is similar (9–11°) to values observed in other related complexes containing the $C_5H_4Bu^t$ ring.[26] (4) Fe–C(ring) distances are all close to 2.10 Å and do not reveal that the Fe has been displaced from the ring center. The C(ring)–C(ring) distances are all close to 1.41 Å, where significance cannot be attached to the differences in length as they lie in the range of standard deviations. (5) If the cyclopentadienyl ring is regarded as occupying 3 coordination sites, a near-octahedral arrangement of ligands is observed with P–Fe–I (97.0 (1)°), P–Fe–CO (91.4 (2)°), and I–Fe–CO (89.4 (2)°) angles being close to 90°.

Conclusion. The use of the bulkier substituent on the cyclopentadienyl ligand has resulted in the detection of preferred conformers for all of the new complexes $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(L)I]$. The preferred conformation with L near trans to the ring substituent is readily confirmed by NMR spectroscopy (P–H and P–C coupling constants, nOe spectra), molecular mechanics calculations, and an X-ray crystal structure determination (L = PPh_3). The effect is clearly related to steric effects associated with both the ligand set and the ring substituent.

(26) (a) Howie, R. A.; McQuillan, G. P.; Thompson, D. W.; Lock, G. A. *J. Organomet. Chem.* **1986**, *303*, 213. (b) Howie, R. A.; McQuillan, G. P.; Thompson, D. W. *J. Organomet. Chem.* **1984**, *268*, 149. (c) Erker, G.; Muhlenberndt, T.; Benn, R.; Rubinska, A.; Tsay, Y.-H.; Krüger, C. *Angew Chem., Int. Ed. Engl.* **1985**, *24*, 321.

Acknowledgment. We wish to thank the University of the Witwatersrand and the FRD for financial support, Dr. S. Dobson and C. Allen for assistance with the crystal structure determination, and S. Heiss for running NMR spectra. We also thank a reviewer and Prof. J. W. Faller for helpful comments.

Registry No. $[Fe_2(CO)_9]$, 15321-51-4; $C_5H_5Bu^+$, 41539-65-5; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2]_2$, 95765-96-1; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)_2I]$, 122189-23-5; $P(OCH_2)_3CCH_3$, 1449-91-8; $P(OMe)_3$, 121-45-9; $P(O\text{-}o\text{-}CH_3C_6H_4)_3$, 2622-08-4; $P[OCH_2C(CH_3)_3]_3$, 14540-52-4; $P[OCH(CH_3)_2]_3$, 116-17-6; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(OCH_2)_3CCH_3)I]$, 122189-24-6; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(OMe)_3)I]$, 122189-25-7; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P[OCH(CH_3)_2]_3)I]$, 122189-26-8; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P[OCH_2C(CH_3)_3]_3)I]$, 122189-27-9; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)]$, 122189-28-0; $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(P(O\text{-}o\text{-}CH_3C_6H_4)_3)I]$, 122212-53-7; $[(\eta^5\text{-}C_5H_4D)Fe(CO)(PMePh_2)I]$, 122189-29-1; $PMePh_2$, 1486-28-8; $[(\eta^5\text{-}C_5H_4D)Fe(CO)_2I]$, 122189-30-4; $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$, 12154-95-9.

Supplementary Material Available: Tables listing details of the force field in the molecular mechanics calculations, parameters of nonbonded interactions (Buckingham potential), and fractional coordinates ($\times 10^4$) and common isotropic temperature factors ($Å^2 \times 10^3$) for hydrogen atoms, anisotropic temperature factors ($Å^2 \times 10^3$) for non-hydrogen atoms, and bond lengths (Å) and angles (deg) for $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$ (6 pages); a structure factor table for $[(\eta^5\text{-}C_5H_4Bu^t)Fe(CO)(PPh_3)I]$ (28 pages). Ordering information is given on any current masthead page.

Contribution from the Carl S. Marvel Laboratories of Chemistry, Department of Chemistry, University of Arizona, Tucson, Arizona 85721

Preparation and Properties of Tantalum Imido Complexes and Their Reactions with Alkynes. Coordination Control through Multiple Metal–Ligand Bonding

Yuan-Wei Chao, Pamela A. Wexler, and David E. Wigley*

Received April 5, 1989

The reaction of $TaCl_5$ with $Me_3SiNHAr$ (NAr = N-2,6-C_6H_3-*i*-Pr_2), in the presence of donor solvents, provides the imido complexes $Ta(NAr)Cl_3L_2$ (L = tetrahydrofuran (THF, **1**), $^1/_2$ dimethoxyethane (dme, **2**), pyridine (py, **3**), tetrahydrothiophene (THT, **4**)) in high yield. These adducts are shown to exhibit a *cis,mer* geometry. The reaction of these compounds with 1 equiv of lithium alkoxides produces the imido alkoxide metathesis products $Ta(NAr)(OR)Cl_2L_2$ (**5**, OR = O-2,6-C_6H_3-*i*-Pr_2 (DIPP), L = THF; **6**, OR = DIPP, L = $^1/_2$ dme; **7**, OR = DIPP, L = py; **8**, OR = O-2,6-$C_6H_3Me_2$ (DMP), L = py). The reaction of Me_3SiNEt_2 with $TaCl_5$ in toluene/diethyl ether gives a high yield of dimeric $[Ta(NEt_2)_2Cl_3]_2$ (**9**), from which the imido amide $Ta(NAr)(NEt_2)Cl_2(py)_2$ (**11**) can be prepared by the reaction of **9** with LiNHAr. Dimeric **9** can be converted easily to the monomeric adduct $Ta(NEt_2)_2Cl_3(py)$ (**10**) upon reaction with pyridine. When these tantalum imides are reduced in the presence of alkynes, either alkyne adducts or metallacyclopentadienes are isolated. Thus, the compounds $(EtC{\equiv}CEt)Ta(NAr)Cl(py)_2$ (**12**), $(PhC{\equiv}CPh)Ta(NAr)Cl(py)_2$ (**13**), $(Me_3SiC{\equiv}CMe)Ta(NAr)Cl(py)_2$ (**14**), $(C(CMe_3){=}CHCH{=}C(CMe_3))Ta(NAr)Cl(py)_2$ (**15**), $(EtC{\equiv}CEt)Ta(NAr)(DIPP)(py)_2$ (**16**), and $(PrC{\equiv}CPr)Ta(NAr)(DIPP)(py)_2$ (**17**) are prepared from the two-electron reduction of either $Ta(NAr)Cl_3(py)_2$ (**3**) or $Ta(NAr)(DIPP)Cl_2(py)_2$ (**7**) in the presence of the appropriate alkyne. Crystals of the imido alkoxide Ta(N-2,6-C_6H_3-*i*-Pr_2)(O-2,6-$C_6H_3Me_2$)$Cl_2(C_5H_5N)_2$ (**8**) belong to the monoclinic space group $P2_1/c$ with a = 9.547 (2) Å, b = 17.089 (3) Å, c = 19.135 (3) Å, β = 91.86 (1)°, and V = 3120.4 $Å^3$ for Z = 4 with ρ(calcd) = 1.50 g/cm^3. The X-ray structural study on **8** reveals a six-coordinate structure with cis-phenylimide and alkoxide ligands and mutually trans-chloride ligands. The imido linkage features a Ta–N bond of 1.769 (5) Å and Ta–N–C_{ipso} angle of 179.1 (5)°, suggesting a Ta–N bond order between 2 and 3 and emphasizing the additional π donation of the nitrogen lone pair to an empty metal orbital. The phenoxide ligand is characterized by a Ta–O distance of 1.905 (5) Å and Ta–O–C_{ipso} angle of 145.1 (5)°.

Introduction

The control of reactivity at a transition-metal center by steric manipulations is effected typically by varying the size of its anionic ligands[1] or controlling the "cone angle" of its neutral ligands,[2] which often promote coordinative unsaturation by ligand dissociation.[3] A more extreme method of steric control uses a formal dianionic ligand—occupying a single coordination site—in the place of two monoanions. Therefore, by the introduction of metal–ligand multiple bonding at this site,[4] the coordination number of the metal is decreased while its oxidation state is sustained. This approach has been used in designing olefin metathesis catalysts,[5] in developing reactive compounds for alkane

(1) See, for example: (a) Kruse, W. *J. Organomet. Chem.* **1972**, *42*, C39. (b) Giering, W. P.; Rosenblum, M. *J. Organomet. Chem.* **1970**, *25*, C71. (c) Listemann, M. L.; Schrock, R. R.; Dewan, J. C.; Kolodziej, R. M. *Inorg. Chem.* **1988**, *27*, 264. (d) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Little, D.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2266.

(2) See, for example: (a) Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313. (b) Bartik, T.; Himmler, T.; Schulte, H.-G.; Seevogel, K. *J. Organomet. Chem.* **1984**, *272*, 29. (c) Tolman, C. A.; Seidel, W. C.; Gosser, L. W. *Organometallics* **1983**, *2*, 1391.

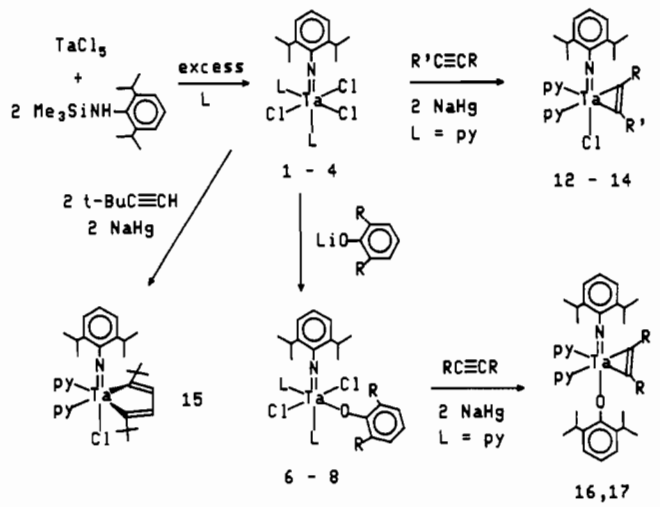
(3) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

(4) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley-Interscience: New York, 1988.

(5) (a) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423. (b) Schaverien, C. J.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2771. (c) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373.

0020-1669/89/1328-3860$01.50/0

Scheme I

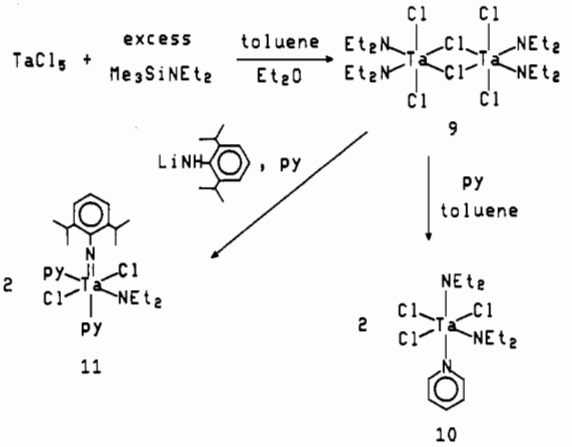


1, L = THF
2, L = 1/2 dme
3, L = py
4, L = THT
6, R = i-Pr, L = 1/2 dme
7, R = i-Pr, L = py
8, R = Me, L = py
12, R = R' = Et
13, R = R' = Ph
14, R = Me_3Si, R' = Me
16, R = Et
17, R = n-Pr

activation,[6] and in providing living catalysts for the ring-opening polymerization of norbornene.[7]

Alkyne cyclization by reduced tantalum compounds provides Ta(III) arene species[8] that can engage in intramolecular C–H activations,[9] although these reactions are quite susceptible to steric effects.[10] Such a system may be suitable for *inter*molecular C–H activations if metal–ligand multiple bonding—increasingly important in alkane activation[6,11]—can be incorporated as a part of steric control. We have begun, therefore, to explore the use of dianionic, monodentate ligands as a means of providing steric unsaturation and multiple metal–ligand bonding to certain tantalum complexes. Since the bulky phenoxide ligand O-2,6-C_6H_3-*i*-Pr_2 is useful in promoting alkyne cyclization chemistry and in stabilizing Ta(III) arenes,[8] we turned to its phenylimide analogue N-2,6-C_6H_3-*i*-Pr_2 (NAr) to fulfill this purpose. The considerable general interest in organoimide compounds[12] lies in their study as models for such industrially relevant processes as the ammoxidation of propylene,[13] nitrile reduction,[14] and the Haber

Scheme II



process[15] and in their potential importance as π donors in olefin metathesis chemistry.[16] In this paper we report the first stages of this study, namely the synthesis and characterization of new tantalum phenylimido complexes and an examination of their reactivity toward alkynes.

Results

The transformations observed in this study are summarized in Schemes I and II. Spectroscopic data for the compounds are given in the Experimental Section. Abbreviations used in this paper are listed in ref 17.

Tantalum Imido Halide Complexes. When a toluene slurry of $TaCl_5$ is stirred with 2 equiv of $Me_3SiNHAr$ dissolved in a donor solvent, smooth reaction occurs to provide solutions from which the imido complexes $Ta(NAr)Cl_3L_2$ can be isolated in high yield (Scheme I; **1**, L = THF; **2**, L = $^1/_2$ dme; **3**, L = py; **4**, L = THT).[17] The generality of this reaction is seen in the facile formation of N-, O-, and S-donor adducts and in the fact that the order of addition of the reagents ($Me_3SiNHAr$ or L) does not appear critical to its success. These reactions are described in eq 1, which is supported by the isolation of 1.02 mmol of H_2NAr

$$TaCl_5 + 2Me_3SiNHAr \xrightarrow[-2Me_3SiCl]{} \text{“}Ta(NHAr)_2Cl_3\text{”} \xrightarrow{L} Ta(NAr)Cl_3L_2 + H_2NAr \quad (1)$$

from the reaction of 1.06 mmol of $TaCl_5$ (in benzene) with 2.12 mmol of $Me_3SiNHAr$ (in pyridine).[18] When the reaction is restricted to 1 equiv of $Me_3SiNHAr$ in pyridine (3 equiv per Ta), the pyridinium salt $[C_5H_5NH]Cl$ is not isolated and simply a lower yield of $Ta(NAr)Cl_3(py)_2$ (**3**) is formed. Thus, a formal analogy between imido (RN^{2-}) and alkylidene (RHC^{2-}) ligands is clear when these structures are compared to those of the related *cis,mer*-$Ta(=CHCMe_3)Cl_3L_2$ complexes[19] and is affirmed by the α-hydrogen abstraction[20] analogy in their preparation.

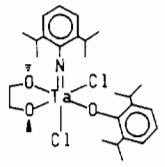
The solvent ligands in $Ta(NAr)Cl_3L_2$ (**1**–**4**) are inequivalent by ^1H and ^{13}C NMR spectroscopy, which requires the *cis,mer* configuration depicted in Scheme I. For example, the pyridine derivative clearly exhibits two resonances each for the pyridine $(CH)_{ortho}$, $(CH)_{meta}$, and $(CH)_{para}$ by NMR analysis. These structures are analogous to a number of six-coordinate tantalum

(6) (a) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 8729. (b) Cummins, C. C.; Baxter, S. M.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 8731.
(7) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169.
(8) Bruck, M. A.; Copenhaver, A. S.; Wigley, D. E. *J. Am. Chem. Soc.* **1987**, *109*, 6525.
(9) Ballard, K. R.; Gardiner, I. M.; Wigley, D. E. *J. Am. Chem. Soc.* **1989**, *111*, 2159.
(10) Strickler, J. R.; Wexler, P. A.; Wigley, D. E. *Organometallics* **1988**, *7*, 2067.
(11) (a) McDade, C.; Green, J. C.; Bercaw, J. E. *Organometallics* **1982**, *1*, 1629. (b) Bulls, A. R.; Schaefer, W. P.; Serfas, M.; Bercaw, J. E. *Organometallics* **1987**, *6*, 1219. (c) Cook, B. R.; Reinert, T. J.; Suslick, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 7281. (d) Chamberlain, L. R.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 1502.
(12) For reviews, see ref 12a,b. For tantalum imides, see ref 12c. (a) Chisholm, M. H.; Rothwell, I. P. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 2, pp 161–188. (b) Nugent, W. A.; Haymore, B. L. *Coord. Chem. Rev.* **1980**, *31*, 123. (c) Hubert-Pfalzgraf, L. G.; Postel, M.; Riess, J. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon Press: Oxford, England, 1987; Vol. 3, pp 585–697.
(13) (a) Maatta, E. A.; Du, Y. *J. Am. Chem. Soc.* **1988**, *110*, 8249. (b) Burrington, J. D.; Grasselli, R. K. *J. Catal.* **1979**, *59*, 79. (c) Nugent, W. A.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 1759. (d) Grasselli, R. K.; Burrington, J. D. *Adv. Catal.* **1981**, *30*, 133. (e) Burrington, J. D.; Katisek, C. T.; Grasselli, R. K. *J. Catal.* **1983**, *81*, 489. (f) Burrington, J. D.; Kartisek, C. T.; Grasselli, R. K. *J. Catal.* **1984**, *87*, 363.
(14) (a) Bakir, M.; Fanwick, P. E.; Walton, R. A. *Inorg. Chem.* **1988**, *27*, 2017. (b) Rhodes, L. F.; Venanzi, L. M. *Inorg. Chem.* **1987**, *26*, 2692. (c) Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1979**, *101*, 7255. (d) Han, S. H.; Geoffroy, G. L. *Polyhedron* **1988**, *7*, 2331.
(15) Fjare, D. E.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1981**, *103*, 1572.
(16) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1982**, *104*, 448.
(17) Abbreviations used in this paper: THF = tetrahydrofuran, dme = 1,2-dimethoxyethane, py = pyridine, THT = tetrahydrothiophene, DIPP = O-2,6-C_6H_3-*i*-Pr_2, DMP = O-2,6-$C_6H_3Me_2$, NAr = N-2,6-C_6H_3-*i*-Pr_2.
(18) For related reactions, see: (a) Jones, T. C.; Nielson, A. J.; Rickard, C. E. F. *J. Chem. Soc., Chem. Commun.* **1984**, 205. (b) Bates, P. A.; Nielson, A. J.; Waters, J. M. *Polyhedron* **1985**, *4*, 1391.
(19) Rupprecht, G. A.; Messerle, L. W.; Fellmann, J. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 6236.
(20) (a) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98. (b) Mayer, J. M.; Curtis, C. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2651.

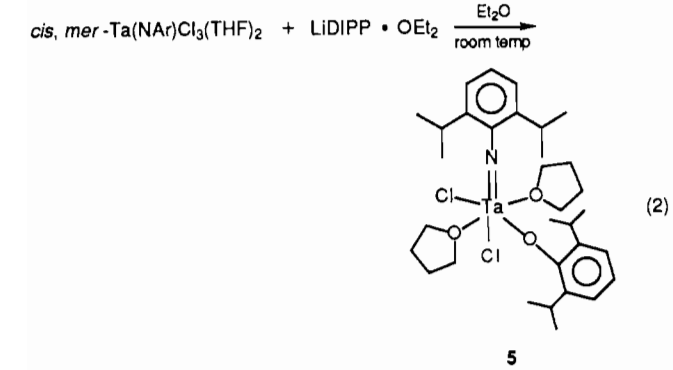
and niobium complexes of the general formula $RN{=}MX_3L_2$ (M = Nb, Ta), including $Ta(=NPh)Cl_3L_2$ (L_2 = $(THF)_2$,[21] $(PMe_3)_2$,[21] $(THF)(PEt_3)$[22]), $[M(=NPh)Cl_3(SMe_2)]_2(\mu\text{-}Cl)_2$,[23,24] $[(NbCl_4(NCMe))_2(\mu\text{-}NCMe{=}CMeN)]^{2-}$,[25] and $[TaCl_3(THF)_2]_2(\mu\text{-}NCMe{=}CMeN)$.[26] This structural comparison extends to formal μ-hydrazido(4-) compounds such as $[TaCl_3(THF)(PBz_3)]_2(\mu\text{-}N_2)$ (Bz = CH_2Ph).[27]

Tantalum Imido Alkoxide Complexes. Metathesis of the chloride ligands in $Ta(NAr)Cl_3L_2$ can be effected with lithium alkoxide salts to provide a route to new imido alkoxide derivatives. Thus, $Ta(NAr)Cl_3L_2$ reacts smoothly with 1 equiv of LiDIPP·OEt_2 (DIPP = 2,6-diisopropylphenoxide) or LiDMP (DMP = 2,6-dimethylphenoxide) to form the complexes $Ta(NAr)(OR)Cl_2L_2$ in high yield (Scheme I; **6**, OR = DIPP and L = $^1/_2$ dme; **7**, OR = DIPP and L = py; **8**, OR = DMP and L = py).[17] ^1H and ^{13}C NMR data reveal inequivalent pyridine ligands in compounds **7** and **8**, which requires the phenoxide ligand to be oriented cis to the phenylimide as depicted in Scheme I and confirmed in the crystal structure determination of $Ta(NAr)(DMP)Cl_2(py)_2$ (**8**, vide infra). Since alkoxide ligands are better π donors than chlorides, it is perhaps not surprising that the DIPP and DMP ligands are oriented cis to the strong π-donor imide ligand in these d^0 structures.[28]

Inequivalent CH_3- groups in the dme adduct **6** (by ^1H and ^{13}C NMR spectroscopy) are constrained to be cis to each other and could imply either the trans-chloride structure presented in Scheme I, analogous to the case for the pyridine adducts, or an "all-cis" structure:



However, the all-cis structure shown here is ruled out for $Ta(NAr)(DIPP)Cl_2(dme)$ (**6**) on the basis of the simplicity of the $CHMe_2$ resonances in the ^1H and ^{13}C NMR spectra; only one type of $CHMe_2$ group *each* is observed for the NAr and DIPP ligands, and a more complex pattern is expected for an all-cis structure with no molecular plane of symmetry. However, ambiguity exists in the structure of the THF adduct $Ta(NAr)(DIPP)Cl_2(THF)_2$·OEt_2 (**5**), formed according to eq 2, as its



(2)

5

Table I. Crystallographic Data for $Ta(NAr)(DMP)Cl_2(py)_2$ (**8**)

chem formula: $C_{30}H_{36}Cl_2TaN_3O$	fw: 706.49
space group: $P2_1/c$ (No. 14)	T = 23 ± 1 °C
a = 9.547 (2) Å	λ = 0.71073 Å
b = 17.089 (3) Å	ρ_{calcd} = 1.50 g cm^{-3}
c = 19.135 (3) Å	μ = 36.8 cm^{-1}
β = 91.86 (1)°	transm coeff: 0.800–1.202
V = 3120.4 Å^3	R = 0.035
Z = 4	R_w = 0.040

Table II. Relevant Bond Distances (Å) for $Ta(NAr)(DMP)Cl_2(py)_2$ (**8**)

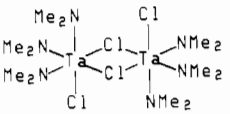
Ta–Cl(1)	2.391 (2)	Ta–N(3)	2.348 (6)
Ta–Cl(2)	2.401 (2)	Ta–N(4)	2.408 (6)
Ta–O(1)	1.905 (5)	O(1)–C(11)	1.377 (9)
Ta–N(2)	1.769 (5)	N(2)–C(21)	1.404 (8)

Table III. Selected Bond Angles (deg) for $Ta(NAr)(DMP)Cl_2(py)_2$ (**8**)

Cl(1)–Ta–Cl(2)	157.19 (8)	O(1)–Ta–N(2)	102.1 (2)
Cl(1)–Ta–O(1)	95.1 (2)	O(1)–Ta–N(3)	166.3 (2)
Cl(1)–Ta–N(2)	99.3 (2)	O(1)–Ta–N(4)	81.7 (2)
Cl(1)–Ta–N(3)	82.2 (1)	N(2)–Ta–N(3)	91.6 (2)
Cl(1)–Ta–N(4)	80.5 (1)	N(2)–Ta–N(4)	176.2 (2)
Cl(2)–Ta–O(1)	97.1 (1)	N(3)–Ta–N(4)	84.6 (2)
Cl(2)–Ta–N(2)	96.8 (2)	Ta–O(1)–C(11)	145.1 (5)
Cl(2)–Ta–N(3)	81.4 (2)	Ta–N(2)–C(21)	179.1 (5)
Cl(2)–Ta–N(4)	82.3 (1)		

spectroscopic data require *equivalent* THF ligands. If we constrain the alkoxide ligand to be cis to the imide in order to maximize the number of π interactions in this d^0 molecule (vide infra), then structure **5** shown in eq 2 is the only one consistent with all these data.

Tantalum Imido Amide Complexes. We were interested in preparing other $Ta(NAr)(\pi\text{-donor})X_2L_n$ compounds where the π donor was not restricted to an alkoxide and therefore have explored the use of dialkylamido ligands in this regard. Chisholm has reported the preparation of $[Ta(NMe_2)_3Cl_2]_2$ by the reaction of $Ta(NMe_2)_5$ with Me_3SiCl.[29] An X-ray crystallographic study of this molecule revealed the dimeric molecular structure[29]



We have found that the simple reaction of $TaCl_5$ with Me_3SiNEt_2 in toluene/diethyl ether provides an almost quantitative yield of the compound $[Ta(NEt_2)_2Cl_3]_2$ (**9**), which we formulate as a dimer on the basis of molecular weight measurements (Scheme II). From the equivalency of all the ethyl groups in the NEt_2 ligands, and the presumably related structure of $[Ta(NMe_2)_3Cl_2]_2$, we can propose the structure shown in Scheme II for compound **9**. Pyridine reacts quickly with solutions of **9** to disrupt the dimer and form the adduct $Ta(NEt_2)_2Cl_3(py)$ (**10**). The ^1H and ^{13}C NMR data for **10** reveal inequivalent amide ligands, which is consistent with the *cis,mer* conformation seen, for example, in $Ta(NMe_2)_2Cl_3(HNMe_2)$ in Chisholm's study.[29]

When $[Ta(NEt_2)_2Cl_3]_2$ (**9**) is dissolved in Et_2O and reacted with 1 equiv of LiNHAr, the solution slowly develops a yellow color and, upon the addition of pyridine, the compound $Ta(NAr)(NEt_2)Cl_2(py)_2$ (**11**) is isolated in high yield (Scheme II). This

(21) (a) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1982**, *104*, 3077. (b) Rocklage, S. M.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7808.
(22) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 223.
(23) Cotton, F. A.; Duraj, S. A.; Roth, W. J. *J. Am. Chem. Soc.* **1984**, *106*, 4749.
(24) Canich, J. A. M.; Cotton, F. A.; Duraj, S. A.; Roth, W. J. *Polyhedron* **1986**, *5*, 895.
(25) Finn, P. A.; Schaefer-King, M.; Kilty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220.
(26) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.
(27) Churchill, M. R.; Wasserman, H. J. *Inorg. Chem.* **1982**, *21*, 218.
(28) (a) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335. (b) In the case of π-acid ligands, the trans influence of the ligand seems to be more important then its π-bonding ability in determining which ligands are mutually cis;[28a] this has not been established for π donors.
(29) Chisholm, M. H.; Huffman, J. C.; Tan, L.-S. *Inorg. Chem.* **1981**, *20*, 1859.
(30) Bradley, D. C.; Hursthouse, M. B.; Abdul Malik, K. M.; Nielson, A. J.; Chota Vuru, G. B. *J. Chem. Soc., Dalton Trans.* **1984**, 1069.
(31) Nugent, W. A.; Harlow, R. L. *J. Chem. Soc., Chem. Commun.* **1978**, 579.
(32) Schrock, R. R.; Wesolek, M.; Liu, A. H.; Wallace, K. C.; Dewan, J. C. *Inorg. Chem.* **1988**, *27*, 2050.

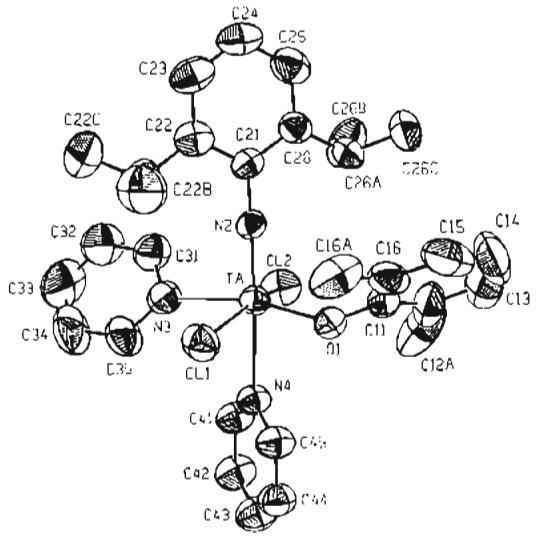


Figure 1. ORTEP drawing of $Ta(NAr)(DMP)Cl_2(py)_2$ (**8**; NAr = N-2,6-C_6H_3-*i*-Pr_2; DMP = O-2,6-$C_6H_3Me_2$).

reaction proceeds presumably via the intermediate $Ta(NHAr)(NEt_2)_2Cl_2$, which eliminates $HNEt_2$ readily to provide the product. By NMR spectroscopy, we propose the structure shown in Scheme II; thus, in **11** as in the other d^0 compounds **5**–**8**, the better π donor amide is cis to the phenylimide ligand.[28]

Structural Study of Ta(N-2,6-C_6H_3-*i*-Pr_2)(O-2,6-$C_6H_3Me_2$)-$Cl_2(C_5H_5N)_2$ (8). Yellow single crystals of **8** suitable for an X-ray analysis were grown from THF/pentane solution at −30 °C. A summary of the crystal data and the structural analysis is given in Table I; important bond distances are given in Table II and relevant angles in Table III.

Figure 1 presents the molecular structure of Ta(N-2,6-C_6H_3-*i*-Pr_2)(O-2,6-$C_6H_3Me_2$)$Cl_2(C_5H_5N)_2$ (**8**) and confirms the geometry predicted from the NMR data. The overall octahedral structure is distorted away from the N-2,6-C_6H_3-*i*-Pr_2 ligand: N(imido)–Ta–ligand(cis) angles average 97.5° and range from 91.6 (2)° for N(2)–Ta–N(3) to 102.1 (2)° for N(2)–Ta–O(1) (Table III). However, the steric bulk imposed by the imide ligand may not be responsible for this distortion, as a similar effect has been reported in the unsubstituted phenylimide complex $Ta(NPh)Cl_3(THF)(PEt_3)$,[22] in the dinuclear $[TaCl_3(THF)_2]_2(\mu$-NCMe=CMeN),[26] and in the μ-hydrazido(4−) complex $[TaCl_3(THF)(PBz_3)]_2(\mu$-$N_2)$,[27] all of which possess relatively uncongested coordination spheres. The Ta–O bond distance (1.905 (5) Å) of the alkoxide and the Ta–O–C_{ipso} angle (145.1 (5)°) do not indicate the considerable steric congestion at the metal which would induce large Ta–O–C_{ipso} angles.[10]

The salient feature of this structure is the linearity of the phenylimido linkage (Ta–N–C_{ipso} = 179.1 (5)°) and the short Ta–N(imido) bond (1.769 (5) Å). A comparison of this bond with those in other selected Ta–imido moieties is presented in Table IV. These data are consistent with a tantalum–nitrogen bond order somewhat greater than 2 and reflect the additional π donation of the nitrogen lone pair, i.e. formal bonding as shown here:

$$L_nTa{\equiv}NAr$$

Since the alkoxide ligand is oriented cis to the imide, this molecule can maximize the number of π interactions between these ligands and the d^0 metal, thereby imparting maximum stabilization of the nitrogen and oxygen pπ lone pairs.[33] The Ta(V) center in **8** can be considered to have an 18-valence-electron count if the arylimide is a four-electron (neutral) donor and the alkoxide a three-electron donor.[12b] The imide ligand, therefore, can be considered to π donate into both d_{xz} and d_{yz} metal orbitals. The metal d_{xy} is the remaining orbital capable of interacting in a π fashion with the alkoxide ligand:

This fact accounts for the cis orientation of the alkoxide,[33] as well as the relative orientation of the phenyl ring of the DMP ligand, since the oxygen pπ orbital *not* interacting with the DMP aromatic π system participates in $Ta(d_{xy})$–$O(p\pi)$ bonding.[34]

Pyridine ligands are trans to both imide and alkoxide ligands in this molecule; therefore, the Ta–N(py) bond lengths can be examined as an internal comparison of the trans influence[28] of these π-donor ligands. The greater structural trans effect of the stronger π-donor imido ligand is evident in the 0.06-Å difference in these bonds, as Ta–N(3)(trans to OR) = 2.348 (6) Å, while Ta–N(4)(trans to NAr) = 2.408 (6) Å. The much greater difference in trans influences of imide vs halide ligands is seen in the 0.20-Å difference in Ta–O(THF) bonds in the complex $[TaCl_3(THF)_2]_2(\mu$-NCMe=CMeN).[26]

One additional interesting feature of this structure is the almost perfect staggering of the phenylimide aromatic ring relative to the vertical planes containing the cis ligands. As seen in Figure 1, this phenyl ring is oriented so as to place the *o*-$CHMe_2$ groups between, not aligned with, the cis ligands. The dihedral angle between the phenylimide ring and the N(2)–N(3)–N(4)–O(1) plane is 45.5° and between the phenylimide and N(2)–Cl(1)–N(4)–Cl(2) plane is 45.4°. This orientation is most likely a manifestation of steric interactions and requires the loss of conjugation of the NAr aromatic π system with the imido nitrogen pπ orbital. With strong interactions between both nitrogen pπ orbitals and the metal d_{xz} and d_{yz} orbitals, the rotational barrier about N–C_{ipso} is lowered and the aromatic ring is free to minimize steric repulsions.

Reactions of Imido Complexes with Alkynes. The reactivity study of new imido compounds with alkynes was initiated by using the pyridine complex **3**, which, due to the high crystallinity generally exhibited by pyridine adducts, aided in the isolation and identification of the reaction products.

By reduction of $Ta(NAr)Cl_3(py)_2$ (**3**) with 2 equiv of NaHg in the presence of an excess of RC≡CR′, the yellow or orange complexes $(RC{\equiv}CR')Ta(NAr)Cl(py)_2$ (**12**, R = R′ = Et; **13**, R = R′ = Ph; **14**, R = Me_3Si, R′ = Me) are obtained (Scheme I). The symmetrical alkyne adducts **12** and **13** are characterized (^1H and ^{13}C NMR spectroscopy) by (i) equivalent ends of the alkyne ligand and (ii) one type of pyridine ligand. Furthermore, since the hydrolysis of compound **13** (1:9 v/v H_2O/acetone)

Table IV. Structural Data for Selected Imido Complexes of Tantalum[17]

compd	Ta–N, Å	Ta–N–R, deg	ref
$Ta(NAr)(DMP)Cl_2(py)_2$	1.769 (5)	179.1 (5)	this work
$[Ta(NPh)Cl_3(SMe_2)]_2$	1.747 (8)	176.4 (8)	24
$Ta(NPh)Cl_3(THF)(PEt_3)$	1.765 (5)	173.27 (40)	22
$[TaCl_3(THF)_2]_2(\mu$-NCMe=CMeN)	1.747 (7)	178.7 (9)	26
$[Ta(NCMe_3)(NHCMe_3)Cl_2$-$(NH_2CMe_3)]_2$	1.61 (3)	169 (2)	18a
$[Ta(NCMe_3)(OEt)Cl_2$-$(NH_2CMe_3)]_2$	1.70 (2)	167 (2)	18b
$Ta(NCMe_3)[N(SiMe_3)_2]_2Cl$	1.763 (6)	165.8 (6)	30
$Ta(NCMe_3)(NMe_2)_3$	1.77 (2)	180[a]	31
$[Ta(DIPP)_3(THF)]_2(\mu$-$N_2)$[b]	1.796 (5)	176.6 (6)	32
$[TaCl_3(THF)(P(CH_2Ph)_3)](\mu$-$N_2)$[b]	1.796 (5)	178.91 (40)	27

[a] Required by symmetry. [b] These formally μ-hydrazido(4−) (Ta=N—N=Ta) complexes are included for comparison. See ref 27 for a discussion of bonding in these compounds.

(33) (a) A similar argument has been made for octahedral group 6 complexes with metal dπ–ligand π conflicts.[33b] (b) Brower, D. C.; Templeton, J. L.; Mingos, D. M. P. *J. Am. Chem. Soc.* **1987**, *109*, 5203.

(34) Coffindaffer, T. W.; Rothwell, I. P.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2906.

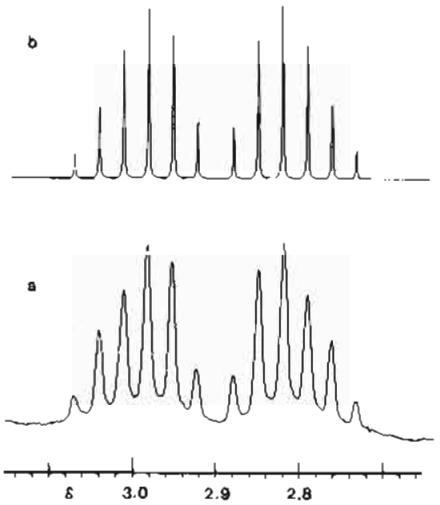


Figure 2. Partial ^{1}H NMR spectra of the EtC≡CEt methylene resonances in (EtC≡CEt)Ta(NAr)(DIPP)(py)$_2$ (**16**): (a) observed; (b) simulated.

produces *cis*-PhCH=CHPh in quantitative yield (^{1}H NMR spectroscopy), we consider the alkyne ligand in these complexes as substantially reduced. Structures **12**–**14**, presented in Scheme I, are in accord with these data. Rapid rotation of the alkyne on the NMR time scale is ruled out since such a process would equilibrate the diastereotopic methylene protons in (EtC≡CEt)Ta(NAr)Cl(py)$_2$ (**12**) and cause them to appear as a quartet as the ligand passed through a molecular plane of symmetry (vide infra). Compound **14**, (Me$_3$SiC≡CMe)Ta(NAr)Cl(py)$_2$, necessarily contains different acetylenic carbons as seen in the ^{13}C NMR spectrum but is almost certainly related structurally to compounds **12** and **13**. One enantiomer of **14** is depicted in Scheme I.

An interesting feature of this chemistry is the isolation of the metallacyclopentadiene complex (C(CMe$_3$)=CHCH=C-(CMe$_3$))Ta(NAr)Cl(py)$_2$ (**15**) from the reduction of the chloride Ta(NAr)Cl$_3$(py)$_2$ (**3**) in the presence of an excess of Me$_3$CC≡CH. When only 1 equiv of this alkyne is used, a lower yield of metallacycle **15** is isolated, along with a complex mixture of other products. These products may include a small amount of an alkyne adduct, analogous to compounds **12**–**14**, since the ^{1}H NMR spectra of these mixtures include a singlet at ca. δ 10.46 (Me$_3$CC≡C*H*), but this product could not be isolated. The α,α'-di-*tert*-butyl metallacycle structure assigned in Scheme I is based upon the gated decoupled ^{13}C NMR spectrum of **15**, in which the β-carbon of the metallacycle is split into a doublet ($J_{C_\beta H}$ = 153.7 Hz), and upon the hydrolysis of **15**, in which the diene (*E*,*E*)-Me$_3$CCH=CHCH=CHCMe$_3$ is observed by ^{1}H NMR spectroscopy.

The alkyne adducts (EtC≡CEt)Ta(NAr)(DIPP)(py)$_2$ (**16**) and (PrC≡CPr)Ta(NAr)(DIPP)(py)$_2$ (**17**) are prepared from the two-electron reduction of Ta(NAr)(DIPP)Cl$_2$(py)$_2$ (**7**) in the presence of 3-hexyne and 4-octyne, respectively. Since both ends of the coordinated alkyne in **16** and **17** are equivalent by ^{1}H and ^{13}C NMR spectroscopy, and since only one type of pyridine ligand is observed, the only consistent structure places the alkoxide ligand trans to the phenylimide (Scheme I). In this orientation, the imide nitrogen pπ and alkoxide oxygen pπ orbitals push the empty metal d_{xz} and d_{yz} levels very high in energy, leaving the filled d_{xy} orbital unperturbed to overlap with the alkyne $\pi_\parallel$* orbital (see Discussion).

With the alkyne effectively locked in this conformation, the methylene protons of coordinated CH$_3$CH$_2$C≡CCH$_2$CH$_3$ in **16** are diastereotopic and therefore exhibit the ABX$_3$ pattern as shown in Figure 2 by coupling to the methyl protons as well as to each other. Although one methylene proton environment is "endo" to NAr and the other type is "exo" to NAr, $^3J_{AX} = {}^3J_{BX}$ as demonstrated by the single triplet observed for the $-CH_3$ protons of the alkyne. This analysis is supported by the simulated spectrum as shown in Figure 2, where $^3J_{AX} = {}^3J_{BX}$ = 7.5 Hz and $^2J_{AB}$ = 15.0 Hz, giving the observed 12-line pattern.

Discussion

The structural analysis of the Ta(V) imido alkoxides (**6**–**8**) and of the Ta(III) alkyne complexes containing these ligands (**16** and **17**) is of interest with respect to the relative orientation of the π-donor ligands and the d^n configuration of the metal. Imido alkyne complexes are rather rare, known examples including the d^2 group 6 species Mo(*p*-NC$_6$H$_4$CH$_3$)(MeO$_2$CC≡CCO$_2$Me)(S$_2$CNEt$_2$)$_2$[35] and W(=NPh)(PhC≡CPh)Cl$_2$(PMe$_3$)$_2$[36] and the μ-hydrazido(4–) complex [W(PhC≡CPh)(dme)Cl$_2$]$_2$-(μ-N$_2$).[37] In all of these compounds, as in complexes **16** and **17**, the alkyne ligand is oriented cis to the imido functionality and the alkyne C–C axis is perpendicular to the metal–imide bond. In a qualitative orbital analysis of adducts **16** and **17**, the alkyne can be considered to lie in the equatorial plane of a trigonal bipyramid and bond to the ML$_4$ fragment, the orbitals of which have been described previously.[38] With the *z* axis chosen to lie along the Ta–NAr vector for simplicity, the alkyne $\pi_\parallel{}^b$ and $\pi_\parallel$* interactions with the metal center, shown as A and B, are

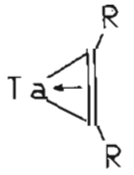
A B

straightforward.[3] In these formally d^2 complexes d_{xy} is filled, so interaction B ($d_{xy} \rightarrow \pi_\parallel$*) is essentially responsible for the perpendicular orientation of the alkyne C–C axis relative to Ta–NAr. The hydrolysis experiment, which suggests a metallacyclopropene contribution to the structure, lends support to the importance of interaction B.

The interactions of the alkyne $\pi_\perp{}^b$ and $\pi_\perp$* set with the metal are not as straightforward, since the imido nitrogen pπ orbitals participate as well. Realizing that three molecular orbitals result from each N–Ta–alkyne ($\pi_\perp$) interaction, we represent the nodal properties of the lowest energy orbital of each set of three for both N p_x–d_{xz}–$\pi_\perp{}^b$ (C) and N p_y–d_{yz}–$\pi_\perp$* (D). Two of the three MOs

C D

to which $\pi_\perp{}^b$ contributes will be filled: C, which is highly alkyne $\pi_\perp{}^b$ in character, and the next highest MO (not shown), which is mostly N 2p_x in character. Therefore, the alkyne can behave as a π donor from $\pi_\perp{}^b \rightarrow d_{xz}$, much like an imido or oxo ligand, and so perhaps is better represented as[39]



A similar interaction has been seen to affect the orientation of an alkyne ligand cis to a π donor oxo ligand in d^2 molybdenum

(35) Devore, D. D.; Maatta, E. A.; Takusagawa, F. *Inorg. Chim. Acta* **1986**, *112*, 87.
(36) Clark, G. R.; Nielson, A. J.; Rickard, C. E. F.; Ware, D. C. *J. Chem. Soc., Chem. Commun.* **1989**, 343.
(37) Churchill, M. R.; Li, Y.-J.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 4472.
(38) (a) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058. (b) Albright, T. A.; Hoffmann, R.; Thibeault, J. C.; Thorn, D. L. *J. Am. Chem. Soc.* **1979**, *101*, 3801. (c) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466.
(39) (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. *Inorg. Chem.* **1981**, *20*, 387.

complexes.[33,40] Thus, compounds **12–14** can be considered as 18-electron species since this π donation shown above is probably significant.[39]

Since the d_{yz} orbital of the ML_4 fragment becomes quite high in energy if L is a π-donor,[38a] and since the alkyne $\pi_\perp$* orbital is also high in energy relative to N $2p_y$ orbital D is largely localized on the nitrogen. This energy mismatch as well as the poor δ-symmetry (d_{yz}–$\pi_\perp$*) overlap combine to make this interaction of little importance to the binding of the alkyne.

Finally we note that in the d^2 rhenium(V) analogues of compounds **6–8**, e.g. $Re(p\text{-}NC_6H_4CH_3)(OEt)(S_2CNMe_2)_2$,[41] $Re(p\text{-}NC_6H_4CH_3)(RN{=}CHC_6H_4O)Cl_2(PPh_3)$,[42] and $Re(O)(OEt)Cl_2(py)_2$,[43] the relative orientation of the imido (or oxo) and alkoxide ligands is trans. The fact that the imido and alkoxide ligands in the alkyne complexes **16** and **17** are trans supports the above orbital analysis in terms of the formal d^2 assignment for these compounds.

Concluding Remarks

This simple entry into $Ta(NAr)X_3L_2$ compounds with use of the trimethylsilyl reagent $Me_3SiNHAr$ has provided a high-yield route to potential precursor molecules for a variety of mid-valent tantalum imides. Their utility has been demonstrated in the preparation of d^2 tantalum alkyne compounds, isolated as their pyridine adducts. We have observed the π bonding of the NAr, DIPP, and alkyne ligands and the metal oxidation state to be paramount in determining the isomerism in these compounds, as well as the relative orientation of the alkyne ligand at a given coordination site.

Our recent preparation of the tantalum(III) arene complexes $(\eta^6\text{-}C_6R_6)Ta(DIPP)_2Cl$[8] and their tantalum(II) analogues $(\eta^6\text{-}C_6R_6)Ta(DIPP)_2$[44] points to the potential synthesis of molecules of the type $(\eta^6\text{-}C_6R_6)Ta(=NR)(OR)$. These compounds would exhibit the same coordination number and geometry as the Ta(II) arenes mentioned above, but multiple metal–ligand bonding would maintain the higher Ta(III) oxidation state. To prepare molecules of this type by cyclization chemistry, the imido precursor will probably have to be an etherate or THF adduct, as the pyridine ligands (which are quite useful for the isolation of crystalline adducts) do not appear to be sufficiently labile to allow the competition of additional molecules of alkyne for their coordination sites.

Experimental Section

General Details. All experiments were performed under a nitrogen atmosphere by standard Schlenk techniques[45] or in a Vacuum Atmospheres HE-493 drybox at room temperature (unless otherwise indicated). Solvents were purified under N_2 by standard techniques[46] and transferred to the drybox without exposure to air. In all preparations, DIPP = 2,6-diisopropylphenoxide, DMP = 2,6-dimethylphenoxide, and NAr = (2,6-diisopropylphenyl)imide (Ar = 2,6-C_6H_3-*i*-Pr_2).[17]

Starting Materials. Tantalum(V) chloride (resublimed) was purchased from Alfa and used as received. Dimethoxyethane was distilled from sodium/benzophenone, and pyridine was predried over 4-Å molecular sieves and distilled before use. 2,6-Diisopropylaniline and tetrahydrothiophene were obtained from Aldrich and vacuum-distilled before use. Trimethylchlorosilane and (diethylamino)trimethylsilane were obtained from Petrarch and used as received. 3-Hexyne, 4-octyne, 1-(trimethylsilyl)-1-propyne, and 3,3-dimethyl-1-butyne were obtained from Farchan Laboratories and passed down a short (5-cm) column of activated alumina (at ca. −10 °C) prior to use. Deuterated NMR solvents were also passed down a short column of activated alumina before use. Diphenylacetylene was obtained from Aldrich and used as received.

Ligand Preparations. The lithium phenoxide salts Li(O-2,6-C_6H_3-*i*-Pr_2) and Li(O-2,6-$C_6H_3Me_2$) were prepared by adding equimolar *n*-butyllithium to a pentane solution of the appropriate phenol at 0 °C, allowing the reaction mixture to warm to room temperature and stirring it overnight, and filtering off the resulting lithium salt. A near-quantitative yield was obtained after washing the lithium phenoxide with pentane and drying the product in vacuo. For the diisopropylphenoxide salt, the highly crystalline monoetherate Li(O-2,6-C_6H_3-*i*-Pr_2)·OEt_2 was obtained by dissolving Li(O-2,6-C_6H_3-*i*-Pr_2) in diethyl ether, followed by ether removal to provide the etherate in an overall 90% isolated yield. Li(NH-2,6-C_6H_3-*i*-Pr_2) was prepared and isolated in a procedure analogous to that used for the alkoxide salts, except that the product was filtered off only 3–4 h after the reaction between 2,6-diisopropylaniline and *n*-butyllithium was initiated.

Me_3SiNH-2,6-C_6H_3-*i*-Pr_2. A solution of 44.5 g (0.25 mol) of H_2N-2,6-C_6H_3-*i*-Pr_2 in 300 mL of pentane was prepared and cooled to 0 °C. To this solution was added slowly 155 mL of an *n*-butyllithium solution (1.6 M in hexane, 0.25 mol). The mixture was stirred at room temperature for 3 h, after which time the resulting lithium salt was filtered off. This salt was completely dissolved in diethyl ether (ca. 500 mL), and the solution was cooled to 0 °C and stirred vigorously while neat Me_3SiCl (27.2 g, 0.25 mol) was added slowly. After 3 h, the mixture was filtered through Celite, and the volatile components were removed from the filtrate in vacuo to provide pure, pale yellow, liquid $Me_3SiNHAr$ in greater than 90% yield. This compound was used without further purification. ^1H NMR (C_6D_6): δ 7.08 (sharp m, 3 H, H_{aryl}), 3.44 (spt, 6.9 Hz, 2 H, C*H*Me_2), 2.00 (br, 1 H, NH), 1.19 (d, 6.9 Hz, 12 H, CH*Me*$_2$), 0.01 (s, 9 H, Me_3Si).

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 $CDCl_3$. Chemical shifts were referenced internally 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. Resonances associated with solvents of crystallization are not reported. Simulated spectra were obtained by using Bruker PANIC software on the Aspect 2000 computer. Infrared spectra were obtained as Nujol mulls, between 4000 and 600 cm^{-1}, on a Perkin-Elmer 1310 spectrometer and were not assigned but used as fingerprints (w = weak, m = medium, s = strong; sh = shoulder, br = broad, v = very). The molecular weight of $[Ta(NMe_2)_2Cl_3]_2$ (**9**) was determined by vapor pressure osmometry in benzene solution.[47] Elemental analyses were performed by Desert Analytics of Tucson, AZ. All samples were handled under nitrogen and were combusted with WO_3.

Preparations. $Ta(NAr)Cl_3(THF)_2$ (1). To a stirred suspension of 2.30 g (6.41 mmol) of $TaCl_5$ in 20 mL of toluene was added slowly a solution of 3.2 g (12.8 mmol) of $Me_3SiNHAr$ in 5 mL of THF. The solution quickly turned orange upon $Me_3SiNHAr$/THF addition. After the solution was stirred for 24 h, the solvent was removed in vacuo to provide an orange oil, which was stirred under 15 mL of pentane (in which it is insoluble) and then allowed to stand at room temperature for 2 days without stirring. Over this time the product crystallized as an orange solid, which was filtered off, washed with small quantities (ca. 3 mL) of diethyl ether followed by pentane, and dried in vacuo to yield 3.20 g (5.24 mmol, 82%) of pure product. The analytically pure compound was obtained by recrystallization from toluene/pentane at −30 °C. ^1H NMR (C_6D_6): δ 7.23 (d, 7.7 Hz, 2 H, H_m), 6.81 (t, 7.7 Hz, 1 H, H_p), 4.76 (spt, 6.8 Hz, 2 H, C*H*Me_2), 4.12 and 3.93 (br, 4 H each, $C_\alpha H_2$, THF), 1.48 (d, 6.8 Hz, 12 H, CH*Me*$_2$), 1.34 and 1.17 (br, 4 H each, $C_\beta H_2$, THF). ^{13}C NMR (C_6D_6): δ 149.3 (C_{ipso}), 148.9 (C_o), 126.1 (C_p), 122.4 (C_m), 77.5 and 72.4 (C_α and C'_α, THF), 27.6 (*C*HMe_2), 25.4 (CH*Me*$_2$), 25.3 (coincident C_β and C'_β, THF). IR: 1350 s, 1295 w, 1250 w, 1173 w, 1100 w, 1040 w, 1000 m–s, 930 w, 915 w, 848 vs, 803 w, 762 m cm^{-1}. Anal. Calcd for $C_{20}H_{33}Cl_3NO_2Ta$: C, 39.59; H, 5.48; Cl, 17.53. Found: C, 40.50; H, 5.67; Cl, 16.87.

$Ta(NAr)Cl_3(dme)$ (2). A suspension of 0.49 g (1.37 mmol) of $TaCl_5$ in 10 mL of toluene was stirred vigorously while a solution of 0.69 g (2.74 mmol) of $Me_3SiNHAr$ in 2 mL of dimethoxyethane was added slowly. The solution immediately turned orange upon $Me_3SiNHAr$/dme addition. After the mixture was stirred at room temperature for 24 h, the resulting orange solution was filtered and the filtrate was pumped to dryness to yield the orange microcrystalline product. Washing these microcrystals with 3–5 mL of pentane provided 0.54 g (0.97 mmol, 71%)

(40) (a) Mingos, D. M. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W. Eds.; Pergamon Press: Oxford, England, 1982; Vol. 3, pp 59–60. (b) Braterman, P. S.; Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1976**, 241.
(41) Goeden, G. V.; Haymore, B. L. *Inorg. Chem.* **1983**, *22*, 157.
(42) Rossi, R.; Marchi, A.; Duatti, A.; Magon, L.; Casellato, U.; Graziani, R.; Polizzotti, G. *Inorg. Chim. Acta* **1984**, *90*, 121.
(43) Lock, C. J. L.; Turner, G. *Can. J. Chem.* **1977**, *55*, 333.
(44) Wexler, P. A.; Wigley, D. E. *J. Chem. Soc., Chem. Commun.* **1989**, 664.
(45) Shriver, D. F.; Drezdzon, M. A. *The Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.
(46) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 3rd ed.; Pergamon Press: Oxford, England, 1988.
(47) Burger, B. J.; Bercaw, J. E. In *Experimental Organometallic Chemistry*; Wayda, A. L., Darensbourg, M. Y., Eds.; ACS Symposium Series 357; American Chemical Society: Washington, DC, 1987; pp 79–98.

of compound sufficiently pure for subsequent reactions. The analytically pure compound was obtained by recrystallization from toluene at −30 °C. ^{1}H NMR (C_6D_6): δ 7.22 (d, 7.7 Hz, 2 H, H_m), 6.83 (t, 7.7 Hz, 1 H, H_p), 4.78 (spt, 6.8 Hz, 2 H, C*H*Me$_2$), 3.41 and 3.26 (s, 3 H each, O*Me*), 2.90 (br s, 4 H, OCH_2), 1.48 (d, 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 149.0 (C_o), 148.5 (C_{ipso}), 126.5 (C_p), 122.5 (C_m), 75.2 and 70.1 (O*Me*), 68.9 and 62.3 (OCH_2), 27.8 (*C*HMe$_2$), 25.1 (CH*Me*$_2$). IR: 1290 w, 1270 w, 1230 w, 1175 br w, 1165 br w, 1095 w, 1062 m–s, 1010 vs, 995 sh, 983 sh, 973 s, 922 w, 842 s, 810 w, 790 m, 750 m cm^{-1}. Anal. Calcd for $C_{16}H_{27}Cl_3NO_2Ta$: C, 34.77; H, 4.92. Found: C, 35.01; H, 5.06.

Ta(NAr)Cl$_3$(py)$_2$ (3). To a stirred suspension of 4.15 g (11.6 mmol) of $TaCl_5$ in 100 mL of benzene was added slowly 8 mL of diethyl ether, which reacted to provide a clear, pale yellow solution. To this solution was added 5.77 g (23.16 mmol) of $Me_3SiNHAr$ dissolved in 5 mL (58.2 mmol) of pyridine. The solution was stirred and heated to 60 °C for 24 h. The resulting red solution was cooled, concentrated to ca. 20 mL in volume, and allowed to stand at room temperature for 6–8 h. Over this time, red-orange crystals formed, were filtered off, and were dried in vacuo to provide 5.23 g (7.84 mmol, 68%) of the benzene solvate Ta(NAr)Cl$_3$(py)$_2$·0.6C$_6$H$_6$. Gentle overnight heating of this solid (ca. 40 °C) under high vacuum (ca. 10^{-5} Torr) was used for complete removal of the benzene. Analytically pure samples are obtained by recrystallization from hot benzene followed by benzene removal as described above. Preparations that call for the use of Ta(NAr)Cl$_3$(py)$_2$ or the solvate Ta(NAr)Cl$_3$(py)$_2$·0.6C$_6$H$_6$ can be performed *with either compound*; therefore, in general, removal of this benzene is not essential. ^{1}H NMR (C_6D_6): δ 9.12 (br, 2 H, H_o, py), 8.75 (m, 2 H, H_o, py), 7.27 (d, 7.6 Hz, 2 H, H_m, NAr), 6.83 and 6.79 (overlapping t, 1 H each, H_p, py and NAr), 6.65 (br t, 1 H, H_p, py), 6.48 and 6.18 (br, 2 H each, H_m, py), 4.73 (spt, 6.8 Hz, 2 H, C*H*Me$_2$), 1.38 (d, 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 152.4 and 151.9 (C_o, py), 148.8 (C_o, NAr), 148.4 (C_{ipso}), 140.2 and 138.8 (C_m, py), 125.4, 124.9, and 124.5 (C_p, NAr and py), 121.8 (C_m, NAr), 27.1 (*C*HMe$_2$), 24.8 (CH*Me*$_2$). IR: 1600 s, 1350 s, 1295 w, 1245 w, 1215 m, 1150 w, 1095 w, 1063 s, 1038 m, 1003 m, 985 m, 930 w, 795 w–m, 755 s, 690 s, 630 w, 620 w cm^{-1}. Anal. Calcd for $C_{22}H_{27}Cl_3N_3Ta$: C, 42.57; H, 4.38; Cl, 17.13. Found: C, 42.64; H, 4.40; Cl, 16.82.

Ta(NAr)Cl$_3$(THT)$_2$ (4). To a room-temperature suspension of 2.3 g (6.4 mmol) of $TaCl_5$ in 100 mL of benzene was added 3.20 g (12.8 mmol) of $Me_3SiNHAr$. This mixture was heated to 60 °C for 1 h, over which time a pink precipitate formed. After the mixture was allowed to cool to ca. 40 °C, tetrahydrothiophene (1.5 mL, 16.4 mmol) was added slowly, which reacted with the pink solid and formed a red-orange solution. After this solution was stirred at room temperature for 8 h, all volatiles were removed in vacuo to provide a red-orange oil. The oil was redissolved in a minimum volume (<5 mL) of toluene and cooled to −30 °C, which resulted in the formation of 2.49 g (3.9 mmol, 61%) of orange crystals, which were filtered off, washed with a few milliliters of cold (ca. −20 °C) pentane, and dried in vacuo. ^{1}H NMR ($CDCl_3$): δ 7.16 (d, 7.7 Hz, 2 H, H_m), 6.82 (t, 7.7 Hz, 1 H, H_p), 4.27 (spt, 6.8 Hz, 2 H, C*H*Me$_2$), 3.33 (br 8 H, $C_\alpha H_2$, THT), 2.00 (br, 8 H, $C_\beta H_2$, THT), 1.28 (d, 6.8 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 149.2 (C_o), 148.9 (C_{ipso}), 126.3 (C_p), 121.6 (C_m), 39.1 and 35.8 (br, C_α and C'_α, THT), 30.3 (coincident C_β and C'_β, THT), 27.5 (*C*HMe$_2$), 24.4 (CH*Me*$_2$). IR: 1341 s, 1296 s, 1271 w, 1256 m, 1176 w, 1100 w, 1056 w, 1017 m, 991 m, 957 w, 936 m, 862 s, 801 s, 760 s, 723 m, 667 m cm^{-1}. Anal. Calcd for $C_{20}H_{33}Cl_3NS_2Ta$: C, 37.60; H, 5.21. Found: C, 37.64; H, 5.36.

Ta(NAr)(DIPP)Cl$_2$(THF)$_2$·OEt$_2$ (5). Solid LiDIPP·OEt$_2$ (0.43 g, 1.75 mmol) was added to a vigorously stirred solution of 1.0 g (1.64 mmol) of Ta(NAr)Cl$_3$(THF)$_2$ (**1**) in 15 mL of diethyl ether. After this mixture was stirred for 6 h at room temperature, the resulting yellow, cloudy solution was filtered and the volatiles removed from the filtrate in vacuo to provide an orange oil. This oil was dissolved in 6 mL of pentane/diethyl ether (1:1, v/v) and cooled to −30 °C to provide 0.88 g (1.07 mmol, 64%) of yellow crystals of the product as the ether solvate Ta(NAr)(DIPP)Cl$_2$(THF)$_2$·OEt$_2$. The analytically pure compound was obtained by recrystallization from Et$_2$O at −30 °C. ^{1}H NMR (C_6D_6): δ 7.14–6.91 (m, 5 H, H_{aryl} (DIPP) and H_m (NAr)), 6.77 (t, 1 H, H_p, 7.7 Hz, NAr), 4.25 and 4.19 (overlapping spt, 6.7 Hz, 2 H each, C*H*Me$_2$), 4.04 (m, 8 H, $C_\alpha H_2$, THF), 1.32 and 1.30 (overlapping d, 6.7 Hz, 12 H each, CH*Me*$_2$), ca. 1.3 (br, 8 H, $C_\beta H_2$, THF; integration of the doublets at δ 1.32 and 1.30 reveals that the THF $C_\beta H_2$ resonances are obscured by these signals). ^{13}C NMR (C_6D_6): δ 158.2 (C_{ipso}, DIPP), 149.6 (C_{ipso}, NAr), 146.7 (C_o, NAr), 138.2 (C_o, DIPP), 124.5 and 122.6 (C_p, NAr and DIPP), 123.7 and 122.3 (C_m, NAr and DIPP), 73.7 (br, C_α, THF), 27.7 and 26.0 (*C*HMe$_2$), 25.4 (C_β, THF), 25.1 and 24.6 (CH*Me*$_2$). IR: 1428 s, 1360 sh, 1350 m–s, 1325 m, 1300 br w, 1250 s, 1190 s, 1105 m, 1095 m, 1035 w–m, 1010 m, 910 m, 890 m, 855 s, 790 w, 740 s, 700 w cm^{-1}. Anal. Calcd for $C_{36}H_{60}Cl_2NO_4Ta$: C, 52.56; H, 7.35. Found: C, 52.49; H, 7.31.

Ta(NAr)(DIPP)Cl$_2$(dme) (6). To a room-temperature solution of 0.42 g (0.76 mmol) of Ta(NAr)Cl$_3$(dme) (**2**) in 10 mL of toluene/ether (4:1, v/v) was added 0.196 g (0.76 mmol) of LiDIPP·OEt$_2$. After this mixture was stirred for 3 h, the yellow solution was pumped to dryness, and the resulting yellow solid was extracted with 30 mL of Et$_2$O and filtered, and the volatiles were removed from the filtrate in vacuo to provide the product as a yellow solid. This solid was washed with 3–5 mL of cold (−20 °C) Et$_2$O followed by cold pentane and dried in vacuo to provide 0.26 g (0.37 mmol, 49%) of yellow Ta(NAr)(DIPP)Cl$_2$(dme). Recrystallization from diethyl ether at −30 °C provided the analytically pure compound. ^{1}H NMR (C_6D_6): δ 7.15–6.92 (m, 5 H, H_{aryl} (DIPP) and H_m (NAr)), 6.80 (t, 7.6 Hz, 1 H, H_p, NAr), 4.40 and 4.28 (spt, 6.8 Hz, 2 H each, C*H*Me$_2$), 3.39 and 3.28 (s, 3 H each, OCH_3), 2.97 (s, 4 H, OCH_2), 1.36 and 1.33 (overlapping d, 6.8 Hz, 12 H each, CH*Me*$_2$). ^{13}C NMR (C_6D_6): δ 157.8 (C_{ipso}, DIPP), 149.2 (C_{ipso}, NAr), 146.9 (C_o, NAr), 138.5 (C_o, DIPP), 124.6 and 123.4 (C_p, NAr and DIPP), 124.0 and 122.6 (C_m, NAr and DIPP), 73.8 and 70.4 (OCH_3), 67.7 and 61.5 (OCH_2), 27.7 and 26.1 (*C*HMe$_2$), 25.1 and 24.8 (CH*Me*$_2$). Anal. Calcd for $C_{28}H_{44}Cl_2NO_3Ta$: C, 48.42; H, 6.39. Found: C, 48.49; H, 6.48.

Ta(NAr)(DIPP)Cl$_2$(py)$_2$·OEt$_2$ (7). A solution of 1.0 g (1.61 mmol) of Ta(NAr)Cl$_3$(py)$_2$ (**3**) in 15 mL of Et$_2$O/THF (2:1, v/v) was stirred vigorously while solid LiDIPP·OEt$_2$ (0.42 g, 1.62 mmol) was added. After it was stirred at room temperature for 4 h, the resulting yellow, cloudy solution was filtered and the filtrate reduced in volume in vacuo to a yellow oil. This oil was redissolved in 5 mL of diethyl ether and the solution cooled to −30 °C to provide 0.97 g (1.16 mmol, 72%) of yellow crystals of the monoetherate Ta(NAr)(DIPP)Cl$_2$(py)$_2$·OEt$_2$. Recrystallization from Et$_2$O at −30 °C provided the analytically pure compound. ^{1}H NMR (C_6D_6): δ 9.05 (br, 2 H, H_o, py), 8.93 (m, 2 H, H_o, py), 7.21–6.95 (m, 5 H, H_{aryl} (DIPP) and H_m (NAr)), 6.82 (br t, 2 H, H_p, py and NAr), 6.67 (br t, 1 H, H_p, py), 6.48 and 6.24 (m, 2 H each, H_m, py), 4.34 and 4.23 (overlapping spt, 6.8 Hz, 2 H each, C*H*Me$_2$), 1.28 and 1.26 (overlapping d, 6.8 Hz, 12 H each, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 157.8 (C_{ipso}, DIPP), 152.5 and 151.3 (C_o, py), 148.9 (C_{ipso}, NAr), 146.8 (C_o, NAr), 139.1 and 138.4 (C_p, py), 137.8 (C_o, DIPP), 124.4 and 124.1 (C_m, py), 123.4 and 121.3 (C_p, NAr and DIPP), 123.0 and 121.6 (C_m, NAr and DIPP), 27.0 and 25.5 (*C*HMe$_2$), 24.4 and 23.8 (CH*Me*$_2$). IR: 1600 m, 1330 m, 1295 w, 1250 m–s, 1220 w, 1190 m, 1148 w, 1105 br w, 1062 m, 1045 m, 1005 w–m, 980 w, 925 w, 875 m, 860 m, 790 br w, 745 s, 690 s cm^{-1}. Anal. Calcd for $C_{38}H_{54}Cl_2N_3O_2Ta$: C, 54.55; H, 6.51; Cl, 8.47. Found: C, 54.63; H, 6.67; Cl, 7.99.

Ta(NAr)(DMP)Cl$_2$(py)$_2$ (8). A 0.18-g (1.42-mmol) amount of LiDMP was added directly to a solution of 0.87 g (1.40 mmol) of Ta(NAr)Cl$_3$(py)$_2$ (**3**) in 15 mL of Et$_2$O/THF (3:1, v/v). After the mixture was stirred at room temperature for 8 h, the resulting yellow solution was filtered and the filtrate reduced in volume in vacuo to provide an orange oil. The oil was dissolved in 2–3 mL of Et$_2$O and cooled to −30 °C to yield 0.63 g (0.89 mmol, 64%) of yellow crystals of Ta(NAr)(DMP)Cl$_2$(py)$_2$. Recrystallization from diethyl ether at −30 °C provided the analytically pure compound. ^{1}H NMR (C_6D_6): δ 9.01 and 8.93 (m, 2 H each, H_o, py), 7.23 (d, 7.7 Hz, 2 H, H_m, NAr), 6.98–6.65 (m, 6 H, H_{aryl} (DMP) and H_p (NAr and py)), 6.45 and 6.26 (m, 2 H each, H_m, py), 4.34 (spt, 6.9 Hz, 2 H, C*H*Me$_2$), 2.58 (s, 6 H, CH_3, DMP), 1.28 (d, 6.9 Hz, 12 H, CH*Me*$_2$). ^{13}C NMR ($CDCl_3$): δ 160.7 (C_{ipso}, DMP), 152.5 and 151.3 (C_o, py), 148.8 (C_{ipso}, NAr), 147.2 (C_o, NAr), 139.2 and 138.6 (C_p, py), 128.0 (C_m, DMP), 127.4 (C_o, DMP), 124.4 and 124.2 (C_m, py), 123.5 (C_p, DMP), 121.8 (C_m, NAr), 120.8 (C_p, NAr), 26.9 (*C*HMe$_2$), 24.4 (CH*Me*$_2$), 17.6 (CH_3, DMP). Anal. Calcd for $C_{30}H_{36}Cl_2N_3OTa$: C, 51.00; H, 5.14; N, 5.95. Found: C, 50.14; H, 5.12; N, 5.82.

[Ta(NEt$_2$)$_2$Cl$_3$]$_2$ (9). Excess Me_3SiNEt_2 (1.08 g, 8 mmol) was added (neat) to a solution of $TaCl_5$ (0.72 g, 2 mmol) in 20 mL of toluene/diethyl ether (3:1, v/v) at room temperature. The solution immediately turned red-orange. After the mixture was stirred for 24 h, the solution was pumped to dryness to yield the product as red-orange microcrystals, which were washed with 20 mL of pentane and dried in vacuo; the yield of [Ta(NEt$_2$)$_2$Cl$_3$]$_2$ was 0.70 g (0.81 mmol) or 81%. This solid was sufficiently pure for further reactions, but the analytically pure compound can be crystallized from toluene/pentane solutions at −30 °C. ^{1}H NMR (C_6D_6): δ 3.92 (q, 7.0 Hz, 2 H, NCH_2CH$_3$), 0.87 (t, 7.0 Hz, 3 H, NCH$_2$CH_3). ^{13}C NMR (C_6D_6): δ 46.2 (NCH$_2$CH$_3$), 12.2 (NCH$_2$CH$_3$). IR: 1290 sh, 1260 br, w, 1174 m, 1112 m, 1075 m, 1052 m, 1022 m–s, 990 s, 980 s, 895 sh, 887 s, 873 s, 780 s, 710 w cm^{-1}. Molecular weight (C_6H_6 solution): calcd for dimer 863; found, 951. Anal. Calcd for $C_{16}H_{40}Cl_6N_4Ta_2$: C, 22.26; H, 4.67. Found: C, 22.51; H, 4.92.

Ta(NEt$_2$)$_2$Cl$_3$(py) (10). A 1.5-mL amount of pyridine was added to a solution of [Ta(NEt$_2$)$_2$Cl$_3$]$_2$ (**9**, 0.60 g, 0.69 mmol) in 10 mL of toluene at room temperature. The solution became a darker red-orange upon pyridine addition. After it was stirred for 1 h, the solution was pumped to dryness to yield an orange solid, which was washed with cold (ca. −20

°C) pentane and dried in vacuo to provide 0.60 g (1.17 mmol, 88%) of pure red to red-orange $Ta(NEt_2)_2Cl_3(py)$. Recrystallization from diethyl ether at −30 °C provides an analytically pure sample. ^1H NMR (C_6D_6): δ 9.10 (br, 2 H, H_o), 6.75 (m, 1 H, H_p), 6.46 (m, 2 H, H_m), 4.47 and 3.87 (br, 4 H each, NCH_2CH_3), 1.08 and 0.97 (br, 6 H each, NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 151.8 (C_o), 138.9 (C_p), 124.4 (C_m), 47.9 and 45.6 (NCH_2CH_3), 11.9 and 11.2 (NCH_2CH_3). IR: 1597 m, 1440 s, 1180 w, 1120 w–m, 1088 m, 1057 m, 1035 m, 1000 s, 990 s, 905 sh, 890 sh, 880 m, 788 s, 755 m, 690 s, 623 m cm^{-1}. Anal. Calcd for $C_{13}H_{25}Cl_3N_3Ta$: C, 30.58; H, 4.93; N, 8.23. Found: C, 30.68; H, 4.97; N, 8.14.

$Ta(NAr)(NEt_2)Cl_2(py)_2$ (11). A 1.12-g (1.34-mmol) amount of $[Ta(NEt_2)_2Cl_3]_2$ (**9**) was dissolved in 15 mL of diethyl ether, and the solution was stirred vigorously while 0.49 g (2.68 mmol) of solid LiNHAr was added. A precipitate formed slowly as the solution turned yellow. After this mixture was stirred for 2 h, 0.5 mL (6.2 mmol) of neat pyridine was added dropwise, which immediately produced an orange color. This solution was stirred for another 2 h and filtered, and the filtrate was pumped to dryness to provide an orange solid. The solid was dissolved in 15 mL of diethyl ether, and the solution was concentrated to 5 mL and cooled to −30 °C to yield 1.06 g (1.61 mmol, 60%) of orange crystals of $Ta(NAr)(NEt_2)Cl_2(py)_2$. This compound can be recrystallized from diethyl ether solutions at −30 °C. ^1H NMR (C_6D_6): δ 9.22 and 8.83 (br, 2 H each, H_o, py), 7.26 (d, 7.7 Hz, 2 H, H_m, NAr), 6.91 (t, 7.7 Hz, 1 H, H_p, NAr), 6.76 (br, 2 H, H_p, py), 6.38 (br, 4 H, H_m, py), 4.86 (spt, 6.8 Hz, 2 H, $CHMe_2$), 4.14 (br, 4 H, NCH_2CH_3), 1.44 (d, 6.8 Hz, 12 H, $CHMe_2$), 1.24 (t, 7.0 Hz, 6 H, NCH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 151.7 (C_o, py), 149.4 (C_{ipso}, NAr), 147.3 (C_o, NAr), 138.1 (C_p, py), 124.1 (C_m, py), 122.8 (C_p, NAr), 122.0 (C_m, NAr), 50.0 (br, NCH_2CH_3), 26.7 ($CHMe_2$), 24.5 ($CHMe_2$), 13.0 (NCH_2CH_3). IR: 1603 s, 1485 sh, 1363 sh, 1350 sh, 1296 m, 1219 m, 1087 w, 1156 m, 1141 m, 1100 w, 1069 s, 1041 s, 1008 s, 986 m, 933 w, 892 m, 794 m, 755 s, 723 m, 697 s, 627 m cm^{-1}. Anal. Calcd for $C_{26}H_{37}Cl_2N_4Ta$: C, 47.50; H, 5.67. Found: C, 48.12; H, 6.12.

(EtC≡CEt)Ta(NAr)Cl(py)$_2$ (12). To a solution of 0.72 g (1.08 mmol) of $Ta(NAr)Cl_3(py)_2 \cdot 0.6C_6H_6$ (**3**·0.6C_6H_6) in 15 mL of diethyl ether/THF (2:1) were added slightly more than 1 equiv of 3-hexyne (136 μL, 1.19 mmol) and 2 equiv of NaHg amalgam (0.5%, 0.73 mL). After this mixture was stirred at room temperature for 16 h, the yellow-brown solution was filtered through Celite and the filtrate was pumped to dryness. The resulting yellow solid was extracted with 15 mL of pentane, and the extract was filtered and concentrated to ca. 4 mL volume. Cooling the solution to −30 °C resulted in the formation of a crop of yellow crystals of $(EtC{\equiv}CEt)Ta(NAr)Cl(py)_2$ (0.22 g, 0.35 mmol, 32%). This compound can be recrystallized from pentane at −30 °C. ^1H NMR (C_6D_6): δ 9.08 (m, 4 H, H_o, py), 7.30 (d, 7.6 Hz, 2 H, H_m, NAr), 7.00 (t, 7.6 Hz, 1 H, H_p, NAr), 6.74 (m, 2 H, H_p, py), 6.38 (m, 4 H, H_m, py), 4.21 (spt, 6.9 Hz, 2 H, $CHMe_2$), 2.82 and 2.64 (ABX_3 multiplet, 2 H each, CH_2CH_3), 1.29 (d, 6.9 Hz, 12 H, $CHMe_2$), 1.08 (t, 6 H, 7.5 Hz, CH_2CH_3). ^{13}C NMR (C_6D_6): δ 194.3 (C_{acet}), 152.8 (C_o, py), 152.7 (C_{ipso}, NAr), 144.0 (C_o, NAr), 136.7 (C_p, py), 124.1 (C_m, py), 122.8 (C_m, NAr), 122.1 (C_p, NAr), 27.6 ($CHMe_2$), 27.4 (CH_2CH_3), 24.1 ($CHMe_2$), 14.9 (CH_2CH_3). IR: 1599 m, 1364 s, 1350 sh, 1296 m, 1212 m, 1151 m, 1098 w, 1068 m, 1042 m, 1011 w, 978 m, 932 w, 801 w, 758 s, 697 s cm^{-1}. Anal. Calcd for $C_{28}H_{37}ClN_3Ta$: C, 53.21; H, 5.90. Found: C, 53.44; H, 6.05.

(PhC≡CPh)Ta(NAr)Cl(py)$_2$ (13). To a solution of 0.513 g (0.77 mmol) of $Ta(NAr)Cl_3(py)_2 \cdot 0.6C_6H_6$ (**3**·0.6C_6H_6) in 15 mL of diethyl ether/THF (2:1) were added 0.153 g (0.85 mmol) of PhC≡CPh and 0.53 mL of a 0.5% NaHg amalgam (1.54 mmol). After this mixture was stirred at room temperature for 12 h, the resulting yellow-brown solution was filtered through Celite and the filtrate was pumped to dryness to provide a yellow-brown solid. The solid was dissolved in Et_2O, reduced in volume in vacuo to ca. 5 mL, and cooled to −30 °C to yield 0.32 g (0.44 mmol, 57%) of yellow $(PhC{\equiv}CPh)Ta(NAr)Cl(py)_2$. This compound can be recrystallized from pentane or diethyl ether at −30 °C to provide crystals of the analytically pure product. ^1H NMR (C_6D_6): δ 9.09 (m, 4 H, H_o, py), 7.27 (d, 7.7 Hz, 2 H, H_m, NAr), 7.08–6.87 (m, 11 H, C_6H_5 and H_p, NAr), 6.67 (m, 2 H, H_p, py), 6.29 (m, 4 H, H_m, py), 4.34 (spt, 6.9 Hz, 2 H, $CHMe_2$), 1.26 (d, 6.9 Hz, 12 H, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 195.9 (C_{acet}), 153.0 (C_o, py), 152.5 (C_{ipso}, C_6H_5), 144.6 (C_o, NAr), 144.2 (C_{ipso}, NAr), 136.9 (C_p, py), 128.2, 127.7, 125.8 (C_o, C_m, C_p; C_6H_5), 124.4 (C_m, py), 123.0 (C_p, NAr), 122.9 (C_m, NAr), 27.7 ($CHMe_2$), 24.3 ($CHMe_2$). IR: 1640 m, 1594 m, 1586 sh, 1290 m, 1250 w, 1206 m–s, 1143 m, 1105 w, 1088 w, 1060 m–s, 1035 m, 1018 w, 1002 w, 973 m, 923 m, 788 w–m, 765 s, 748 s, 686 vs, 622 w cm^{-1}. Anal. Calcd for $C_{36}H_{37}ClN_3Ta$: C, 59.39; H, 5.12. Found: C, 59.54; H, 5.37.

(Me$_3$SiC≡CMe)Ta(NAr)Cl(py)$_2$ (14). Orange crystals of compound **14** were prepared and recrystallized in 52% yield by a procedure analogous to that used in the preparation of $(PhC{\equiv}CPh)Ta(NAr)Cl(py)_2$ (**13**). ^1H NMR (C_6D_6): δ 9.20 and 8.94 (m, 2 H each, H_o, py), 7.29 (d, 7.7 Hz, 2 H, H_m, NAr), 6.99 (t, 7.7 Hz, 1 H, H_p, NAr), 6.74 and 6.69 (overlapping m, 1 H each, H_p, py), 6.37 and 6.33 (overlapping m, 2 H each, H_m, py), 4.08 (spt, 6.8 Hz, 2 H, $CHMe_2$), 2.52 (s, 3 H, $Me_3SiC{\equiv}CMe$), 1.31 and 1.23 (d, 6.8 Hz, 6 H each, $CHMe_2$), 0.085 (s, 9 H, $Me_3SiC{\equiv}CMe$). ^{13}C NMR (C_6D_6): δ 217.4 and 186.2 (C_{acet}), 153.3 and 152.4 (C_o, py), 152.6 (C_o, NAr), 136.9 and 136.4 (C_m, py), 124.1 (both C_p, py), 122.8 (C_m, NAr), 122.3 (C_p, NAr), 27.7 ($CHMe_2$), 24.3 and 23.7 ($CHMe_2$), 21.4 (CH_3, acet), 1.15 (Me_3Si, acet). The C_{ipso} (NAr) resonance is not observed even in concentrated solutions and is probably coincident with C_o (NAr). IR: 1625 m, 1595 m, 1360 s, 1345 sh, 1290 m, 1235 m, 1210 m, 1145 m, 1085 w, 1065 m, 1050 m, 1005 w, 975 m, 930 w, 845 s, 828 s, 750 s, 690 s cm^{-1}.

(C(CMe$_3$)=CHCH=C(CMe$_3$))Ta(NAr)Cl(py)$_2$ (15). Compound **15** was prepared and recrystallized by a procedure completely analogous to that used in the preparation of $(PhC{\equiv}CPh)Ta(NAr)Cl(py)_2$ (**13**), with use of 2 equiv of $Me_3CC{\equiv}CH$/equiv of tantalum. This procedure provided a 41% yield of reddish brown crystals of $(C(CMe_3)=CHCH=C(CMe_3))Ta(NAr)Cl(py)_2$. ^1H NMR (C_6D_6): δ 9.18 (br, 4 H, H_o, py), 7.31 (d, 7.6 Hz, 2 H, H_m, NAr), 7.08 (s, 2 H, $C_\beta H$), 6.98 (t, 7.6 Hz, 1 H, H_p, NAr), 6.87 (m, 2 H, H_p, py), 6.54 (m, 4 H, H_m, py), 4.87 (spt, 6.9 Hz, 2 H, $CHMe_2$), 1.49 (d, 6.9 Hz, 12 H, $CHMe_2$), 1.09 (s, 18 H, $C_\alpha CMe_3$). ^{13}C NMR ($CDCl_3$): δ 224.3 (C_α), 151.1 (C_o, py), 148.4 (C_o, NAr), 137.9 (C_p, py), 124.2 (C_m, py), 122.1 (C_m, NAr), 121.9 (C_p, NAr), 106.3 (C_β), 40.5 ($C_\alpha CMe_3$), 30.7 ($C_\alpha CMe_3$), 26.8 ($CHMe_2$), 24.9 ($CHMe_2$). The C_{ipso} (NAr) resonance is not observed and is probably coincident with C_o (NAr). IR: 1600 m, 1483 sh, 1356 w, 1340 m, 1293 m, 1253 w, 1223 m, 1216 m, 1150 m, 1110 w, 1068 m, 1040 m, 1007 m, 979 m, 936 w, 832 m, 809 w, 797 m, 753 s, 700 s cm^{-1}. Anal. Calcd for $C_{34}H_{47}ClN_3Ta$: C, 57.18; H, 6.63. Found: C, 56.94; H, 6.76.

(EtC≡CEt)Ta(NAr)(DIPP)(py)$_2$ (16). To a −30 °C solution of 0.62 g (0.74 mmol) of $Ta(NAr)(DIPP)Cl_2(py)_2 \cdot OEt_2$ (**7**) in 15 mL of diethyl ether was added an excess of 3-hexyne (125 μL, 1.11 mmol) and 0.51 mL of 0.5% NaHg amalgam (1.48 mmol). After this mixture was stirred at room temperture for 8 h, the resulting orange-brown solution was filtered through Celite and the solvent removed from the filtrate in vacuo to yield a yellow-brown, oily solid. The solid was extracted with pentane, the extract was filtered, and the filtrate was concentrated and cooled to −30 °C to provide 0.27 g (0.35 mmol, 47%) of orange crystalline $(EtC{\equiv}CEt)Ta(NAr)(DIPP)(py)_2$. Recrystallization can be effected from pentane solutions at −30 °C. ^1H NMR (C_6D_6): δ 8.87 (m, 4 H, H_o, py), 7.36–6.90 (m, 6 H, H_{aryl}, DIPP and NAr), 6.63 (m, 2 H, H_p, py), 6.23 (m, 4 H, H_m, py), 4.24 (spt, 6.9 Hz, 2 H, $CHMe_2$), 3.61 and 3.45 (spt, 6.9 Hz each, 1 H each, $CHMe_2$), 3.00 and 2.81 (ABX_3 multiplets, 2 H each, CH_2CH_3), 1.33 and 1.31 (overlapping d, 6.9 Hz each, 6 H and 12 H, $CHMe_2$), 1.11 (t, 7.5 Hz, 6 H, CH_2CH_3), 1.00 (d, 6.9 Hz, 6 H, $CHMe_2$). ^{13}C NMR (C_6D_6): δ 188.4 (C_{acet}), 157.2 (C_{ipso}, DIPP), 153.5 (C_o, NAr), 152.2 (C_o, py), 137.6 and 136.5 (C_o, DIPP), 136.8 (C_m, py), 124.0 (C_p, py), 123.8 and 123.5 (C_m, DIPP), 122.6 (C_m, NAr), 120.3 and 119.3 (C_p, NAr and DIPP), 27.6 (CH_2CH_3, acet), 27.5 and 22.6 ($CHMe_2$, DIPP), 26.5 ($CHMe_2$, NAr), 24.5 ($CHMe_2$, NAr), 24.0 and 23.8 ($CHMe_2$, DIPP), 15.0 (CH_2CH_3, acet). C_{ipso} (NAr) could not be definitively assigned. IR: 1592 w, 1575 w, 1410 s, 1355 sh, 1325 s, 1290 w, 1265 s, 1255 sh, 1205 m, 1145 w, 1110 w, 1085 w, 1060 w, 1035 w, 1000 w, 960 w, 925 w, 885 m, 865 m, 755 m, 740 s, 690 s cm^{-1}. Anal. Calcd for $C_{40}H_{54}N_3OTa$: C, 62.09; H, 7.03; N, 5.43. Found: C, 62.36; H, 7.28; N, 5.28.

(PrC≡CPr)Ta(NAr)(DIPP)(py)$_2$ (17). Compound **17** was prepared and recrystallized by a procedure completely analogous to that used in the preparation of $(EtC{\equiv}CEt)Ta(NAr)(DIPP)(py)_2$ (**16**). This procedure provided a 51% yield of orange crystals of $(PrC{\equiv}CPr)Ta(NAr)(DIPP)(py)_2$. This compound was formulated on the basis of its spectroscopic properties. ^1H NMR (C_6D_6): δ 8.88 (m, 4 H, H_o, py), 7.35 (d, 7.6 Hz, 2 H, H_m, NAr), 7.26–6.89 (m, 4 H, H_{aryl} (DIPP) and H_p (NAr)), 6.65 (m, 2 H, H_p, py), 6.25 (m, 4 H, H_m, py), 4.24 (spt, 6.9 Hz, 2 H, $CHMe_2$), 3.62 and 3.47 (spt, 6.9 Hz each, 1 H each, $CHMe_2$), 2.97 and 2.81 (ABX_3 multiplets, 2 H each, $CH_2CH_2CH_3$), 1.51 (m, 4 H, $CH_2CH_2CH_3$), 1.35 and 1.32 (overlapping d, 6.9 Hz each, 6 H and 12 H, $CHMe_2$), 1.00 (d, 6.9 Hz, 6 H, $CHMe_2$), 0.98 (t, 7.5 Hz, 6 H, $CH_2CH_2CH_3$). ^{13}C NMR (C_6D_6): δ 187.5 (C_{acet}), 157.0 (C_{ipso}, DIPP), 153.5 (C_o, NAr), 152.2 (C_o, py), 137.6 and 136.5 (C_o, DIPP), 136.8 (C_m, py), 124.0 (C_p, py), 123.7 and 123.5 (C_m, DIPP), 122.6 (C_m, NAr), 120.3 and 119.3 (C_p, NAr and DIPP), 36.8 ($CH_2CH_2CH_3$, acet), 27.4 and 26.5 ($CHMe_2$, NAr and DIPP), 25.0 ($CHMe_2$, DIPP), 24.6 ($CHMe_2$, NAr), 24.2 and 23.8 ($CHMe_2$, DIPP), 23.7 ($CH_2CH_2CH_3$, acet), 15.3 ($CH_2CH_2CH_3$, acet). C_{ipso} (NAr) could not be definitively assigned.

Structural Determination of Ta(N-2,6-C$_6$H$_3$-*i*-Pr$_2$)(O-2,6-C$_6$H$_3$Me$_2$)Cl$_2$(C$_5$H$_5$N)$_2$ (8). A yellow rectangular crystal (approximate dimensions 0.50 × 0.50 × 0.29 mm) was mounted in a glass capillary in a random

orientation. Preliminary examination and data collection were performed on a Syntex $P2_1$ diffractometer as described in Table I. Two check reflections were measured after every 98 data reflections; the intensities of these standards remained constant within experimental error throughout data collection. From the systematic absences of $h0l$ ($l = 2n$) and $0k0$ ($k = 2n$) and from the subsequent least-squares refinement, the space group was determined to be $P2_1/c$ [No. 14]. A total of 6210 reflections were collected in the $+h,+k,\pm l$ octants (5541 unique) in the range $2° \leq 2\theta \leq 50°$, with 3355 reflections having $I \geq 3\sigma(I)$. Lorentz and polarization corrections were applied to the data, and an empirical absorption correction was made.[48] The agreement factors for the 561 observed and accepted reflections were 3.2% on the basis of I and 2.3% on the basis of F_o. The structure was solved by using the Patterson heavy-atom method and difference Fourier syntheses and refined in full-matrix least squares. Hydrogen atoms were placed in calculated positions (C-H = 0.95 Å), constrained to ride on the atom to which they were bonded, and included in the refinement. The largest peak in the final difference Fourier map was 1.13 (10) e/Å^3. All calculations were performed on a VAX computer using SDP/VAX.[49]

Hydrolysis of (PhC≡CPh)Ta(NAr)Cl(py)$_2$ (13) and (C(CMe$_3$)=CHCH=C(CMe$_3$))Ta(NAr)Cl(py)$_2$ (15). A 0.054-g amount of (PhC≡CPh)Ta(NAr)Cl(py)$_2$ (**13**) was dissolved in 10 mL of Et_2O, and an excess of water (0.5 mL of 1:9 v/v H_2O/acetone) was added dropwise at room temperature. This mixture was stirred for 20 min, over which time the yellow solution decolorized and a white precipitate formed. The solvent was removed from this mixture, and the hydrolysis products were extracted with 10 mL of Et_2O and filtered through Celite. The solvent was removed in vacuo to provide a white oily solid. Only *cis*-PhCH=CHPh (and no free PhC≡CPh) was observed in the hydrolysis products by ^{1}H NMR (C_6D_6). Compound **15**, (C(CMe$_3$)=CHCH=C(CMe$_3$))Ta(NAr)Cl(py)$_2$, was hydrolyzed, and the hydrolysis product was identified as (*E*,*E*)-Me$_3$CCH=CHCH=CHCMe$_3$, by a workup procedure analogous to that described above for compound **13**. These hydrolysis reactions also produce H_2NAr in high yield (^{1}H NMR spectroscopy).

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We also acknowledge support from the U.S. Army Research Office (Short Term Innovative Research Program). We thank Drs. Ian M. Gardiner and Roy L. Johnston for helpful discussions and Pamela S. Nicholls for experimental assistance in the early stages of this research.

Supplementary Material Available: Full details of the structure solution, tables of atomic positional and thermal parameters for Ta(N-2,6-C_6H_3-*i*-Pr$_2$)(O-2,6-C_6H_3Me$_2$)Cl$_2$(C_5H_5N)$_2$, full tables of bond distances and angles, and tables of least-squares planes and dihedral angles (15 pages); listings of observed and calculated structure factor amplitudes (32 pages). Ordering information is given on any current masthead page.

(48) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158.
(49) Frenz, B. A. In *Computing in Crystallography*; Schenk, H., Olthof-Hazelkamp, R., van Konigsveld, H., Bassi, G. C., Eds.; Delft University Press: Delft, Holland, 1978; pp 64-71.

Contribution from the Zettlemoyer Center for Surface Studies and Department of Chemistry, Sinclair Laboratory No. 7, Lehigh University, Bethlehem, Pennsylvania 18015

Methanol Synthesis Catalysts Based on Cs/Cu/ZnO/M_2O_3 (M = Al, Cr, Ga): Genesis from Coprecipitated Hydrotalcite-like Precursors, Solid-State Chemistry, Morphology, and Stability

John G. Nunan,[†] Paul B. Himelfarb,[‡] Richard G. Herman,* Kamil Klier, Charles E. Bogdan,[§] and Gary W. Simmons

Received March 15, 1989

The formation, decomposition, and reconstitution of hydrotalcite-like hydroxy carbonates $(Cu_{0.4}Zn_{0.6})_6M_2(OH)_{16}CO_3{\cdot}4H_2O$ (M = Al, Cr, Ga) have been studied to determine the causes of the high long-lasting catalytic activity (M = Cr) and the severe deactivation (M = Al, Ga) of the Cu/ZnO/M_2O_3 methanol synthesis catalysts doped with cesium after thermal decomposition of the hydrotalcite-like precursors. The alumina-based (M = Al) and gallia-based (M = Ga), but not the chromia-based (M = Cr), CuO/ZnO/M_2O_3 mixed oxides that were produced by thermal treatment at 623 K of the hydrotalcite-like compounds reconstituted the original hydrotalcite-type compounds during the aqueous doping procedure carried out with the cesium formate promoter, CsOOCH. The re-formation of the Al- and Ga-containing catalysts to their hydrotalcite-like precursors is due to incomplete decomposition of the hydroxy carbonates prior to doping. Electron diffraction and transmission electron microscopy give evidence for the reconstitution reactions. The alkali-metal-promoted methanol synthesis catalyst of choice from hydrotalcite-type precursors is based on chromia.

Introduction

The most active and selective low-temperature (<573 K) low-pressure (<10 kPa) methanol synthesis catalysts are based on an intimate mixture of Cu/ZnO prepared by calcination of the coprecipitated precursors.[1,2] With these binary catalysts, it was found that the composition that gives the highest activity for methanol synthesis[3] and for methanol decomposition[4] corresponded to Cu/Zn = 30/70 mol %. It was subsequently shown that preparation of this optimized catalyst by the usual method of carbonate coprecipitation resulted in the formation of a single-phase aurichalcite precursor, $(Cu_{0.3}Zn_{0.7})_5(OH)_6(CO_3)_2$.[5] Calcination and reduction of this hydroxy carbonate resulted in a dispersed Cu/ZnO catalyst, where a significant fraction of the

[†] Present address: Allied Signal, P.O. Box 5016, Des Plaines, IL 60017.
[‡] Present address: Shell Development Co., P.O. Box 1380, Houston, TX 77001.
[§] Present address: J. T. Baker, Inc., 222 Red School Lane, Phillipsburg, NJ 08865.

(1) (a) Natta, G. In *Catalysis*; Emmett, P. H., Ed.; Reinhold: New York, 1955; Vol. 3, Chapter 8. (b) Frolich, P. K.; Fenske, M. R.; Quiggle, D. *Ind. Eng. Chem.* **1928**, *20*, 694. (c) Kostelitz, O.; Huttig, G. F. *Kolloid-Z.* **1934**, *67*, 265. (d) Collins, B. M. German Patent 2,302,658 (to Imperial Chemical Industries, Ltd.), Aug 2, 1973. (e) Davies, P.; Snowdon, F. F. U.S. Patent 3,326,956 (to Imperial Chemical Industries, Ltd.), June 20, 1967. (f) Stiles, A. B. U.S. Patent 4,111,847 (to E. I. Du Pont de Nemours and Co.), Sept 5, 1978.
(2) Klier, K. *Adv. Catal.* **1982**, *31*, 243.
(3) Herman, R. G.; Klier, K.; Simmons, G. W.; Finn, B. P.; Bulko, J. B.; Kobylinski, T. P. *J. Catal.* **1979**, *56*, 407.
(4) Frolich, P. K.; Fenske, M. R.; Taylor, P. S.; Southwich, C. A., Jr. *Ind. Eng. Chem.* **1928**, *20*, 1327.
(5) Himelfarb, P. B.; Simmons, G. W.; Klier, K.; Herman, R. G. *J. Catal.* **1985**, *93*, 442.

0020-1669/89/1328-3868$01.50/0