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Conformationally Rigid Diamide Complexes: Synthesis and Structure of Tantalum(III) Alkyne Derivatives[†]

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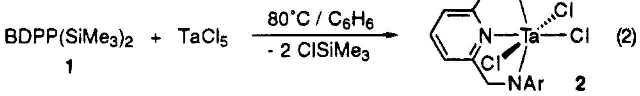
*Summary: The chelating diamide complexes mer-$TaCl_3$-(BDPP) (**2**), mer-$TaCl_3$(BDPP) (**3**), and (BDPP)Ta(η^2-RC≡CR)Cl (**4a**, R = Pr; **4b**, R = Et; **4c**, R = Ph) (BDPP = 2,6-$(ArNCH_2)_2$-NC_5H_3; Ar = 2,6-$^iPr_2$-C_6H_3), have been prepared. Proton and carbon NMR data suggest that the alkynes in **4a**–**c** rotate rapidly on the NMR time scale. An X-ray study of (BDPP)Ta(η^2-PrC≡CPr)Cl (**4a**) revealed a distorted-square-pyramidal geometry with the chloride occupying the apical position.*

Certain group 5 metal complexes are active catalysts for the polymerization and cyclization of alkynes.[1–4] The polymerization of alkynes can occur by two different pathways: cycloaddition of an alkyne to a carbene to yield a vinylcarbene upon ring-opening[5] and the insertion of an alkyne into a metal–carbon bond.[6] Complexes of the type $L_nTa(\eta^2\text{-}RC{\equiv}CR)X$ (X = alkyl, hydride, chloride)[7–10] are ideally suited for studying the latter mechanism. Cyclization reactions are highly dependent on the steric and electronic properties of the ancillary ligands. For example, the two-electron reduction of $(DIPP)_2TaCl_3(OEt_2)$ (DIPP = 2,6-diisopropylphenoxide) in the presence of excess 3-hexyne yields the arene complex $(DIPP)_2Ta(\eta^6\text{-}C_6Et_6)Cl$ and hexaethylbenzene.[4] Under similar conditions the complex $(DIPP)_3TaCl_2(OEt_2)$, which bears one additional bulky alkoxide ligand, yields only the metallacyclopentadiene complex $(DIPP)_3Ta(C_4Et_4)$.[11] A flexible ligand array is common to the complexes mentioned above. Our interest in the steric and electronic effects of conformationally rigid ligands led us to explore the synthesis of bulky chelating diamide ancillaries,[12–14] in particular, amides which bear the voluminous 2,6-diisopropylphenyl moiety. We report here the synthesis of monoalkyne complexes of tantalum stabilized by a new conformationally rigid diamide ligand.

2,6-Bis(bromomethyl)pyridine[15] was treated with 2 equiv of $LiNAr(SiMe_3)$[16] to yield the silylated ligand precursor $BDPP(SiMe_3)_2$ (**1**)[17] as a white crystalline solid (eq 1).

$$2LiNAr(SiMe_3) + 2,6\text{-}(BrCH_2)_2\text{-}NC_5H_3 \xrightarrow[-2LiBr]{-40\text{ to }+25\ ^\circ C/DME} \underset{\mathbf{1}}{2,6\text{-}[NAr(Me_3Si)CH_2]_2\text{-}NC_5H_3} \qquad (1)$$

$BDPP(SiMe_3)_2$ reacts cleanly with $TaCl_5$ to give 2 equiv of $ClSiMe_3$ (confirmed by ^1H NMR spectroscopy) and the yellow trichloride complex *mer*-(BDPP)$TaCl_3$ (**2**) in high yield (eq 2).



Proton and carbon NMR spectra[18] of complex **2** are consistent with a meridional coordination of the ligand, as evidenced by the singlet observed at 5.84 ppm for the methylene protons (CH_2N) of the BDPP unit. Interestingly, the isopropyl methyl groups of the arene are diastereotopic, which we interpret as a consequence of restricted rotation about the N–C_{ipso} bond. The proton NMR spectrum of complex **2** remains unchanged at 80 °C.

Compound **2** can be alkylated with 3 equiv of MeMgBr to give the trimethyl derivative *mer*-(DBPP)$TaMe_3$ (**3**), in good yield (eq 3; RT = room temperature).

$$\underset{\mathbf{2}}{mer\text{-}(BDPP)TaCl_3} + 3MeMgBr \xrightarrow[-3ClMgBr]{Et_2O/RT} \underset{\mathbf{3}}{mer\text{-}(BDPP)TaMe_3} \qquad (3)$$

[†] Dedicated to the memory of Professor Kenneth G. Rutherford.

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(17) $BDPP(SiMe_3)_2$ (**1**): ^1H NMR (C_6D_6, 300 MHz) δ 7.15 (t, 2H, Ar), 7.02 (d, 4H, Ar), 6.48 (t, 1H, py), 6.47 (d, 2H, py), 4.28 (s, 4H, NCH_2), 3.31 (sept, 4H, $CHMe_2$), 1.17 (d, 12H, $CHMe_2$), 0.90 (d, 12H, $CHMe_2$), 0.27 (s, 18H, $SiMe_3$); $^{13}C\{^1H\}$ NMR δ 159.88, 148.69, 143.40, 135.88, 126.30, 124.24, 122.28, 58.78, 27.94, 25.18, 1.06; MS (EI) *m/z* 601.423 (M^+), calcd for $C_{37}H_{59}N_3Si_2$ 601.424.

(18) *mer*-(BDPP)$TaCl_3$ (**2**): ^1H NMR (C_6D_6, 300 MHz) δ 7.14 (m, 6H, Ar), 6.84 (t, 1H, py), 6.38 (d, 2H, py), 5.84 (s, 4H, NCH_2), 3.80 (sept, 4H, $CHMe_2$), 1.52 (d, 12H, $CHMe_2$), 1.12 (d, 12H, $CHMe_2$); $^{13}C\{^1H\}$ NMR δ 161.64, 148.84, 146.56, 139.66, 125.35, 122.28, 117.51, 71.78, 28.89, 27.57, 23.64. Anal. Calcd for $C_{31}H_{41}N_3TaCl_3$: C, 50.11; H, 5.56; N, 5.66. Found: C, 50.25; H, 5.68; N, 5.11.

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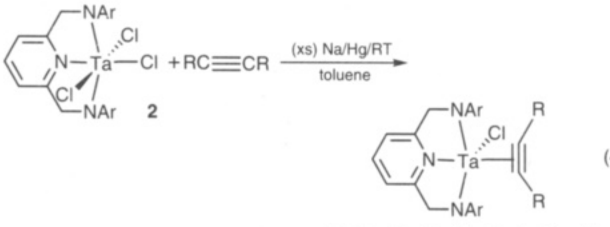
The proton and carbon NMR spectra[19] of compound **3** suggest that the meridional coordination of the BDPP ligand is retained. Furthermore, two different Ta–Me groups are observed: one trans to the pyridine of the BDPP unit and two cis. A similar restricted rotation about the N–C_{ipso} bond is proposed on the basis of the presence of diastereotopic isopropyl methyl groups. Other metathetical reactions involving larger alkylating reagents (e.g., $PhCH_2MgCl$ and Me_3SiCH_2Li) yield intractable materials.

The reduction of *mer*-(BDPP)$TaCl_3$ with excess Na/Hg in the presence of alkynes yields the pseudo five-coordinate Ta(III) derivatives (BDPP)Ta(η^2-RC≡CR)Cl (**4a**, R = Pr; **4b**, R = Et; **4c**, R = Ph) (eq 4).



(4)

4a, R = Pr; **4b**, R = Et; **4c**, R = Ph

A single low-field acetylenic carbon resonance is observed in the $^{13}C\{^1H\}$ NMR spectra[20] of complexes **4a**–**c**, suggesting that the alkyne acts as a four-electron donor.[21] The BDPP methylene protons (CH_2NAr) are diastereotopic in the ^1H NMR spectra of complexes **4a**–**c**, indicating some asymmetry above and below the N_3 plane of the ligand. However, the presence of two isopropyl methine and four isopropyl methyl resonances in the proton and carbon NMR spectra of complexes **4a**–**c** again supports the notion of a restricted rotation about the N-C_{ipso} bond. Given the above-mentioned asymmetry of the ligand and since both ends of the coordinated alkynes are equivalent by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, a rapid rotation of the alkynes on the NMR time scale is advanced.

Yellow single crystals of (BDPP)Ta(η^2-PrC≡CPr)Cl (**4a**) suitable for an X-ray analysis were grown from a saturated ether solution at −30 °C.[22] The molecular structure of complex **4a** is shown in Figure 1, and selected bond distances and angles are given in Table 1. Overall, the molecular structure is best described as a distorted square pyramid with the chloride (Cl(1)) occupying the apical position. The 4-octyne unit is located trans to the pyridine of the BDPP ligand and is rotated by 50° with respect to the Cl(1)–Ta(1)–N(2) plane (Figure 1, bottom). The bond distances in the Ta–alkyne moiety are comparable to those reported for other mononuclear Ta(III) alkyne complexes.[11,23–25]

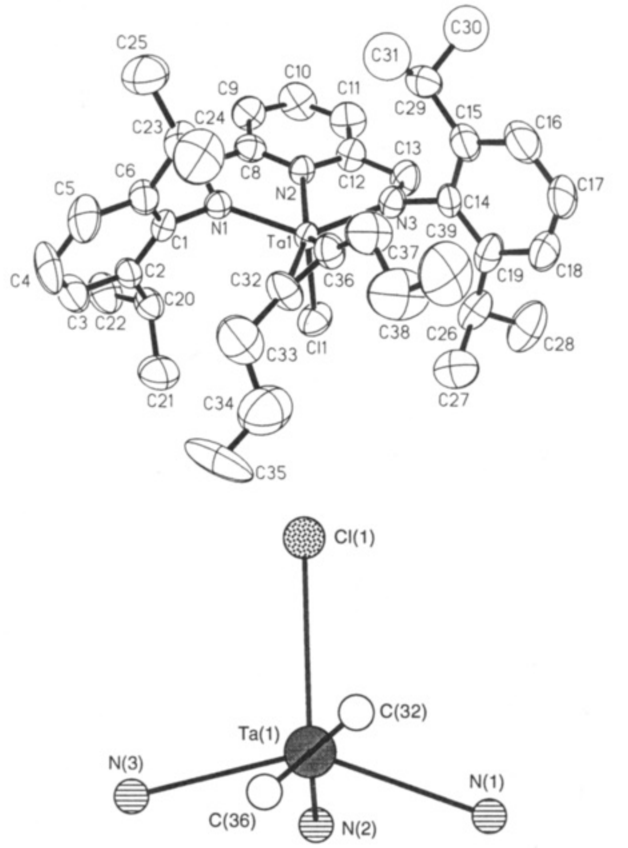


Figure 1. (top) ORTEP drawing of (BDPP)Ta(η^2-PrC≡CPr)Cl (**4a**) with thermal ellipsoids at the 50% probability level. Three orientations of C(30) and C(31) were located in the final difference Fourier map. (bottom) Chem 3D Plus representation of the core of **4a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for (BDPP)Ta(η^2-PrC≡CPr)Cl (4a)

Bond Distances			
Ta(1)–N(1)	2.053(6)	Ta(1)–N(2)	2.255(6)
Ta(1)–N(3)	2.033(6)	Ta(1)–Cl(1)	2.361(2)
Ta(1)–C(32)	2.062(7)	Ta(1)–C(36)	2.085(7)
C(32)–C(36)	1.287(11)	C(32)–C(33)	1.527(9)
C(36)–C(37)	1.522(8)	Acet*–Ta[a]	1.97
Bond Angles			
N(3)–Ta(1)–N(1)	137.2(2)	N(1)–Ta(1)–N(2)	71.4(2)
N(3)–Ta(1)–N(2)	71.9(2)	N(1)–Ta(1)–Cl(1)	106.6(2)
N(2)–Ta(1)–Cl(1)	93.7(2)	N(3)–Ta(1)–Cl(1)	96.9(2)
C(36)–C(32)–C(33)	132.6(8)	C(32)–C(36)–C(37)	137.2(8)
C(1)–N(1)–Ta(1)	126.3(5)	C(1)–N(1)–C(7)	108.7(5)
C(7)–N(1)–Ta(1)	124.5(5)	C(14)–N(3)–C(13)	109.3(6)
C(14)–N(3)–Ta(1)	130.2(5)	C(13)–N(3)–Ta(1)	120.4(5)

[a] Acet* = midpoint of C(32)–C(36).

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(19) *mer*-(BDPP)$TaMe_3$ (**3**): ^1H NMR (C_6D_6, 300 MHz) δ 7.14 (m, 6H, Ar), 6.84 (t, 1H, py), 6.63 (d, 2H, py), 5.04 (s, 4H, NCH_2), 3.56 (sept, 4H, CHMe$_2$), 1.42 (d, 12H, CHMe_2), 1.39 (s, 3H, TaMe), 1.16 (d, 12H, CHMe_2), 0.86 (s, 6H, TaMe); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.46 MHz) δ 161.27, 151.30, 145.28, 138.38, 126.36, 124.49, 116.78, 71.14, 69.09 (TaCH_3), 65.80 (TaCH_3), 28.44, 27.46, 23.95. Anal. Calcd for $C_{34}H_{50}N_3Ta$: C, 59.90; H, 7.39; N, 6.16. Found: C, 59.43; H, 7.35; N, 5.73.

(20) (BDPP)Ta(η^2-PrC≡CPr)Cl (**4a**): ^1H NMR (C_6D_6, 300 MHz) δ 7.19 (t, 2H, Ar), 7.13 (d, 4H, Ar), 6.85 (t, 1H, py), 6.39 (d, 2H, py), 5.12 (AB quartet, $^2J_{HH}$ = 20.1, 4H, NCH_2), 3.79 (sept, 2H, CHMe$_2$), 3.15 (sept, 2H, CHMe$_2$), 2.51 (m, 4H, ≡CCH_2), 1.46 (d, 6H, CHMe_2), 1.34 (m, 4H, CH_2CH$_3$), 1.32 (d, 6H, CHMe_2), 1.24 (d, 6H, CHMe_2), 1.01 (d, 6H, CHMe_2), 0.84 (t, 6H, CH$_2$$CH_3$); $^{13}C\{^1H\}$ NMR δ 237.01 (C≡C), 160.77, 154.41, 145.19, 138.41, 125.49, 124.32, 123.57, 116.99, 70.95, 40.02, 28.60, 27.95, 26.66, 25.76, 24.61, 23.80, 21.94, 15.45. Anal. Calcd for $C_{39}H_{55}N_3TaCl$: C, 59.88; H, 7.09; N, 5.37. Found: C, 59.62; H, 7.19; N, 5.16. Spectroscopic details for compounds **4b** and **4c** are available in the supporting information.

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(22) X-ray data for (BDPP)Ta(η^2-PrC≡CPr)Cl (**4a**): Data were collected at 23 °C on a Siemens P4 diffractometer using graphite-monochromated Mo Kα radiation. A total of 6078 reflections were collected in the θ range 1.9–23°, of which 5179 were unique (R_{int} = 0.0284). The structure was solved by a combination of Patterson and difference Fourier techniques. Non-hydrogen atoms were refined anisotropically, except C(30) and C(31), which were refined isotropically. In the final least-squares refinement cycle on F^2, the model converged at R1= 0.0401, wR2 = 0.0946, and GOF = 1.037 for 4463 reflections with $F_o \geq 4\sigma(F_o)$ and 408 parameters. Crystal data: a = 9.936(2) Å, b = 11.558(1) Å, c = 17.689(2) Å, α = 74.997(6)°, β = 87.424(10)°, γ = 75.372(9)°, V = 1898.0(5) $Å^3$, space group $P\bar{1}$, Z = 2, mol wt 792.36, and ρ(calcd) = 1.386 g/cm^3.

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Each amide is sp^2-hybridized, as evidenced by the sum of the angles about each nitrogen (N(1) = 359.5° and N(3) = 359.9°). The rigid coordination of the ligand and enforced location of the aryl isopropyl groups creates a "pocket" opposite the pyridine and necessarily protects the metal above and below the N_3 plane.

Finally, we are also exploring the catalytic activity of derivatives of complex **4a**.[26] The alkyl complexes (BDPP)Ta(η^2-PrC≡CPr)R (R = alkyl), where the apical chloride has been replaced with an alkyl group, are being pursued as alkyne polymerization catalysts.[1-3] In addition, we are exploring the catalytic alkyne cyclization[1,4] reactivity of *in situ* prepared cationic derivatives (e.g., $[(BDPP)Ta(\eta^2\text{-PrC}{\equiv}\text{CPr})]^+$).

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Supporting Information Available: Text giving experimental details for compounds **1**–**3** and **4a**–**c** and tables of crystal data, data collection details, final positional parameters, all bond distances and angles, torsion angles, and least-squares planes for **4a** (15 pages). Ordering information is given on any current masthead page.

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