nucleophilic attack on carbonyl functionalities by early-transition-metal alkyls, when coordinated by π-donor ancillary ligands (e.g. $(RO)_3TiR$, $(RO)_3ZrR$, and $(R_2N)_3TiR$), is an extremely useful methodology in organic synthesis.[24b] (b) Weidmann, B.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 31.

[25] (a) The mechanism of aqueous base-induced disproportionation of aldehydes has been clearly elucidated.[25b] (b) Swain, C. G.; Powell, A. L.; Sheppard, W. A.; Morgan, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 3576.

[26] (a) Steffey, B. D.; Chesnut, R. W.; Kerschner, J. L.; Pellechia, P. J.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1989**, *111*, 378. (b) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162. (c) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 448. (d) Ballard, K. R.; Gardiner, I. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 2159.

[27] March, J. *Advanced Organic Chemistry*; Wiley: New York, 1985; pp 829–845.

[28] Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

[29] Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

precipitate formed and the solution color changed to yellow. After the reaction mixture was filtered through Celite, the solvent was removed from the filtrate in vacuo to provide a yellow oil. When this oil was triturated with pentane, a yellow solid formed immediately. The solvent was again removed in vacuo to provide a yellow solid. The solid was collected, washed with pentane, and dried in vacuo to provide 20.03 g (23.35 mmol, 70%) of $Ta(DIPP)_3Cl_2\cdot OEt_2$. Additional crops of product (up to 84% total yield) may be obtained by concentrating and cooling the filtrate. This product is sufficiently pure for further reactions but can be recrystallized from diethyl ether/pentane at −40 °C. ^1H NMR ($CDCl_3$): δ 7.09–6.89 (m, 9 H, H_{aryl}), 4.28 (br, 4 H, OCH_2CH_3), 3.78 (br, 6 H, $CHMe_2$), 1.37 (t, 6 H, OCH_2CH_3), 1.07 (br, 36 H, $CHMe_2$). ^{13}C NMR ($CDCl_3$): δ 155.2 (br, C_{ipso}), 139.7 (C_o), 123.5 (coincident C_m and C_p), 66.8 (OCH_2CH_3), 26.0 ($CHMe_2$), 24.5 ($CHMe_2$), 12.2 (OCH_2CH_3). IR: 1580 w, 1356 m, 1322 s, 1245 s, 1180 br s, 1140 m, 1094 s, 1052 m, 1044 m, 1010 m, 983 m, 927 m, 895 s, 871 s, 821 w, 790 s, 762 m, 742 s, 704 s, 670 w. Anal. Calcd for $C_{40}Cl_2H_{61}O_4Ta$: C, 56.01; H, 7.17. Found: C, 56.11; H, 7.31. The non-etherate of this molecule has been used previously.[23e]

Physical Measurements. ^1H (250 MHz) and ^{13}C (62.9 MHz) NMR spectra were recorded at probe temperature on a Bruker WM-250 spectrometer in C_6D_6 or $CDCl_3$ solvent. Chemical shifts were referenced to protio solvent impurities (δ 7.15, C_6D_6; δ 7.24, $CDCl_3$) and solvent ^{13}C resonances (δ 128.0, C_6D_6; δ 77.0, $CDCl_3$) and are reported in ppm downfield of Me_4Si. Assignments of ^{13}C resonances were assisted by attached proton tests or off-resonance-decoupled spectra. Infrared spectra (reported in cm^{-1}) were recorded as Nujol mulls between 4000 and 600 cm^{-1} with use of a Perkin-Elmer 1310 spectrometer and were not assigned but used as fingerprints (w = weak, m = medium, s = strong intensities; sh = shoulder, br = broad, v = very). All microanalytical samples were handled under nitrogen and were combusted with WO_3 (Desert Analytics, Tucson, AZ).

Preparations. $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1). To a solution of 3.06 g (3.57 mmol) of $Ta(DIPP)_3Cl_2\cdot OEt_2$ in 40 mL of diethyl ether were added 1.08 g (6.06 mmol) of diphenylacetylene and 2.02 mL of 0.6% Na/Hg amalgam (7.2 mmol). This mixture was stirred at room temperature overnight (ca. 16 h), over which time the solution developed an orange color. After the reaction mixture was filtered through Celite, the solvent was removed from the filtrate in vacuo to provide an orange oil. This oil was dissolved in pentane, and when the solution was cooled to −40 °C, pale yellow crystals of impure product formed. The crystals were filtered off and dried in vacuo, and excess diphenylacetylene was removed by sublimation (5×10^{-5} Torr, room temperature). The product that remained was sufficiently pure for further reactions but could be recrystallized from pentane at −40 °C. From 2.32 g of impure product that was isolated in this manner, 1.80 g (2.02 mmol, 57%) of recrystallized compound was obtained. ^1H NMR ($CDCl_3$): δ 7.37–7.13 (m, 19 H, H_{aryl} and $C_2(C_6H_5)_2$), 3.57 (spt, 6 H, $CHMe_2$), 1.21 (d, 36 H, $CHMe_2$). ^{13}C NMR ($CDCl_3$): δ 216.2 (C_{alkyne}), 157.4 (C_{ipso}, DIPP), 141.5 (C_{ipso}, C_6H_5), 137.6 (C_o, DIPP), 128.9, 128.0 (C_o and C_m, C_6H_5), 127.6 (C_p, C_6H_5), 123.1 (C_m, DIPP), 122.7 (C_p, DIPP), 27.1 ($CHMe_2$), 23.3 ($CHMe_2$) IR: 1580 br w, 1428 s, 1358 m, 1320 s, 1248 s, 1194 s, 1103 m, 1098 sh, 1052 w, 1038 m, 1022 w, 930 sh, 915 sh, 890 s, 870 m, 800 sh, 786 m, 760 w, 742 s, 697 s. Anal. Calcd for $C_{50}H_{61}O_3Ta$: C, 67.40; H, 6.90. Found: C, 67.69; H, 7.01.

$(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$ (2). To a solution of 1.0 g (1.12 mmol) of $Ta(DIPP)_3Cl_2.OEt_2$ in 20 mL of diethyl ether was added 0.34 mL (2.32 mmol) of $Me_3SiC{\equiv}CMe$ and 1.00 mL of 0.5% Na/Hg amalgam (2.3 mmol). The solution was stirred at room temperature overnight (ca. 24 h). The resulting mixture was filtered through Celite, and all volatiles were removed from the filtrate in vacuo to provide the product as a yellow oil. This oil was pure by ^1H and ^{13}C NMR spectroscopy and was used without further purification in the following preparations. Since this compound has not been induced to crystallize, no analyses were attempted. ^1H NMR (C_6D_6): δ 7.09–6.90 (m, 9 H, H_{aryl}), 3.46 (spt, 6 H, $CHMe_2$), 2.54 (s, 3 H, $Me_3SiC{\equiv}CMe$), 1.17 (d, 36 H, $CHMe_2$), −0.005 (s, 9 H, $Me_3SiC{\equiv}CMe$). ^{13}C NMR (C_6D_6): δ 226.0 (C_{alkyne}), 224.4 (C'_{alkyne}), 158.2 (C_{ipso}), 137.7 (C_o), 124.5 (C_m), 123.1 (C_p), 27.3 ($CHMe_2$), 24.6 ($CH_3C{\equiv}CSiMe_3$), 23.8 ($CHMe_2$), 0.5 ($CH_3C{\equiv}CSiMe_3$). IR: 1574 br, 1558 br, 1430 s, 1323 s, 1245 s, 1186 s, 1105 m, 1091 sh, 1038 m, 1022 m, 917 sh, 892 s, 870 m, 837 s, 786 m, 743 s, 700 m.

$(DIPP)_3Ta(CPh{=}CPhCMe(Ph)O)$ (3). Acetophenone (0.10 mL, 0.86 mmol) was added to a −40 °C solution of 0.50 g (0.56 mmol) of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1) in 20 mL of diethyl ether. The solution was stirred at room temperature for 24 h, over which time its color lightened to pale yellow. All volatiles were then removed in vacuo to provide an oil. This oil was dissolved in pentane (ca. 5 mL), and when the solution was cooled to −40 °C, a pale yellow, crystalline product was obtained. The crystals were collected, washed with a minimum volume of cold (ca. −30 °C) pentane, and dried in vacuo; yield 0.52 g (0.51 mmol, 92%). Analytically pure samples were obtained by recrystallization from Et_2O/pentane solution at −40 °C. ^1H NMR (C_6D_6): δ 7.52–7.48 and 7.05–6.47 (m, 24 H, H_{aryl} and $C_{\alpha,\beta,\gamma}C_6H_5$), 3.76 (spt, 6 H, $CHMe_2$), 1.84 (s, 3 H, $C_\gamma Me$), 1.23 (d, 18 H, $CHMe_2$), 1.15 (d, 18 H, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 199.9 (C_α), 175.3 (C_β), 157.1 (C_{ipso}, DIPP), 147.1, 144.5, 140.1 (C_{ipso}, $C_{\alpha,\beta,\gamma}C_6H_5$), 138.5 ($C_o$, DIPP), 129.5, 128.3, 127.5, 127.3, 126.9, 126.8, 126.7, 124.5 (C_o, C_m, C_p; $C_{\alpha,\beta,\gamma}C_6H_5$), 123.7 ($C_m$, DIPP), 123.6 ($C_p$, DIPP), 96.5 ($C_\gamma$), 27.9 ($C_\gamma Me$), 27.5 ($CHMe_2$), 24.3, 24.1 ($CHMe_2$). One ^{13}C resonance for $C_{\alpha,\beta,\gamma}C_6H_5$ has not been located. IR: 1580 br w, 1535 br w, 1320 s, 1246 s, 1175 br s, 1095 s, 1059 m, 1036 m, 945 m, 930 w, 896 s, 872 m, 800 w, 786 m, 767 m, 741 s, 705 m, 690 s, 674 m, 630 m. Anal. Calcd for $C_{58}H_{69}O_4Ta$: C, 68.90; H, 6.88. Found: C, 69.14; H, 7.12.

$(DIPP)_3Ta(C(SiMe_3){=}CMeCPh_2O)$ (4). A 1.07-g (1.30-mmol) quantity of $(DIPP)_3Ta(Me_3SiC{\equiv}CMe)$ (2) was dissolved in 10 mL of diethyl ether, and a slight excess of benzophenone (0.26 g, 1.40 mmol) was added to the solution. An immediate color change from yellow to red-orange was observed upon $Ph_2C{=}O$ addition, and within 15 min the solution color had changed back to yellow. The solution was stirred at room temperature for 24 h, over which time the product was observed to precipitate as a white solid. This solid was filtered off, washed with cold (ca. −30 °C) pentane, and dried in vacuo; yield 0.61 g (0.60 mmol, 52%). Analytically pure samples were obtained by recrystallization from Et_2O/pentane solution at −40 °C. ^1H NMR (C_6D_6): δ 7.28–6.95 (m, 19 H, H_{aryl} (DIPP) and $C_\gamma C_6H_5$), 3.49 (spt, 6 H, $CHMe_2$), 2.21 (s, 3 H, $C_\beta Me$), 1.09 (d, 36 H, $CHMe_2$), 0.13 (s, 9 H, $SiMe_3$). ^{13}C NMR (C_6D_6): δ 207.5 (C_α), 174.3 (C_β), 157.0 (C_{ipso}, DIPP), 147.5 (C_{ipso}, C_6H_5), 138.3 (C_o, DIPP), 128.3, 128.2, 126.9 (C_o, C_p, C_m; C_6H_5), 123.9, 123.8 (C_p and C_m, DIPP), 109.8 (C_γ), 27.7 ($CHMe_2$), 24.8 ($C_\beta Me$), 24.4 ($CHMe_2$), 2.1 ($SiMe_3$). IR: 1580 w, 1532 w, 1312 br m, 1248 m, 1236 m, 1175 s, 1105 m, 1095 m, 1087 m, 1036 m, 1022 w, 982 w, 960 w, 915 m, 898 s, 886 m, 843 m, 825 w, 788 w, 772 m–w, 742 s, 692 m, 638 w. Anal. Calcd for $C_{55}H_{73}SiO_4Ta$: C, 65.59; H, 7.30. Found: C, 65.00; H, 7.28.

$(DIPP)_3Ta(CPh{=}CPhCH(Ph)O)$ (5). To a −40 °C solution of 0.70 g (0.78 mmol) of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1) in 20 mL of diethyl ether was added exactly 1 equiv (0.079 mL, 0.78 mmol) of benzaldehyde. After the mixture was stirred for ca. 16 h at room temperature, the solvent was removed in vacuo to provide a yellow oil. The oil was dissolved in a minimum of diethyl ether, the volume of this ether solution was approximately tripled by adding acetonitrile, and when the Et_2O/MeCN solution was cooled to −40 °C, the product was obtained as a pale yellow solid. The crystals were collected, washed with a minimum volume of cold (ca. −30 °C) acetonitrile, and dried in vacuo; yield 0.54 g (0.54 mmol, 68%). Recrystallizing the compound from Et_2O/MeCN at −40 °C provided analytically pure samples of **5**. ^1H NMR ($CDCl_3$): δ 7.31 (s, 1 H, $C_\gamma HPh$), 7.20–6.54 (m, 24 H, H_{aryl}(DIPP) and $C_{\alpha,\beta,\gamma}C_6H_5$), 3.49 (spt, 6 H, $CHMe_2$), 1.13 (d, 18 H, $CHMe_2$), 1.04 (d, 18 H, $CHMe_2$). ^{13}C NMR ($CDCl_3$): δ 202.8 (C_α), 164.3 (C_β), 156.6 (C_{ipso}, DIPP), 145.9, 141.5, 138.6 (C_{ipso}, $C_{\alpha,\beta,\gamma}C_6H_5$), 138.2 ($C_o$, DIPP), 128.7, 128.0, 127.8, 127.6, 127.5, 127.4, 127.0, 126.5, 124.3 (C_o, C_m, C_p; $C_{\alpha,\beta,\gamma}C_6H_5$), 123.1 (br; coincident C_m and C_p, DIPP), 95.7 (C_γ), 27.3 ($CHMe_2$), 23.9, 23.8 ($CHMe_2$). IR: 1585 br w, 1429 s, 1359 m, 1321 s, 1248 br s, 1182, br s, 1102 m, 1094 m, 1060 w, 1037 m, 1005 m, 915 sh, 897 s, 872 m, 833 w, 800 w, 786 m, 747 w, 741 s, 691 s, 653 m, 615 w. Anal. Calcd for $C_{57}H_{67}O_4Ta$: C, 68.66; H, 6.77. Found: C, 68.58; H, 7.00.

$(DIPP)_3(PhCH_2O)Ta(\eta^2\text{-}CPh{=}CPhCPh{=}O)$ (6). To a −40 °C solution of 0.51 g (0.57 mmol) of $(DIPP)_3Ta(PhC{\equiv}CPh)$ (1)

in 20 mL of diethyl ether was added 0.11 mL (1.1 mmol) of benzaldehyde. An immediate color change from pale yellow to orange-red was observed. The solution was stirred at room temperature for 24 h, after which time the solvent was removed in vacuo to provide a red oil. The oil was dissolved in a minimum volume of pentane, and when the solution was cooled to −40 °C, red crystals were isolated. These crystals were collected, washed with a minimum volume of cold (ca. −30 °C) pentane, and dried in vacuo; yield 0.39 g (0.36 mmol, 62%, 2 crops). Analytically pure samples were obtained by recrystallization from Et$_2$O/pentane solution at −40 °C. ^{1}H NMR (CDCl$_3$): δ 7.61–6.65 (m, 29 H, H$_{\text{aryl}}$ (DIPP), $C_{\alpha,\beta,\gamma}C_6H_5$, and OCH$_2$*Ph*), 5.19 (s, 2 H, OC*H*$_2$Ph), 3.87 (spt, 2 H, C*H*Me$_2$), 3.56 (spt, 4 H, C*H*Me$_2$), 1.02, 0.83, 0.79 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 245.5 (s, C$_\gamma$), 204.7 (s, C$_\alpha$), 157.2, 156.5 (s, C$_{\text{ipso}}$ (DIPP)), 147.6, 147.0, 137.6, 135.3 (s, C$_{\text{ipso}}$ ($C_{\alpha,\beta,\gamma}C_6H_5$ and OCH$_2$*C*$_6$H$_5$), 139.6, 138.2 (s, C$_o$, DIPP), 134.6, 132.4, 130.4, 128.1, 128.0, 127.7, 127.4, 127.3, 127.2, 127.0, 126.1, 125.6 (d; C$_o$, C$_m$, C$_p$, $C_{\alpha,\beta,\gamma}C_6H_5$ and OCH$_2$*C*$_6$H$_5$), 123.1, 122.8 (d, C$_m$, DIPP), 121.4, 120.8 (d, C$_p$, DIPP), 76.1 (t, O*C*H$_2$C$_6$H$_5$), 26.2, 24.3 (d, *C*HMe$_2$), 24.1, 23.9 (q, CH*Me*$_2$). One CH*Me*$_2$ ^{13}C signal was apparently obscured, and C$_\beta$ could not be located. IR: 1591 m, 1578 m, 1530 m, 1422 s, 1322 s, 1290 m, 1265 m, 1250 s, 1195 s, 1107 m, 1096 m, 1082 m, 1050 s, 1019 m, 942 m, 935 w, 904 m, 888 s, 869 s, 828 w, 796 w, 783 m, 741 s, 725 m, 694 s, 665 m, 635 m. Anal. Calcd for $C_{64}H_{73}O_5Ta$: C, 69.68; H, 6.67. Found: C, 70.00; H, 6.85.

(DIPP)$_3$(PhCD$_2$O)Ta(η^2-CPh=CPhCPh=O) (6-d_2). The reaction of (DIPP)$_3$Ta(PhC≡CPh) (1; 0.37 g, 0.41 mmol) with benzaldehyde-α-*d* (0.94 g, 0.88 mmol), by the procedure used to prepare **6**, provided 0.35 g (0.32 mmol, 76%) of red crystals of compound **6**-d_2. All NMR resonances remained unaffected except for the following. ^{1}H NMR: δ 5.19 resonance is no longer observed. ^{13}C NMR: δ 76.1 resonance (O*C*D$_2$Ph) is sufficiently broadened to not be observed.

(DIPP)$_3$(PhCHDO)Ta(η^2-CPh=CPhCPh=O) (6-*d*). To a −40 °C solution of 0.21 g (0.24 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 20 mL of diethyl ether was added 0.025 g (0.23 mmol) of benzaldehyde-α-*d*. After the mixture was stirred at room temperature for 1 h, 0.030 mL (0.30 mmol) of unlabeled benzaldehyde was added to the solution. This mixture was stirred overnight (ca. 24 h), over which time the solution had turned orange-red. The solvent was removed in vacuo to provide an orange-red oil. The oil was dissolved in pentane (ca. 3 mL), and when the solution was cooled to −40 °C, an orange-red solid was obtained. The solid was filtered off, washed with cold pentane, and dried in vacuo; yield 0.15 g (0.14 mmol, 57%). Partial ^{1}H NMR (CDCl$_3$): δ 5.18 (broad s, 1 H, OC*H*DPh); $^1J_{\text{HD}}$ is not resolved at 250 MHz. Partial ^{13}C NMR (CDCl$_3$): δ 75.7 (O*C*HDPh, triplet in broad-band-decoupled spectrum). All other resonances remained unaffected.

(DIPP)$_3$(PhCH$_2$O)Ta(η^2-C(SiMe$_3$)=CMeCPh=O) (7). A 0.87-g (1.05-mmol) amount of (DIPP)$_3$Ta(Me$_3$SiC≡CMe) (**2**) was dissolved in 10 mL of diethyl ether. Benzaldehyde (0.24 mL, 2.32 mmol) was added to this solution, and the mixture was stirred at room temperature overnight (ca. 24 h), over which time the solution color changed to red-orange. All volatiles were removed in vacuo to provide a red-orange oil. The oil was dissolved in pentane (ca. 8 mL), and when this solution was cooled to −40 °C, a red-orange crystalline product was obtained. The crystals were filtered off, washed with cold pentane, and dried in vacuo; yield 0.41 g (0.40 mmol, 34%). Analytically pure samples were obtained by recrystallization from pentane at −40 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.67–7.64 and 7.28–6.84 (m, 19 H, H$_{\text{aryl}}$ (DIPP), C$_\gamma$C$_6$H$_5$, and OCH$_2$*Ph*), 6.30 (s, 2 H, OC*H*$_2$Ph), 3.91 (spt, 2 H, C*H*Me$_2$), 3.55 (spt, 4 H, C*H*Me$_2$), 1.92 (s, 3 H, C$_\beta$*Me*), 1.17, 1.15, 0.95 (d, 12 H each, CH*Me*$_2$), 0.37 (s, 9 H, Si*Me*$_3$). ^{13}C NMR (C$_6$D$_6$): δ 257.3 (C$_\gamma$), 205.9 (C$_\alpha$), 156.9, 156.6 (C$_{\text{ipso}}$, DIPP), 150.8 (C$_\beta$), 140.6 (C$_{\text{ipso}}$, OCH$_2$*C*$_6$H$_5$), 139.7, 138.7 (C$_o$, DIPP), 137.2 (C$_{\text{ipso}}$, C$_\gamma$*C*$_6$H$_5$), 132.6, 129.1, 128.7 (C$_p$, C$_o$, C$_m$; C$_\gamma$*C*$_6$H$_5$), 128.5, 127.8, 126.5 (C$_o$, C$_p$, C$_m$; OCH$_2$*C*$_6$H$_5$), 123.7, 123.3 (C$_p$, DIPP), 122.5, 121.8, (C$_m$, DIPP), 77.5 (O*C*H$_2$C$_6$H$_5$), 26.6, 25.1 (*C*HMe$_2$), 24.6, 24.2 (CH*Me*$_2$), 23.9 (C$_\beta$*Me*), 2.8 (SiMe$_3$). One CH*Me*$_2$ ^{13}C signal was apparently obscured and could not be located. IR: 1591 m–w, 1538 m, 1430 s, 1320 s, 1300 w, 1270 m, 1250 s, 1190 s, 1122 m, 1103 w, 1086 m, 1053 s, 1038 m, 1020 w, 992 w, 978 m, 916 w, 903 m, 890 m, 882 m, 858 s, 842 s, 826 m, 785 m, 751 m–w, 742 s, 706 m, 691 m, 628 w, 608 w. Anal. Calcd for $C_{56}H_{75}O_5SiTa$: C, 64.84; H, 7.29. Found: C, 64.88; H, 7.34.

(DIPP)$_3$(CH$_3$CH$_2$O)Ta(η^2-CPh=CPhCPh=O) (8). To a −40 °C solution of 0.49 g (0.55 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 20 mL of diethyl ether was added 0.058 mL (0.57 mmol) of benzaldehyde. After this mixture was stirred at room temperature for 3 h, 0.070 mL (1.2 mmol) of acetaldehyde was added to the solution. An immediate color change from pale yellow to red occurred. The solution was stirred overnight (ca. 24 h), after which time the solvent was removed under reduced pressure to produce a red oil. The oil was dissolved in a minimum volume of pentane, and when the solution was cooled to −40 °C, red crystals of product were obtained. The crystals were collected, washed with a minimum volume of cold (ca. −30 °C) pentane, and dried in vacuo; yield 0.24 g (0.23 mmol, 42%). Recrystallizing this compound from Et$_2$O/pentane at −40 °C provided analytically pure samples. ^{1}H NMR (CDCl$_3$): δ 7.60–6.57 (m, 24 H, H$_{\text{aryl}}$ (DIPP) and $C_{\alpha,\beta,\gamma}C_6H_5$), 4.22 (q, 2 H, OC*H*$_2CH_3$), 3.90 (spt, 2 H, C*H*Me$_2$), 3.56 (spt, 4 H, C*H*Me$_2$), 1.07 (t, 3 H, OCH$_2$C*H*$_3$), 1.07, 0.93, 0.90 (d, 12 H each, CH*Me*$_2$). ^{13}C NMR (CDCl$_3$): δ 244.8 (C$_\gamma$), 203.6 (C$_\alpha$), 157.3, 156.6 (C$_{\text{ipso}}$, DIPP), 147.1, 147.05, 137.7, 135.4 (C$_\beta$ and C$_{\text{ipso}}$, $C_{\alpha,\beta,\gamma}C_6H_5$), 139.4, 138.1 (C$_o$, DIPP), 134.4, 132.3, 130.4, 128.0, 127.7, 127.0, 126.9, 126.2 (C$_o$, C$_m$, C$_p$; $C_{\alpha,\beta,\gamma}C_6H_5$), 123.0, 122.7 (C$_m$, DIPP), 121.7, 121.2 (C$_p$, DIPP), 70.5 (O*C*H$_2CH_3$), 26.3, 26.2 (*C*HMe$_2$), 24.2, 24.1, 23.8 (CH*Me*$_2$), 17.8 (OCH$_2$*C*H$_3$). One resonance (for C$_o$, C$_m$, C$_p$; $C_{\alpha,\beta,\gamma}C_6H_5$) has not been located. IR: 1585 br w, 1531 m, 1415 sh, 1322 br, s, 1308 m, 1290 m, 1250 br s, 1195 br s, 1154 w, 1119 s, 1105 s, 1072 s, 1038 m, 1020 m, 945 m, 930 m, 907 m, 888 s, 869 s, 828 m, 788 m, 743 s, 723 m, 691 s, 677 w, 670 m, 639 w, 618 w. Anal. Calcd for $C_{59}H_{71}O_5Ta$: C, 68.06; H, 6.87. Found: C, 68.04; H, 6.95.

(DIPP)$_3$(CH$_3$CH$_2$(CH$_3$)CHO)Ta(η^2-CPh=CPhCPh=O) (9). To a −40 °C solution of 0.75 g (0.84 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 20 mL of diethyl ether was added 0.085 mL (0.84 mmol) of benzaldehyde. After this mixture was stirred at room temperature for 3 h, 0.15 mL (1.7 mmol) of 2-butanone was added. An immediate color change from pale yellow to red occurred. The solution was stirred overnight (ca. 24 h), after which time the solvent was removed under reduced pressure to produce a red oil. The oil was dissolved in a minimum volume of diethyl ether. Acetonitrile (ca. 10 mL) was added to this solution, and when this mixture was cooled to +5 °C, the product was obtained as a sticky red solid. The air-stable product was collected, washed with a minimum volume of cold acetonitrile, and dried in vacuo; yield 0.27 g (0.25 mmol, 30%). This compound was recrystallized from Et$_2$O/MeCN at +5 °C. ^{1}H NMR (C$_6$D$_6$): δ 7.64–7.60 and 7.23–6.72 (m, 24 H, H$_{\text{aryl}}$ (DIPP) and $C_{\alpha,\beta,\gamma}C_6H_5$), 4.65 (m, 1 H, OC*H*(Me)Et), 4.21 (broad, 2 H, C*H*Me$_2$), 3.84 (spt, 4 H, C*H*Me$_2$), 1.54, 1.39 (m, 1 H each, C*H*$_2$CH$_3$), 1.31, 1.29 (d, 6 H each, CH*Me*$_2$), 1.14, 1.09 (d, 12 H each, CH*Me*$_2$), 1.06 (d, 3 H, CHC*H*$_3$), 0.59 (t, 3 H, CH$_2$C*H*$_3$). The resonances at δ 1.39 and 1.06 were partially obscured by other signals. ^{13}C NMR (C$_6$D$_6$): δ 245.1 (s, C$_\gamma$), 203.9 (s, C$_\alpha$), 157.8, 157.2 (s, C$_{\text{ipso}}$, DIPP), 148.6, 148.2, 138.3, 136.2 (s, C$_{\text{ipso}}$ ($C_{\alpha,\beta,\gamma}C_6H_5$) and C$_\beta$), 139.8, 138.5 (s, C$_o$, DIPP), 134.2, 132.4, 131.0, 128.1, 127.7, 127.4, 127.3, 126.6, 126.5 (d; C$_o$, C$_m$, C$_p$; $C_{\alpha,\beta,\gamma}C_6H_5$), 123.7, 123.6 (d, C$_m$, DIPP), 122.1, 121.7 (d, C$_p$, DIPP), 84.3 (d, O*C*H), 31.9 (t, *C*H$_2$CH$_3$), 26.7, 26.4 (d, *C*HMe$_2$), 24.8, 24.7, 24.6 (q, CH*Me*$_2$), 21.4 (q, CH*C*H$_3$), 10.5 (q, CH$_2$*C*H$_3$). IR: 1591 m, 1579 m, 1531 br m, 1430 sh, 1320 s, 1286 w, 1245 s, 1190 s, 1095 s, 1036 s, 997 m, 945 m, 930 m, 900 w, 881 s, 861 s, 836 w, 798 m, 783 w, 741 s, 694 s, 680 w, 665 w, 630 m, 615 w. Anal. Calcd for $C_{61}H_{75}O_5Ta$: C, 68.52; H, 7.07. Found: C, 67.87; H, 7.18.

(DIPP)$_3$(η^1-EtCN)$\overline{\textbf{Ta(CPh=CPhCH(Ph)O}}$) (11). To a −40 °C solution of 0.61 g (0.68 mmol) of (DIPP)$_3$Ta(PhC≡CPh) (1) in 20 mL of diethyl ether was added 0.072 mL (0.71 mmol) of benzaldehyde. After this mixture was stirred at room temperature for 45 min, 0.15 mL (2.1 mmol) of propionitrile was added to the solution. The solution was stirred overnight (ca. 24 h), and the solvent was removed under reduced pressure to produce a pale orange oil. The oil was dissolved in a minimum volume of pentane, and when the solution was cooled to −40 °C, the product formed as a yellow solid. This solid was filtered off, washed with cold pentane, and dried in vacuo; yield 0.51 g (0.54 mmol, 79%). Recrystallizing this compound from Et$_2$O/pentane at −40 °C provided analytically pure samples. ^{1}H NMR (C$_6$D$_6$): δ 7.43 (s, 1 H, C$_\gamma$*H*Ph), 7.32–7.29 and 7.05–6.58 (m, 24 H, H$_{\text{aryl}}$ (DIPP) and

$C_{\alpha,\beta,\gamma}C_6H_5$), 3.76 (spt, 6 H, C*H*Me$_2$), 1.22 (d, 18 H, CH*Me*$_2$), 1.15 (d, 18 H, CH*Me*$_2$), 0.40 (t, 3 H, C*H*$_3$CH$_2$CN). The resonances for the CH$_3$C*H*$_2$CN protons are partially obscured by the CH*Me*$_2$ doublets. ^{13}C NMR (C_6D_6): 202.7 (C_α), 165.1 (C_β), 157.0 (C_{ipso}, DIPP), 146.8, 142.3, 139.2 (C_{ipso}, $C_{\alpha,\beta,\gamma}C_6H_5$), 138.6 ($C_o$, DIPP), 129.2, 128.3, 128.2, 127.9, 127.7, 127.5, 126.9, 124.9 (C_o, C_m, C_p; $C_{\alpha,\beta,\gamma}C_6H_5$), 123.7 ($C_p$), 123.6 ($C_m$, DIPP), 95.9 ($C_\gamma$), 27.5 (*C*HMe$_2$), 24.3, 24.2 (CH*Me*$_2$), 10.3 (CH$_3$*C*H$_2$CN), 10.0 (*C*H$_3CH_2$CN). One resonance (for C_o, C_m, C_p; $C_{\alpha,\beta,\gamma}C_6H_5$) and the Et*C*N signal have not been observed. IR: 2275 w, 1580 br w, 1429 s, 1322 s, 1245 s, 1182 s, 1105 m, 1093 m, 1061 m, 1038 m, 1008 m, 914 sh, 897 s, 888 sh, 870 m, 831 w, 800 w, 788 m, 772 w, 742 s, 690 s, 643 m. Anal. Calcd for $C_{60}H_{72}NO_4Ta$: C, 68.49; H, 6.90; N, 1.33. Found: C, 68.75; H, 7.51; N, 1.15.

X-ray Structural Determination of (DIPP)$_3$(PhCH$_2$O)-Ta(η^2-CPh═CPhCPh═O) (6). A red irregular block crystal of 6, grown from a toluene/pentane solution at 5 °C, was mounted in air on a glass fiber in a random orientation and examined on a Syntex-Nicolet P2$_1$ diffractometer using Mo Kα radiation monochromatized with graphite (λ = 0.71037 Å). Table I summarizes the crystal data and structure refinement results. Two check reflections were measured every 98 data reflections; the intensities of these standards remained constant within experimental error throughout the data collection. No decay correction was applied. Lorentz and polarization corrections were applied. An empirical absorption correction based on a series of ψ scans was applied to the data. Relative transmission coefficients ranged from 0.777 to 0.999 with an average value of 0.904. The structure was solved by using the Patterson heavy-atom method and refined in full-matrix least squares. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The largest peak in the final difference Fourier map was 0.58 (5) e/Å^3. All calculations were performed on a VAX computer using SDP/VAX.

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Supplementary Material Available: Full details of the structure solution, tables of bond distances and angles, atomic positional and thermal parameters, and least-squares planes and dihedral angles, and a figure showing an additional ORTEP view of (DIPP)$_3$(PhCH$_2$O)Ta(η^2-CPh═CPhCPh═O) (6) (19 pages); a listing of observed and calculated structure factors (26 pages). Ordering information is given on any current masthead page.

Communications

Stereoselective Formation of (C_s-Symmetrical π-allyl)palladium Complexes

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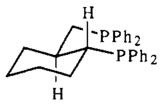
Summary: The complexation of C_s-symmetrical allyl moieties derived from 1-acetoxy-2-propene, 1-acetoxy-1,3-diphenyl-2-propene, and 1-acetoxy-2-cyclohexene to chiral (diphosphine)palladium species containing either of the two new chiral diphosphine ligands **1** and **2** proceeds in up to 88:12 stereoselectivity. Palladium complexes of diphosphine ligands **1** and **2** are unique in that they form *trans*-decalin-like structures possessing C_s symmetry local to the metal.

Interest in the enantioselective metal-catalyzed nucleophilic substitution of allylic acetates has grown in response to the need for new efficient methods for asymmetric carbon–carbon and carbon–heteroatom bond formation.[1] Although good procedures have been developed for the catalytic enantioselective alkylation of unsymmetrical allylic acetates,[2] the situation for C_s-symmetrical substrates is less developed.[3] A promising approach for these latter cases has been developed by Faller for (π-allyl)molybdenum complexes, yet it suffers from low catalytic activity.[4] This unique method relies on the selective formation of one (π-allyl)metal complex followed by the electronic, through-bond activation of one end of the coordinated allyl toward nucleophilic addition.[5] We have undertaken the development of conceptually similar, but potentially catalytically more active, chiral (diphosphine)palladium catalysts. We communicate here our efforts at meeting the first requirement for successful application of these catalysts, the ability to induce the stereoselective coordination of C_s-symmetrical π-allyls to chiral (diphosphine)palladium species. Utilizing the two new chiral diphosphine ligands 1 and 2 to enforce a local C_s-symmetrical environment near the palladium leads to the formation of complexes with selectivities up to 88:12. These (π-allyl)palladium complexes are the first reported examples of isolated stereoisomers of C_s-symmetrical allyls. This ability to control C_s-symmetrical π-allyl complexation enables further studies concerning the asymmetric alkyl-



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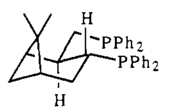

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