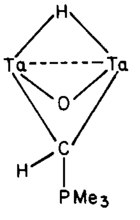
asymmetric (four-electron) system Ta(1)–C(1)–Ta(2) and the asymmetric (two-electron) system Ta(1)–H–Ta(2).

It is also worthy of note that the Ta(1)···Ta(2) distance of 2.992 (1) Å is ~0.12 Å greater than the Ta–Ta single bond length of ~2.872 Å predicted from the average Ta–Cl distance of 2.426 Å found in the present complex and the accepted covalent radius for chlorine of 0.99 Å.[19] This difference of ~0.12 Å is precisely that which we found between M–(H)–M and M–M distance in a variety of $\mu_2$-hydrido-bridged species.[20]

It would appear that the present complex has sufficiently unusual characteristics as to merit a *neutron*-diffraction study.

The analysis strongly suggests that the complex should be written as $[(\eta^5\text{-}C_5Me_4Et)TaCl_2]_2(\mu\text{-}H)(\mu\text{-}CHPMe_3)(\mu\text{-}O)$ with a central *core* as in **4**. Angles at the bridging atoms are as follows: Ta(1)–C(1)–Ta(2) = 82.3 (6)° and Ta(1)–O–Ta(2) = 101.9 (5)°. The geometry of this bridge is illustrated in Figure 5.



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Other points of interest are as follows: (1) The C(1)···O distance in the "disrupted formyl" system is 2.580 (20) Å.

(2) The >CH–PMe₃ system is best regarded as a phosphonium ylide, the C(1)–P distance of 1.751 (19) Å being substantially shorter than the three equivalent P–Me distances [P–C(2) = 1.846 (26) Å, P–C(3) = 1.835 (21) Å, and P–C(4) = 1.838 (22) Å]. A similar pattern was found within the $Fe_2(CO)_6[C(CHO)P(Ph_2C_6H_4)]$ molecule.[21]

(3) The cyclopentadienyl systems are planar within the limits of experimental error (cf. Table VI). In each case the substituents are displaced from the pentaatomic carbocyclic system with the terminal $CH_3$ group of the $CH_2CH_3$ group pointing directly *away* from the appropriate tantalum atom.

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**Registry No.** **2**, 74167-07-0.

**Supplementary Material Available:** Listings of observed and calculated structure factors and data-processing formulas (15 pages). Ordering information is given on any current masthead page.

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(19) Pauling, L. "The Nature of the Chemical Bond", 2nd ed.; Cornell University Press: Ithaca, N.Y., 1960; Table 7-2, p 224.

(20) Churchill, M. R. *Adv. Chem. Ser.* **1978**, *No. 167*, 36–60.

(21) Churchill, M. R.; Rotella F. J. *Inorg. Chem.* **1978**, *17*, 2614–2621.

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# Synthesis of Alkyne Complexes of the Type $Ta(\eta^5\text{-}C_5Me_5)(alkyne)Cl_2$ and Crystal Structure of $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$

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$Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$ complexes (olefin = styrene or cyclooctene) react with alkynes (PhC≡CPh, PhC≡CH, 2-butyne, 3-hexyne, HC≡CH) to give analogous $Ta(\eta^5\text{-}C_5Me_5)(alkyne)Cl_2$ complexes which do not react with additional alkyne, CO, HCl, or ethylene with one exception; $Ta(\eta^5\text{-}C_5Me_5)(HC{\equiv}CH)Cl_2$ reacts with ethylene at 80 °C to give $(\eta^5\text{-}C_5Me_5)Cl_2\overline{TaCH{=}CHCH_2CH_2}$ irreversibly. The diphenylacetylene ligand in $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$ is bonded parallel to the $\eta^5\text{-}C_5Me_5$ ring with a long "acetylenic" linkage (1.337 (8) Å) and short Ta–C(alkyne) bonds (2.067 (6) Å and 2.075 (6) Å), consistent with it being a 4-electron donor. The lack of reactivity of these alkyne complexes is postulated to be due to this strong metal–alkyne bond.

## Introduction

We recently prepared several benzyne complexes of the type $M(\eta^5\text{-}C_5Me_5)(C_6H_4)X_2$ (M = Nb, X = Me; M = Ta, X = Cl or Me).[1] An X-ray structure of one of them[2] (M = Ta, X = Me) showed that the benzyne ligand was oriented perpendicular to the $\eta^5\text{-}C_5Me_5$ ring. This would be unusual if the benzyne ligand were behaving strictly as an alkyne because simple alkyne (and olefin) ligands bond more or less parallel to the ring in monocyclopentadienyl complexes of many metals. Therefore we became interested in making analogous complexes of "normal" alkynes in order to compare them structurally and chemically with the benzyne complexes. At first this did not seem as though it would be a simple task. We thought that the obvious route, displacement of an olefin from $Ta(\eta^5\text{-}C_5Me_5)(olefin)Cl_2$,[3] would not work since the resulting acetylene complex should react with a second equivalent of acetylene to give a tantalacyclopentadiene complex. However, this approach was successful since the alkyne complexes, like the benzyne complexes, are surprisingly unreactive. We report here the preparation and characterization of several alkyne complexes of this type, including one of acetylene itself, along with an X-ray structural study of the diphenylacetylene complex.

## Results

**Preparation and Reactions of $Ta(\eta^5\text{-}C_5Me_5)(alkyne)Cl_2$ Complexes.** When 1 equiv of diphenylacetylene was added to a toluene solution of $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$, the color slowly changed from purple to red-orange over several hours. Removal of the solvent in vacuo gave an orange, crystalline

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(1) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263–265.

(2) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697–1702.

(3) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558–4570.

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**Table I.** $^{13}C$ NMR Chemical Shifts of $Ta(\eta^5\text{-}C_5Me_5)(alkyne)X_2$ Complexes[a]

| complex | solvent | $C_{alkyne}$ | $C_5Me_5$ | other |
|---|---|---|---|---|
| $Ta(\eta^5\text{-}C_5Me_5)(PhCCPh)Cl_2$ | $CD_2Cl_2$ | 222.3 | 121.8, 12.2 | 141.2 ($C_{ipso}$), 130.3, 128.7, 129.1 |
| $Ta(\eta^5\text{-}C_5Me_5)(MeCCMe)Cl_2$ | $C_6D_6$ | 226.7 | 119.7, 11.5 | 21.2 |
| $Ta(\eta^5\text{-}C_5Me_5)(EtCCEt)Cl_2$ | $CDCl_3$ (−10 °C) | 231.4 | 120.0, 11.7 | 14.2 ($CH_3$), 30.9 ($CH_2$) |
| $Ta(\eta^5\text{-}C_5Me_5)(PhCCH)Cl_2$ | $CDCl_3$ | 215.0 (CH),[b] 228.3 (CPh) | 120.8, 11.9 | 138.3, 132.4, 129.5, 128.6 |
| $Ta(\eta^5\text{-}C_5Me_5)(EtCCEt)Br_2$ | $CDCl_3$ | 234.0 | 120.1, 12.3 | 14.2, 32.1 |
| $Ta(\eta^5\text{-}C_5Me_5)(HCCH)Cl_2$ | $C_6D_6$ | 218.1[c] | 120.4, 11.9 | |
| $Ta(\eta^5\text{-}C_5Me_5)(PhCCPh)(OMe)Cl$ | $CDCl_3$ (−10 °C) | 207.8 | 118.2, 11.3 | 140.3, 129.6, 128.2, 127.6, 62.9 (OMe) |
| $Ta(\eta^5\text{-}C_5Me_5)(PhCCPh)(OMe)Cl$ | $CDCl_3$ (−70 °C) | 206.3, 204.5 | 117.8, 11.3 | 139.6, 138.8, 129.8, 128.1[d] |
| $Ta(\eta^5\text{-}C_5Me_5)(PhCCPh)(OMe)_2$ | $CDCl_3$ | 210.1 | 116.8, 10.9 | 142.4, 128.4, 128.1, 126.4, 61.3 (OMe) |
| $Ta(\eta^5\text{-}C_5Me_5)(benzyne)Cl_2$[1] | $C_6D_6$ | 230.5 | 115.3, 11.0 | 131.8, 132.4, 52.7 (TaMe) |

[a] Spectra were recorded at 22.5 MHz and 38 °C in ppm downfield from $Me_4Si$ unless otherwise noted. Coupling constants were obtained from gated $^1H$-decoupled spectra and were normal in all cases: for $C_{aliphatic}$, $J_{CH} \approx 126$ Hz; for $OCH_3$, $J_{CH} \approx 140$ Hz; for TaMe, $J_{CH} = 120$ Hz. [b] $J_{CH} = 183$ Hz. [c] $J_{CH} = 189$ Hz. [d] Not all phenyl carbon resonances could be resolved at this field strength. At this temperature the δ 128.1 peak is broad.

solid whose $^{13}C\{^1H\}$ NMR spectrum was characteristic of a complex of diphenylacetylene of the type $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$. Displacement of olefin by an alkyne proved to be a general reaction for $Ta(\eta^5\text{-}C_5Me_5)(olefin)X_2$ complexes, where the olefin can be (most conveniently) styrene or cyclooctene and X can be Cl or Br (eq 1).[3] We have prepared

$$Ta(\eta^5\text{-}C_5Me_5)(olefin)X_2 + alkyne \rightarrow Ta(\eta^5\text{-}C_5Me_5)(alkyne)X_2 + olefin \quad (1)$$

examples containing 2-butyne (X = Cl), 3-hexyne (X = Cl or Br), phenylacetylene (X = Cl), and acetylene itself (X = Cl). The $^{13}C\{^1H\}$ NMR spectra all exhibit characteristic resonances which are easily assigned on the basis of their chemical shifts and C–H coupling constants (Table I). In all cases the acetylenic carbon resonances fall in the range 200–250 ppm.

The rate of formation of these acetylene complexes varies with the halide (Cl > Br) and the acetylene ($HC{\equiv}CH > RC{\equiv}CR \approx PhC{\equiv}CH \gg PhC{\equiv}CPh$). The latter could be attributed almost entirely to steric factors. That this is the case is suggested by the fact that $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$ did not react with neat $Me_3SiC{\equiv}CSiMe_3$ in 48 h at 60 °C.

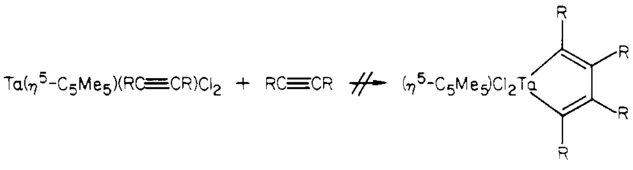
The diphenylacetylene (tolane) complex reacts cleanly with 1 or 2 equiv of NaOMe to give the corresponding monomethoxy and dimethoxy species in high yield (eq 2). In

$$Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2 + y NaOMe \rightarrow Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_{2-y}(OMe)_y \quad (2)$$

$$y = 1, 2$$

$Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)(Cl)(OMe)$ the two acetylenic carbon atoms are inequivalent at −70 °C. The signals for them coalesce at −55 °C ($\Delta G^{\ddagger} = 11 \pm 1$ kcal $mol^{-1}$) to give a single resonance at 208 ppm (−10 °C).

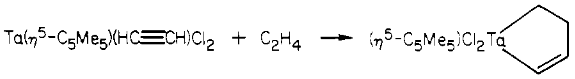
$Ta(\eta^5\text{-}C_5Me_5)(acetylene)X_2$ complexes are quite stable thermally and, except for sensitivity to oxygen in solution, fairly unreactive. Solutions can be heated for 48 h at 110 °C without change. Samples of the diphenylacetylene complex plus 2-butyne and the 2-butyne complex plus diphenylacetylene showed no evidence for acetylene exchange after 48 h at 60 °C. Surprisingly, no alkyne complex reacted readily with more alkyne to give a tantalacyclopentadiene complex (eq 3). Also



(3)

none (except the acetylene complex; see below) reacts with 40 psi of $H_2$, CO, or $C_2H_4$ in 48 h at 110 °C, and even after several hours the acetylene complex is unchanged in the presence of HCl in ether.

The exception to the above list of nonreactions is the reaction of $Ta(\eta^5\text{-}C_5Me_5)(HC{\equiv}CH)Cl_2$ with ethylene (40 psi). In 8 h at 80 °C a green, crystalline complex forms whose $^{13}C\{^1H\}$ NMR spectrum exhibits four resonances in addition to the two at 124.0 and 12.3 ppm due to the $\eta^5\text{-}C_5Me_5$ ligand. In the $^1H$ gated decoupled $^{13}C$ spectrum, the resonances at 210.7 and 150.8 ppm appear as doublets ($^1J_{CH} = 140 \pm 5$ Hz) while those at 96.9 and 44.1 ppm appear as triplets ($^1J_{CH} = 123 \pm 5$ Hz). Therefore they are assigned to the olefinic carbon atoms, $C_{\alpha}^{ol}$ and $C_{\beta}^{ol}$, and the aliphatic carbon atoms, $C_{\alpha}$ and $C_{\beta}$, respectively, in a tantalacyclopentene complex (eq 4). The high-field



(4)

$^1H$ NMR spectrum (250 MHz, 68 °C) consists of an AB pattern centered at δ 7.93 (2 H), a broad multiplet at δ 3.31 (2 H), and a broad triplet at δ 2.70 (2 H). The AB pattern we ascribe to the protons attached to $C_{\alpha}^{ol}$ and $C_{\beta}^{ol}$ and the two other resonances to the protons attached to $C_{\alpha}$ (at δ 3.31) and $C_{\beta}$ (at δ 2.70).

**Crystal Structure of $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$.** An X-ray structural determination (see Experimental Section) yielded the results listed in Tables II–VII and Figures 1–4.

The molecule contains a central tantalum atom linked to an $\eta^5\text{-}C_5Me_5$ ligand, a $PhC{\equiv}CPh$ ligand, and two chloride ions. The coordination geometry about the tantalum atom may be viewed (in the simplest possible description) as pseudotetrahedral. Within the framework of this description, the appropriate angles between "Cp" (the centroid of the cyclopentadienyl ring), "Ac" (the midpoint of the C(11)–C(21) linkage), and the two chloride ligands are Cp–Ta–Ac = 116.11°, Cp–Ta–Cl(1) = 114.67°, Cp–Ta–Cl(2) = 115.70°, Ac–Ta–Cl(1) = 106.73°, Ac–Ta–Cl(2) = 104.39°, and Cl(1)–Ta–Cl(2) = 97.08°.

The tantalum–chlorine bond lengths observed in $Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}PhC{\equiv}CPh)Cl_2$ (Ta–Cl(1) = 2.355 (2) Å and Ta–Cl(2) = 2.352 (2) Å) are comparable to those found in $(\eta^5\text{-}C_5Me_5)Cl_2\overline{TaCH_2CH_2CH_2CH_2}$ (Ta–Cl = 2.366 (2) Å)[4] and $(\eta^5\text{-}C_5Me_5)Cl_2\overline{TaCH_2CH(C_3H_6)CHCH_2}$ (Ta–Cl = 2.375 (2) and 2.362 (2) Å)[4] but are substantially shorter than the tantalum–chlorine linkage found in $Ta(\eta^5\text{-}C_5Me_5)({\equiv}CPh)(PMe_3)_2Cl$ (Ta–Cl = 2.548 (2) Å).[5,6]

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(4) (a) Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 6462–6463. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3106.

(5) McLain, S. J.; Wood, C. D.; Messerle, L. W.; Schrock, R. R.; Hollander, F. J.; Youngs, W. J.; Churchill, M. R. *J. Am. Chem. Soc.* **1978**, *100*, 5962–5964.

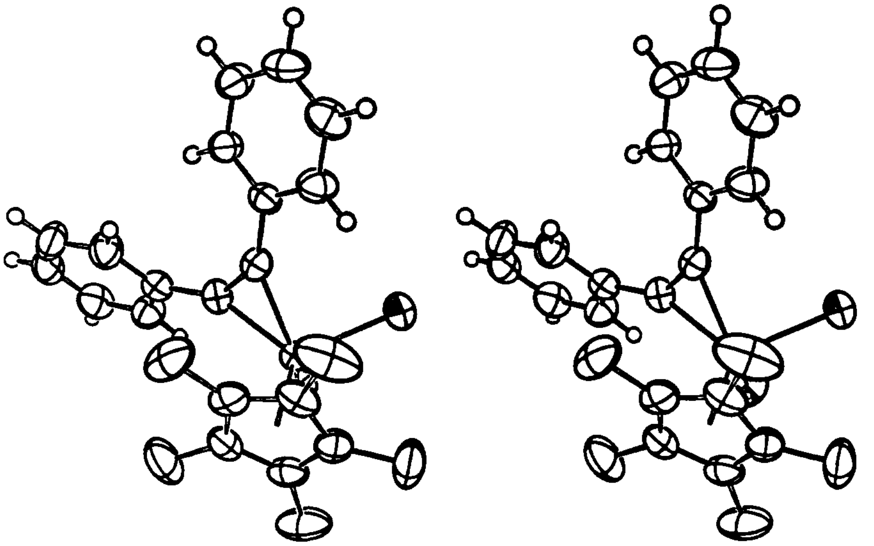

**Figure 1.** Stereoscopic view of the Ta($\eta^5$-$C_5Me_5$)($\eta^2$-PhC≡CPh)$Cl_2$ molecule, showing the coordination geometry about the tantalum atom (ORTEP-II diagram).

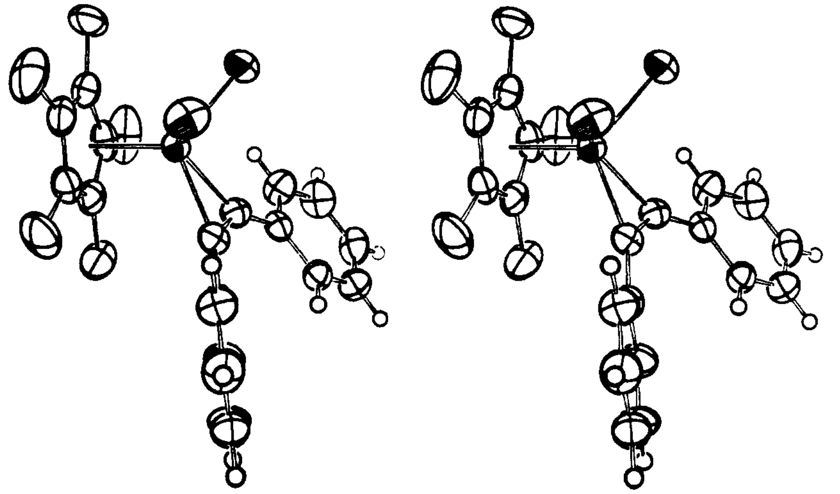

**Figure 2.** Stereoscopic view of the Ta($\eta^5$-$C_5Me_5$)($\eta^2$-PhC≡CPh)$Cl_2$ molecule showing the diphenylacetylene ligand (ORTEP-II diagram).

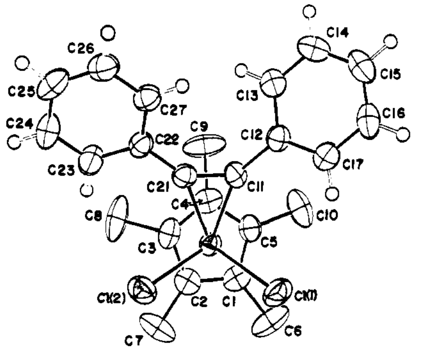

**Figure 3.** The Ta($\eta^5$-$C_5Me_5$)($\eta^2$-PhC≡CPh)$Cl_2$ molecule, projected onto the plane of the $\eta^5$-$C_5Me_5$ ring.

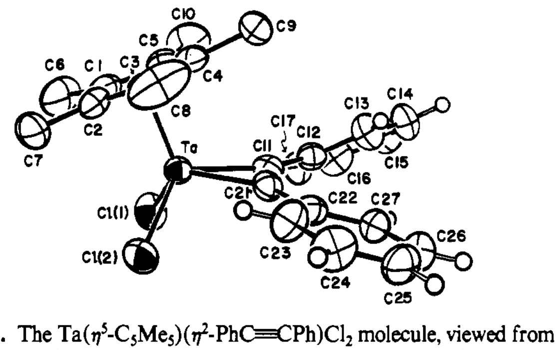

**Figure 4.** The Ta($\eta^5$-$C_5Me_5$)($\eta^2$-PhC≡CPh)$Cl_2$ molecule, viewed from the side and showing the stereochemistry about the tantalum atom.

The $\eta^5$-$C_5Me_5$ ligand is entirely normal. Individual tantalum–carbon bonding distances for the $\eta^5$-pentamethylcyclopentadienyl ligand are Ta–C(1) = 2.435 (6) Å, Ta–C(2) = 2.435 (6) Å, Ta–C(3) = 2.403 (6) Å, Ta–C(4) = 2.422 (6) Å, and Ta–C(5) = 2.404 (6) Å. The root-mean-square deviation from planarity is 0.011 Å for the five atoms of the carbocyclic ring, and the tantalum atom lies 2.102 (2) Å from the cyclopentadienyl plane. The methyl groups of the $\eta^5$-$C_5Me_5$ ligand are displaced from the plane of the carbocyclic ring away from the tantalum atom (see Table VI (C)). Carbon–carbon bond lengths within the $\eta^5$-$C_5Me_5$ ligand are normal, with C(ring)–C(ring) distances ranging from 1.396 (10) to 1.423 (10) Å; the mean value is 1.413 [11] Å. The C(ring)–Me distances range from 1.513 (10) to 1.544 (11) Å, the mean value being 1.528 [11] Å.

The PhC≡CPh ligand is bonded to the tantalum atom symmetrically, the tantalum–carbon bond lengths being Ta–C(11) = 2.067 (6) Å and Ta–C(21) = 2.075 (6) Å. The "acetylenic" linkage (C(11)–C(21) = 1.337 (8) Å) is substantially greater than that in a free acetylene and is close to

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(6) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 171–176.

**Table II.** Final Positional and Isotropic Thermal Parameters, with Esd's

| atom | *x* | *y* | *z* |
|---|---|---|---|
| Ta | 0.23351 (1) | 0.93431 (3) | 0.42371 (2) |
| Cl(1) | 0.31382 (11) | 0.08513 (17) | 0.33033 (13) |
| Cl(2) | 0.11508 (10) | 0.97910 (18) | 0.34020 (12) |
| C(1) | 0.2614 (4) | 0.0967 (7) | 0.5574 (4) |
| C(2) | 0.1810 (4) | 0.0674 (7) | 0.5600 (4) |
| C(3) | 0.1723 (4) | 0.9186 (7) | 0.5791 (4) |
| C(4) | 0.2476 (4) | 0.8578 (7) | 0.5902 (4) |
| C(5) | 0.3037 (4) | −0.0320 (7) | 0.5734 (4) |
| C(6) | 0.2968 (6) | 0.2463 (8) | 0.5450 (6) |
| C(7) | 0.1134 (5) | 1.1744 (9) | 0.5499 (5) |
| C(8) | 0.0945 (4) | 0.8397 (11) | 0.5999 (5) |
| C(9) | 0.2658 (6) | 0.7037 (8) | 0.6196 (5) |
| C(10) | 0.3921 (4) | 0.9540 (10) | 0.5813 (6) |
| C(11) | 0.2986 (3) | 0.7545 (6) | 0.3892 (4) |
| C(12) | 0.3748 (3) | 0.6856 (7) | 0.3741 (4) |
| C(13) | 0.3889 (4) | 0.5433 (7) | 0.4004 (5) |
| C(14) | 0.4603 (4) | 0.4797 (8) | 0.3858 (5) |
| C(15) | 0.5199 (4) | 0.5545 (8) | 0.3432 (5) |
| C(16) | 0.5084 (4) | 0.6942 (9) | 0.3181 (5) |
| C(17) | 0.4367 (4) | 0.7599 (7) | 0.3341 (5) |
| C(21) | 0.2225 (3) | 0.7188 (6) | 0.3888 (4) |
| C(22) | 0.1712 (3) | 0.5980 (6) | 0.3646 (4) |
| C(23) | 0.0907 (4) | 0.6063 (7) | 0.3841 (5) |
| C(24) | 0.0413 (4) | 0.4939 (9) | 0.3599 (5) |
| C(25) | 0.0705 (5) | 0.3729 (8) | 0.3167 (5) |
| C(26) | 0.1494 (4) | 0.3640 (7) | 0.2980 (5) |
| C(27) | 0.1992 (4) | 0.4753 (6) | 0.3210 (4) |
| H(13)[a] | 0.3479 | 0.4893 | 0.4292 |
| H(14) | 0.4685 | 0.3831 | 0.4052 |
| H(15) | 0.5688 | 0.5093 | 0.3313 |
| H(16) | 0.5498 | 0.7469 | 0.2893 |
| H(17) | 0.4299 | 0.8579 | 0.3171 |
| H(23) | 0.0700 | 0.6895 | 0.4140 |
| H(24) | −0.0132 | 0.5005 | 0.3731 |
| H(25) | 0.0365 | 0.2959 | 0.2999 |
| H(26) | 0.1698 | 0.2799 | 0.2687 |
| H(27) | 0.2535 | 0.4675 | 0.3066 |

[a] For all H atoms $B_{iso} = 5.0$ Å$^2$.

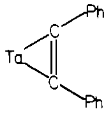
the value expected for a free olefinic linkage. The angles C(21)–C(11)–C(12) = 138.5 (5)° and C(22)–C(21)–C(11) = 140.3 (5)° show the large deviation of the C(ipso) atoms from collinearity with the C(11)–C(21) linkage. Other distances and angles within the $PhC\equiv CPh$ system are in the expected ranges. The "acetylenic" carbons, C(11) and C(21), are bonded to their respective phenyl rings with C(11)–C(12) = 1.465 (8) Å and C(21)–C(22) = 1.462 (8) Å.

The internal angle at C(12), ∠C(13)–C(12)–C(17), is reduced to 116.9 (6)°, and the angle at the para carbon is ∠C(14)–C(15)–C(16) = 119.5 (7)°; angles at the ortho carbons [∠C(12)–C(13)–C(14) = 121.6 (6)° and ∠C(12)–C(17)–C(16) = 121.2 (6)°] and at the meta carbon atoms [∠C(13)–C(14)–C(15) = 120.3 (7)° and ∠C(15)–C(16)–C(17) = 120.4 (6)°] are internally consistent. Similarly, the internal angle at C(22), ∠C(23)–C(22)–C(27), is reduced to 118.1 (5)°, and the angle at the para carbon is ∠C(24)–C(25)–C(26) = 119.5 (7)°; angles at the ortho carbons [∠C(22)–C(23)–C(24) = 120.5 (6)° and ∠C(26)–C(27)–C(22) = 120.8 (6)°] and at the meta carbon atoms [∠C(23)–C(24)–C(25) = 120.3 (7)° and ∠C(25)–C(26)–C(27) = 120.9 (6)°] are also internally consistent. Angles at the ortho and para carbon atoms of both phenyl rings are, presumably, increased from the ideal trigonal value of 120.00° principally to compensate for the compression at C(12) and C(22).

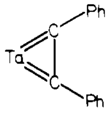
The phenyl group attached to C(11) has a root-mean-square deviation from planarity of 0.008 Å. Carbon–carbon distances within this phenyl ring range from 1.361 (11) to 1.395 (9) Å, the mean value being 1.377 [13] Å. For the phenyl group attached to C(21), the root-mean-square deviation from planarity is only 0.002 Å. Carbon–carbon distances range from 1.371 (11) to 1.399 (9) Å, the mean value being 1.380 [10] Å.

## Discussion

The tantalum-to-tolane bond lengths are comparable to the tantalum-to-benzyne bond lengths observed in $Ta(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}C_6H_4)Me_2$[2] (2.067 (6) and 2.075 (6) vs. 2.059 (4) and 2.091 (4) Å, respectively). In each case, too, the $C\equiv C$ bond length is anomalously long. These parameters closely resemble those found by Cotton and Hall for $[pyH^+][TaCl_4(py)(PhC\equiv CPh)^-]$.[7] These workers concluded that the bonding of the diphenylacetylene ligand to the otherwise electron-deficient tantalum involved the acetylene acting as a 4-electron donor; a bonding scheme involving contributions from both **1** and **2** was invoked. Other examples of an acetylene acting as a "4-electron donor" are $W(CO)(HC\equiv CH)(S_2CNEt_2)_2$[8] and similar complexes.[9] Recently Templeton has suggested that the degree to which an alkyne acts as a greater than 2-electron donor correlates with the chemical shift of the alkyne carbon atoms. By this criterion it is clear that our complexes contain alkynes which are 4-electron donors. Examples where the alkyne is acting as a 2-electron donor (e.g., $Nb(\eta^5\text{-}C_5H_5)_2(PhC\equiv CPh)(O_2CCH_3)$)[10] are 18-electron species and cannot accept any additional electron density from the triple bond.



1



2

We might then ascribe the lack of reactivity of these complexes to the strong metal–acetylene bond and the fact that the product could easily have a lower total valence-electron count. An example of the latter is a 14-electron tantalacyclopentadiene complex. Formation of it then would involve a change in electron count from 16 to 14. Yet the tantalacyclo*pentene* complex is also a 14-electron species and it does not readily lose ethylene to give back the acetylene complex. Therefore the formation of complexes with lower electron counts alone cannot explain why these acetylene complexes are so reluctant to react with more acetylene (or CO, HCl, etc.). Other complexes containing an alkyne that behaves as a 4-electron donor are similarly unreactive.

The orientation of the tolane ligand parallel to the $\eta^5\text{-}C_5Me_5$ ring is the more plausible orientation for steric reasons and the one we expected. We believe the other alkynes, including acetylene itself, also bond parallel to the $\eta^5\text{-}C_5Me_5$ ring. We believe the benzyne ligand bonds "perpendicular" to the $\eta^5\text{-}C_5Me_5$ ring in the solid state[2] because the metal in the pseudo-tetragonal-pyramidal complex thereby can best acquire even more electron density from the π-electron cloud of the benzyne ring and an electron count higher than 16. This must not be an especially strong additional bonding interaction since the benzyne ring rotates readily on the NMR time scale ($\Delta G^{\ddagger} \lesssim 9$ kcal mol$^{-1}$) and the benzyne complex also reacts irreversibly with ethylene to give a benzotantalacyclopentene complex.

## Experimental Section

General procedures can be found elsewhere.[3] Published procedures were used to prepare $Ta(\eta^5\text{-}C_5Me_5)(propylene)Cl_2$, $Ta(\eta^5\text{-}C_5Me_5)(styrene)Cl_2$, $Ta(\eta^5\text{-}C_5Me_5)(cyclooctene)Cl_2$, and $Ta(\eta^5\text{-}C_5Me_5)$(1-

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Table III. Final Anisotropic Thermal Parameters for Nonhydrogen Atoms[a] with Esd's

| atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Ta | 2.687 (12) | 2.691 (12) | 2.455 (12) | −0.155 (10) | 0.115 (7) | 0.176 (9) |
| Cl(1) | 5.01 (9) | 3.74 (8) | 4.84 (8) | −0.50 (7) | 1.56 (7) | 0.94 (7) |
| Cl(2) | 3.95 (8) | 4.32 (8) | 4.57 (8) | 0.53 (6) | −1.16 (6) | 0.01 (6) |
| C(1) | 5.5 (4) | 3.6 (3) | 2.7 (3) | −0.6 (3) | −0.3 (3) | −0.4 (2) |
| C(2) | 4.4 (3) | 4.1 (3) | 2.6 (3) | 0.4 (3) | 0.2 (2) | −0.7 (3) |
| C(3) | 3.9 (3) | 5.3 (4) | 2.5 (3) | −1.3 (3) | 0.3 (2) | −0.0 (3) |
| C(4) | 5.8 (4) | 3.6 (3) | 2.0 (3) | 0.0 (3) | 0.1 (2) | −0.0 (2) |
| C(5) | 3.3 (3) | 4.5 (4) | 3.4 (3) | −0.3 (3) | −0.7 (2) | −0.4 (3) |
| C(6) | 10.7 (6) | 3.8 (4) | 5.4 (4) | −2.8 (4) | −0.1 (4) | −0.2 (3) |
| C(7) | 6.2 (4) | 7.2 (5) | 4.4 (3) | 3.9 (4) | −0.6 (3) | −0.3 (3) |
| C(8) | 5.4 (4) | 10.9 (6) | 4.9 (4) | −4.5 (4) | 2.3 (3) | −1.9 (4) |
| C(9) | 12.0 (6) | 3.4 (4) | 3.4 (3) | 1.1 (4) | −0.2 (4) | 0.8 (3) |
| C(10) | 3.4 (3) | 9.7 (6) | 6.0 (4) | 0.8 (4) | −1.2 (3) | −0.9 (4) |
| C(11) | 2.7 (3) | 3.7 (3) | 2.1 (2) | 0.1 (2) | 0.6 (2) | 0.5 (2) |
| C(12) | 3.0 (3) | 3.4 (3) | 2.8 (2) | −0.2 (2) | 0.0 (2) | 0.1 (2) |
| C(13) | 3.5 (3) | 4.2 (4) | 5.1 (4) | 0.0 (3) | 0.2 (3) | 0.5 (3) |
| C(14) | 4.9 (4) | 3.7 (3) | 5.5 (4) | 1.3 (3) | −0.2 (3) | 0.4 (3) |
| C(15) | 3.2 (3) | 5.6 (4) | 4.6 (3) | 1.1 (3) | −0.0 (3) | −1.1 (3) |
| C(16) | 2.9 (3) | 5.7 (4) | 4.8 (3) | −0.5 (3) | 0.8 (2) | −0.6 (3) |
| C(17) | 3.7 (3) | 3.5 (3) | 4.5 (3) | −0.2 (3) | 0.4 (2) | 0.1 (3) |
| C(21) | 3.3 (3) | 2.9 (3) | 2.8 (2) | 0.0 (2) | 0.3 (2) | 0.5 (2) |
| C(22) | 3.2 (3) | 3.0 (3) | 2.8 (3) | −0.5 (2) | −0.5 (2) | 0.3 (2) |
| C(23) | 3.7 (3) | 4.1 (3) | 4.6 (3) | −0.8 (3) | 0.4 (3) | −0.6 (3) |
| C(24) | 3.4 (3) | 5.4 (4) | 5.5 (4) | −1.4 (3) | 0.3 (3) | 0.1 (3) |
| C(25) | 6.1 (4) | 3.4 (3) | 4.2 (3) | −1.7 (3) | −0.6 (3) | −0.1 (3) |
| C(26) | 4.9 (4) | 3.3 (3) | 4.4 (3) | 0.1 (3) | −0.3 (3) | −0.2 (3) |
| C(27) | 3.8 (3) | 3.0 (3) | 3.4 (3) | −0.2 (2) | −0.3 (2) | −0.2 (2) |

[a] The anisotropic thermal parameters are in the form $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

Table IV. Intramolecular Distances, with Esd's, for Ta($\eta^5$-$C_5Me_5$)($C_6H_5C$≡$CC_6H_5$)$Cl_2$ (Å)

| | | | |
|---|---|---|---|
| (A) Distances from the Tantalum Atom | | | |
| Ta–Cl(1) | 2.355 (2) | Ta–C(1) | 2.435 (6) |
| Ta–Cl(2) | 2.352 (2) | Ta–C(2) | 2.435 (6) |
| Ta–C(11) | 2.067 (6) | Ta–C(3) | 2.403 (6) |
| Ta–C(21) | 2.075 (6) | Ta–C(4) | 2.422 (6) |
| Ta–Cp[a] | 2.100 | Ta–C(5) | 2.404 (6) |
| Ta–Ac[b] | 1.960 | | |
| (B) Distances within the $C_6H_5C$≡$CC_6H_5$ Ligand | | | |
| C(11)–C(21) | 1.337 (8) | | |
| C(11)–C(12) | 1.465 (8) | C(21)–C(22) | 1.462 (8) |
| C(12)–C(13) | 1.395 (9) | C(22)–C(23) | 1.399 (9) |
| C(13)–C(14) | 1.370 (10) | C(23)–C(24) | 1.384 (10) |
| C(14)–C(15) | 1.368 (10) | C(24)–C(25) | 1.372 (10) |
| C(15)–C(16) | 1.361 (11) | C(25)–C(26) | 1.371 (11) |
| C(16)–C(17) | 1.385 (9) | C(26)–C(27) | 1.375 (9) |
| C(17)–C(12) | 1.380 (8) | C(27)–C(22) | 1.381 (8) |
| (C) Distances within the Pentamethylcyclopentadienyl System | | | |
| C(1)–C(2) | 1.396 (10) | C(1)–C(6) | 1.529 (10) |
| C(2)–C(3) | 1.421 (10) | C(2)–C(7) | 1.529 (10) |
| C(3)–C(4) | 1.408 (10) | C(3)–C(8) | 1.544 (11) |
| C(4)–C(5) | 1.423 (10) | C(4)–C(9) | 1.524 (10) |
| C(5)–C(1) | 1.416 (9) | C(5)–C(10) | 1.513 (10) |

[a] Cp is the centroid of the pentaatomic carbocyclic ring, defined by C(1) → C(5). [b] Ac is the midpoint of the C(11)–C(21) acetylenic linkage.

Table V. Selected Interatomic Angles, with Esd's, for Ta($\eta^5$-$C_5Me_5$)($C_6H_5C$≡$CC_6H_5$)$Cl_2$ (Deg)

| | | | |
|---|---|---|---|
| (A) Angles around the Tantalum Atom | | | |
| C(11)–Ta–C(21) | 37.66 (22) | Cp–Ta–C(11) | 113.74 |
| C(11)–Ta–Cl(1) | 92.42 (16) | Cp–Ta–C(21) | 115.50 |
| C(11)–Ta–Cl(2) | 119.26 (16) | Cp–Ta–Cl(1) | 114.67 |
| C(21)–Ta–Cl(1) | 120.12 (16) | Cp–Ta–Cl(2) | 115.70 |
| C(21)–Ta–Cl(2) | 88.99 (16) | Ac–Ta–Cl(1) | 106.73 |
| Cl(1)–Ta–Cl(2) | 97.08 (16) | Ac–Ta–Cl(2) | 104.39 |
| (B) Angles within the $C_6H_5C$≡$CC_6H_5$ Ligand | | | |
| Ta–C(11)–C(12) | 150.0 (4) | Ta–C(21)–C(22) | 148.4 (4) |
| Ta–C(11)–C(21) | 71.5 (3) | Ta–C(21)–C(11) | 70.9 (3) |
| C(12)–C(11)–C(21) | 138.5 (5) | C(22)–C(21)–C(11) | 140.3 (5) |
| C(11)–C(12)–C(13) | 122.0 (5) | C(21)–C(22)–C(23) | 119.8 (5) |
| C(11)–C(12)–C(17) | 121.1 (5) | C(21)–C(22)–C(27) | 122.1 (5) |
| C(13)–C(12)–C(17) | 116.9 (6) | C(23)–C(22)–C(27) | 118.1 (5) |
| C(12)–C(13)–C(14) | 121.6 (6) | C(22)–C(23)–C(24) | 120.5 (6) |
| C(13)–C(14)–C(15) | 120.3 (7) | C(23)–C(24)–C(25) | 120.3 (7) |
| C(14)–C(15)–C(16) | 119.5 (7) | C(24)–C(25)–C(26) | 119.5 (7) |
| C(15)–C(16)–C(17) | 120.4 (6) | C(25)–C(26)–C(27) | 120.9 (6) |
| C(16)–C(17)–C(12) | 121.2 (6) | C(26)–C(27)–C(22) | 120.8 (6) |
| (C) Internal C–C–C Angles within the $\eta^5$-Pentamethylcyclopentadienyl System | | | |
| C(5)–C(1)–C(2) | 109.1 (6) | C(3)–C(4)–C(5) | 107.7 (6) |
| C(1)–C(2)–C(3) | 107.4 (6) | C(4)–C(5)–C(1) | 107.2 (6) |
| C(2)–C(3)–C(4) | 108.5 (6) | | |
| (D) External C–C–C Angles within the $\eta^5$-Pentamethylcyclopentadienyl System | | | |
| C(5)–C(1)–C(6) | 126.2 (6) | C(4)–C(3)–C(8) | 124.7 (6) |
| C(2)–C(1)–C(6) | 124.6 (6) | C(3)–C(4)–C(9) | 126.2 (6) |
| C(1)–C(2)–C(7) | 127.4 (6) | C(5)–C(4)–C(9) | 126.1 (6) |
| C(3)–C(2)–C(7) | 125.1 (6) | C(4)–C(5)–C(10) | 126.5 (6) |
| C(2)–C(3)–C(8) | 126.2 (6) | C(1)–C(5)–C(10) | 126.0 (6) |

pentene)$Cl_2$.[3] The preparation of Ta($\eta^5$-$C_5Me_5$)(cyclooctene)$Br_2$ is analogous to that for the chloro analogue. In general, any olefin complex, Ta($\eta^5$-$C_5Me_5$)(olefin)$X_2$, is suitable starting material for any acetylene complex, Ta($\eta^5$-$C_5Me_5$)(acetylene)$X_2$. $^{13}C$ NMR data for all acetylene complexes can be found in Table I. $^1H$ and $^{13}C$ NMR chemical shifts are given in ppm from $Me_4Si$.

**Preparation of Ta($\eta^5$-$C_5Me_5$)(PhC≡CPh)$Cl_2$.** A toluene solution of diphenylacetylene (0.15 g, 0.814 mmol) was added to Ta($\eta^5$-$C_5Me_5$)(styrene)$Cl_2$ (0.4 g, 0.814 mmol) in 20 mL of toluene. The color changed from purple to red after stirring overnight. Removing the toluene in vacuo left an orange solid. It was dissolved in a minimal amount of $CH_2Cl_2$, and pentane was added until cloudiness persisted. Cooling the solution to −20 °C overnight gave 0.37 g (82%, two crops) of orange crystals. Anal. Calcd for $TaC_{24}H_{25}Cl_2$: C, 50.99; H, 4.46. Found: C, 51.16; H, 4.78. $^1H$ NMR ($CD_2Cl_2$): 7.1–7.8 (m, 10, Ph), 2.1 (s, 15, $C_5Me_5$).

**Preparation of Ta($\eta^5$-$C_5Me_5$)(PhC≡CPh)(OMe)Cl.** Solid NaOMe (0.05 g, 0.89 mmol) was added to a solution of Ta($\eta^5$-$C_5Me_5$)(PhC≡CPh)$Cl_2$ (0.55 g, 0.88 mmol) in 50 mL of 1:1 THF/toluene. The orange solution turned yellow, and a white solid precipitated in 12 h. The mixture was filtered, the solvent removed in vacuo, and the residue recrystallized from a minimal amount of toluene by adding

**Table VI**

Least-Squares Planes[a, b] and Atomic Deviations Therefrom (Å) for $Ta(\eta^5\text{-}C_5Me_5)(C_6H_5C{\equiv}CC_6H_5)Cl_2$

(A) Phenyl Plane Formed by C(12) → C(17)
$-0.3014X - 0.2944Y - 0.9069Z + 8.4969 = 0$

| | | | |
|---|---|---|---|
| C(12)* | 0.009 (6) | C(11) | 0.022 (5) |
| C(13)* | −0.002 (7) | C(21) | 0.515 (6) |
| C(14)* | −0.011 (7) | C(22) | 1.412 (6) |
| C(15)* | 0.011 (7) | C(23) | 1.559 (7) |
| C(16)* | 0.002 (7) | C(24) | 2.425 (7) |
| C(17)* | −0.011 (6) | C(25) | 3.147 (7) |
| Ta | −0.5698 (2) | C(26) | 3.001 (7) |
| Cl(1) | 2.518 (2) | C(27) | 2.153 (6) |
| Cl(2) | 0.960 (2) | | |

(B) Phenyl Plane Formed by C(22) → C(27)
$-0.1531X + 0.4080Y - 0.9001Z + 2.7078 = 0$

| | | | |
|---|---|---|---|
| C(22)* | −0.001 (6) | C(11) | −0.043 (5) |
| C(23)* | −0.001 (7) | C(12) | −0.316 (6) |
| C(24)* | 0.001 (7) | C(13) | −1.221 (7) |
| C(25)* | 0.002 (7) | C(14) | −1.467 (7) |
| C(26)* | −0.004 (7) | C(15) | −0.809 (7) |
| C(27)* | 0.003 (6) | C(16) | 0.065 (7) |
| C(21) | 0.024 (6) | C(17) | 0.303 (6) |
| Ta | 0.3810 (2) | | |
| Cl(1) | −1.896 (2) | | |
| Cl(2) | 1.899 (2) | | |

(C) Cyclopentadienyl Plane
$0.0081X - 0.1972Y - 0.9803Z + 9.5366 = 0$

| | | | |
|---|---|---|---|
| C(1)* | −0.009 (6) | C(6) | −0.111 (8) |
| C(2)* | −0.001 (6) | C(7) | −0.071 (7) |
| C(3)* | 0.011 (6) | C(8) | −0.136 (8) |
| C(4)* | −0.017 (6) | C(9) | −0.131 (7) |
| C(5)* | 0.016 (6) | C(10) | −0.053 (8) |
| Ta | 2.1002 (2) | C(11) | 2.909 (5) |
| | | C(22) | 3.512 (6) |

(D) $0.5213X + 0.2252Y - 0.8231Z + 0.8219 = 0$

| | |
|---|---|
| Ta* | 0.000 |
| Cl(1)* | 0.000 |
| Cl(2)* | 0.000 |

(E) $-0.0576X + 0.2384Y - 0.9695Z + 3.8369 = 0$

| | |
|---|---|
| Ta* | 0.000 |
| C(11)* | 0.000 |
| C(21)* | 0.0000 |

Dihedral Angles, Deg

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| A/B | 42.07 | B/D | 41.16 | A/E | 34.27 | C/E | 25.45 |
| A/C | 19.15 | B/E | 11.86 | B/C | 36.81 | D/E | 34.76 |
| A/D | 58.46 | C/D | 39.94 | | | | |

[a] Orthonormal (Å) coordinates. [b] Atoms marked with asterisks were used in calculating the least-squares plane.

pentane until cloudiness persisted followed by cooling the solution to −30 °C for several hours; yield 0.41 g (83%, two crops).

Anal. Calcd for $TaC_{25}H_{28}ClO$: C, 53.54; H, 5.03. Found: C, 53.64; H, 5.22. $^1H$ NMR ($C_6H_6$): 7.2–7.6 (m, 10, Ph), 4.05 (s, 3, OMe), 1.9 (s, 15, $C_5Me_5$). In the variable-temperature $^{13}C\{^1H\}$ NMR spectra, the coalescence temperature ($T_c$) for the two acetylenic carbon atoms was −55 ± 10 °C and $\Delta\nu$ at −70 °C was 41 ± 10 Hz (defined to be $\Delta\nu_\infty$). $\Delta G^\ddagger$ was calculated with use of the Eyring equation.

**Preparation of $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)(OMe)_2$.** A THF slurry of NaOMe (0.1 g, 1.85 mmol) was added to a 50-mL toluene solution of $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CPh)Cl_2$ (0.5 g, 0.88 mmol). The reaction mixture was heated at reflux overnight. The resulting yellow solution was filtered to remove a white precipitate. Concentration of the filtrate in vacuo gave a yellow oil whose $^1H$ and $^{13}C$ NMR spectra are consistent with its formulation. The complex can be crystallized from THF at −30 °C in 80% yield.

$^1H$ NMR ($CH_2Cl_2$): 7.2–7.6 (m, 10, Ph), 4.3 (s, 6, OMe), 2.1 (s, 15, $C_5Me_5$).

**Preparation of $Ta(\eta^5\text{-}C_5Me_5)$(2-butyne)$Cl_2$, $Ta(\eta^5\text{-}C_5Me_5)$(3-hexyne)$Cl_2$, $Ta(\eta^5\text{-}C_5Me_5)(PhC{\equiv}CH)Cl_2$, and $Ta(\eta^5\text{-}C_5Me_5)$(3-hexyne)$Br_2$.** These complexes were prepared by analogous procedures so only the preparation of the 2-butyne complex will be described in detail. Dimethylacetylene (1 mL, excess) was added as a neat liquid to a 30-mL ether solution of $Ta(\eta^5\text{-}C_5Me_5)$(cyclooctene)$Cl_2$ (0.31 g, 0.68 mmol). In about 10 min, the color of the solution changed from purple to orange. Removal of the solvent in vacuo gave orange crystals of $Ta(\eta^5\text{-}C_5Me_5)$(2-butyne)$Cl_2$ quantitatively. These complexes can be crystallized from ether, toluene, or pentane solutions at −30 °C.

**Table VII.** Experimental Data for the X-ray Diffraction Study of $Ta(\eta^5\text{-}C_5Me_5)(C_6H_5C{\equiv}CC_6H_5)Cl_2$

(A) Crystal Parameters at 25 °C[a]

| | |
|---|---|
| cryst system: monoclinic | $\beta = 90.510\ (15)^\circ$ |
| space group: $P2_1/c$ | $V = 2196.9\ (7)$ Å$^3$ |
| $a = 17.0212\ (35)$ Å | $Z = 4$ |
| $b = 9.3227\ (14)$ Å | mol wt = 565.31 |
| $c = 13.8450\ (23)$ Å | $\rho$(calcd) = 1.85 g cm$^{-3}$ |

(B) Measurement of Intensity Data

radiatn: Mo K$\alpha$ ($\bar{\lambda}$ 0.710 730 Å)
monochromator: highly oriented graphite, $2\theta_{\text{mono}} = 12.2^\circ$, equatorial mode
reflctns measd: $+h, +k, +l$ and $+h, +k, -l$
scan type: coupled $\theta$(cryst)–$2\theta$(counter)
$2\theta$ range: 4.0–45.0°
scan speed: 3.0°/min in $2\theta$
scan width: $[2\theta(\text{Mo K}\alpha_1) - 0.9]^\circ \rightarrow [2\theta(\text{Mo K}\alpha_2) + 0.9]^\circ$
bkgd measmt: stationary crystal, stationary counter at beginning and end of each scan, each for one-fourth of the time taken for the scan
std reflctns: 800, 080, 008; measd after each 97 reflctns
reflctns collected: 3216 total, yielding 2884 symmetry-independent data
abs coeff:[b] $\mu = 55.3$ cm$^{-1}$

[a] Unit cell parameters were derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 24 reflections of the forms $\{055\}$, $\{26\bar{1}\}$, $\{10,3,\bar{2}\}$, $\{119\}$, $\{628\}$, and $\{651\}$, all with $2\theta$ between 20 and 30°. [b] Absorption correction empirical, based on a series of $\chi$ scans. Reflections used, their $2\theta$ values, and max to min intensity ratios: $\{116\}$, 18.39°, 1.26:1; $\{008\}$, 23.64°, 1.22:1; $\{1,0,\overline{10}\}$, 29.75°, 1.19:1; $\{0,0,\overline{12}\}$, 35.79°, 1.15:1.

**$Ta(\eta^5\text{-}C_5Me_5)$(2-butyne)$Cl_2$:** Anal. Calcd for $TaC_{14}H_{21}Cl_2$: C, 38.12; H, 4.80. Found: C, 37.70; H, 4.82. $^1H$ NMR ($CH_2Cl_2$): 2.70 (s, 6, MeCCMe), 2.05 (s, 15, $C_5Me_5$).

**$Ta(\eta^5\text{-}C_5Me_5)$(3-hexyne)$Cl_2$:** $^1H$ NMR ($C_6H_6$): 3.3 (q, $J$ = 7 Hz, 4 H, $MeC\mathit{H}_2C$), 2.2 (s, 15 H, $C_5Me_5$), 1.4 (t, $J$ = 7 Hz, 6 H, $\mathit{Me}CH_2C$).

**$Ta(\eta^5\text{-}C_5Me_5)(PhCCH)Cl_2$:** $^1H$ NMR ($CDCl_3$): 7.2–7.8 (m, PhCCH), 2.1 (s, $C_5Me_5$). Acetylene proton resonance was not recorded.

**$Ta(\eta^5\text{-}C_5Me_5)$(3-hexyne)$Br_2$:** $^1H$ NMR ($C_6H_6$): 3.1 (q, $J$ = 6 Hz, 4 H, $MeC\mathit{H}_2C$), 1.8 (s, $C_5Me_5$), 1.2 (t, $J$ = 6 Hz, 6 H, $\mathit{Me}CH_2C$).

**Preparation of $Ta(\eta^5\text{-}C_5Me_5)(HC{\equiv}CH)Cl_2$.** An ether solution (175 mL) of $Ta(\eta^5\text{-}C_5Me_5)$(cyclooctene)$Cl_2$ (2.05 g, 4.12 mmol) was purged with acetylene, which had been passed, successively, through traps containing a saturated sodium bisulfite solution (to remove acetone) and concentrated sulfuric acid (to remove water). Within 1 min, the color of the solution changed from purple to orange. A small amount of black, totally insoluble solid was filtered off, and the clear, orange filtrate was stripped to an orange solid. Recrystallization from ether at −30 °C gave 1.02 g (60%) in two crops. This complex is extremely sensitive to oxygen.

Anal. Calcd for $TaC_{12}H_{17}Cl_2$: C, 34.89; H, 4.15. Found: C, 34.91; H, 4.29. $^1H$ NMR ($C_6D_6$): 12.5 (s, 2, HCCH), 1.8 (s, 15, $C_5Me_5$).

**Preparation of $(\eta^5\text{-}C_5Me_5)Cl_2\overline{TaCHCHCH_2CH_2}$.** A pressure bomb containing a 6-mL toluene solution of $Ta(\eta^5\text{-}C_5Me_5)(HC{\equiv}CH)Cl_2$ (0.92 g, 2.22 mmol) was pressurized to 40 psi with ethylene. After 8 h at 80 °C the reaction's color changed from orange to green-brown. The solvent was removed in vacuo, and the dark solid residue was recrystallized from tetrahydrofuran (−30 °C) to give pale green crystals (0.76 g, 78%).

$^1H$ NMR ($C_6D_6$, 68 °C): 8.14 (d, 1 H, $\overline{TaC\mathit{H}CHCH_2CH_2}$), 7.71 (d of t, 1 H, $\overline{TaCHC\mathit{H}CH_2CH_2}$), 3.31 (br m, 2 H, $\overline{TaCHCHCH_2C\mathit{H}_2}$), 2.70 (br t, 2 H, $\overline{TaCHCHC\mathit{H}_2CH_2}$), 1.94 (s, 15 H, $C_5Me_5$). $^{13}C$ NMR ($C_6D_6$): 210.7 (d, $J$ = 139 Hz, $\overline{Ta\mathit{C}HCHCH_2CH_2}$), 150.8 (d, $J$ = 145 Hz, $\overline{TaCH\mathit{C}HCH_2CH_2}$), 124.0 (s, $C_5Me_5$), 96.9 (t, $J$ = 122 Hz, $\overline{\mathrm{TaCHCHCH_2}C\mathrm{H_2}}$), 44.2 (t, $J$ = 125 Hz, $\overline{\mathrm{TaCHCH}C\mathrm{H_2}}$), 12.3 (q, $J$ = 128 Hz, $C_5Me_5$).

**Collection of the X-ray Diffraction Data for Ta($\eta^5$-$C_5Me_5$)($C_6H_5C{\equiv}CC_6H_5$)$Cl_2$.** A well-formed orange parallelepiped of approximate dimensions 0.20 × 0.20 × 0.19 mm was carefully wedged into a 0.2-mm diameter thin-walled capillary, which was then purged with argon, flame-sealed, fixed into an aluminum pin with beeswax, and mounted into a eucentric goniometer.

The crystal was aligned and data were collected on our Syntex $P2_1$ automated diffractometer with use of methods described previously.[11] Crystal parameters can be found in Table VII.

**Solution and Refinement of the Structure.** The structure was solved by using the Syntex XTL system on our in-house NOVA 1200 computer. Scattering factors for neutral atoms were used in their analytical forms;[12a] the contributions of all nonhydrogen atoms were corrected for both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion.[12b] The function minimized in the least-squares refinement process was $\sum w(|F_o| - |F_c|)^2$; the weights used ($w$) were derived from the stochastic $\sigma(|F_o|)$ values, modified by an ignorance factor ($p$) of 0.015 (see eq 5).

$$w = [(\sigma(|F_o|))^2 + (p|F_o|)^2]^{-1} \qquad (5)$$

A Patterson synthesis was used to locate the tantalum atom. A series of difference-Fourier syntheses, each being phased by an increasing number of atoms, yielded all 26 remaining nonhydrogen atoms. Hydrogen atoms of the $C_6H_5C{\equiv}CC_6H_5$ ligand were included in calculated positions, based upon $d$(C-H) = 0.95 Å,[13] and were updated as necessary. Full-matrix least-squares refinement led to final convergence with $R_F$ = 3.3%, $R_{wF}$ = 3.1%, and GOF = 1.346 for all 2884 independent reflections (*none* rejected) with 244 variables. The discrepancy indices for those 2571 reflections with $I > 3\sigma(I)$ were $R_F$ = 2.6% and $R_{wF}$ = 3.0%.

A final difference-Fourier synthesis was devoid of significant features. (The highest peak was of height 0.56 e Å$^{-3}$, and there were indications of the positions of some, *but not all*, hydrogen atoms associated with the $\eta^5$-$C_5Me_5$ ligand; this aspect was not further pursued.)

The unusual tests of the residual, $\sum w(|F_o| - |F_c|)^2$, vs. $|F_o|$, $(\sin\theta)/\lambda$, sequence number, and identity or parity of the Miller indices, suggested that the weighting scheme was satisfactory. Final positional and thermal parameters are collected in Tables II and III.

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**Registry No.** Ta($\eta^5$-$C_5Me_5$)(PhC≡CPh)$Cl_2$, 75522-28-0; Ta($\eta^5$-$C_5Me_5$)(PhC≡CPh)(OMe)Cl, 75522-29-1; Ta($\eta^5$-$C_5Me_5$)(PhC≡CPh)$(OMe)_2$, 75522-30-4; Ta($\eta^5$-$C_5Me_5$)(MeC≡CMe)$Cl_2$, 75522-31-5; Ta($\eta^5$-$C_5Me_5$)(EtC≡CEt)$Cl_2$, 75522-32-6; Ta($\eta^5$-$C_5Me_5$)(PhC≡CH)$Cl_2$, 75522-33-7; Ta($\eta^5$-$C_5Me_5$)(EtC≡CEt)$Br_2$, 75522-34-8; Ta($\eta^5$-$C_5Me_5$)(HC≡CH)$Cl_2$, 75522-35-9; ($\eta^5$-$C_5Me_5$)$Cl_2\overline{\mathrm{TaCHCHCH_2CH_2}}$, 75522-36-0; Ta($\eta^5$-$C_5Me_5$)(styrene)$Cl_2$, 71414-50-1; Ta($\eta^5$-$C_5Me_5$)(cyclooctene)$Cl_2$, 71414-52-3; ethylene, 74-85-1; Ta($\eta^5$-$C_5Me_5$)(cyclooctene)$Br_2$, 74594-03-9.

**Supplementary Material Available:** A listing of observed and calculated structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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# ESR Spectra of Cobalt(II)- and Copper(II)-Doped Bis(*N*,*N*-bis(2-(diethylamino)ethyl)((2-hydroxyethyl)amino-*O*)dinickel(II) Diperchlorate. Characterization of Nickel(II)-Cobalt(II) and Nickel(II)-Copper(II) Exchange-Coupled Pairs

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The ESR spectra of cobalt(II)- and copper(II)-doped bis(*N*,*N*-bis(2-(diethylamino)ethyl)((2-hydroxyethyl)amino-*O*)dinickel(II) diperchlorate ($[Ni_2(bdhe)_2](ClO_4)_2$) have shown the presence of nickel(II)-cobalt(II) and nickel(II)-copper(II) pairs. For comparison purposes also the ESR spectra of copper(II)-doped zinc(II) analogue have been recorded. The $g$ values of the pairs have been related to the $g$ values of the individual ions through a vector coupling relation which has been tested with use of available literature data. The effect of large zero field splittings of the individual ions has been discussed. The sign of the interaction has been shown to be antiferromagnetic for the nickel(II)-copper(II) pair, while no safe conclusion was reached for the nickel(II)-cobalt(II) couple.

## Introduction

The spectroscopic and magnetic properties of mixed-transition-metal complexes are attracting increasing interest,[1-7] since they can largely expand the number of experimental data on exchange interactions and give new information to correlate the magnetic properties with the structural features of the complexes.

In general it may be difficult to obtain discrete complexes containing pairs of different metal ions, but it is easier to obtain measurable concentrations of such pairs in the lattices of dinuclear complexes by preparing the compounds starting from variable amounts of two parent metal complexes. Magnetic resonance spectroscopy can then be used in order to reveal the presence of heterodinuclear complexes.[8,9]

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