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Alkyne Coupling with Isonitriles and Carbon Monoxide on Tantalum and Niobium Centers. Molecular Structure of Cp*MeTa(CPhCPhCMeO)

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Reaction of Cp*Ta(η^2-PhCCPh)(CH_3)$_2$ (1) with *tert*-butyl or methyl isocyanides gives high yields of the iminoacyl complexes Cp*Ta(η^2-MeCNR)(η^2-PhCCPh)(Me) (**2a**, R = *tert*-butyl and **2b**, R = methyl). Compound **2a** when heated in refluxing toluene gives the coupled product azatantalacyclopentatriene Cp*Ta(CPhCPhCCH$_3$NR)CH$_3$ (**3**) (R = *tert*-butyl) in high yield. A similar reaction of CO with **1** gives the corresponding metallacycle Cp*Ta(CPhCPhCCH$_3$O)CH$_3$ (**4**). The molecular structure of **4** shows a five-membered "TaC$_3$O" ring folded 124° along the O–Cα axis and containing an alkylidene. The Ta=C bond length is 1.972(8) Å. Crystal data for **4**: $a = 9.010(4)$, $b = 10.742(5)$, $c = 12.945(3)$ Å; $\alpha = 98.16(3)$, $\beta = 101.79(2)$, $\gamma = 75.93(3)°$; $Z = 2$, $V = 1184$ (Å^3), space group = $P\bar{1}$ $d_{calcd} = 1.56$ g/cm^3, $R = 0.0349$, $R_w = 0.0343$. Other three-legged "piano stool" alkyne complexes Cp*Ta(η^2-PhCCPh)(X)(Y) (**5**, X = Cl and Y = CH$_3$; **7**, X = Cl and Y = N(CH$_3$)$_2$) were prepared and spectroscopically characterized. Reduction of Cp*Ta(η^2-PhCCPh)(CH$_3$)(Cl) (**5**) with Na/Hg gives [Cp*Ta(PhCCPh)Cl]$_2$ as the only isolable product. CpNb(η^2-PhCCPh)(CH$_3$)$_2$ reacts with isonitriles, RNC (R = *tert*-butyl or benzyl), to produce the corresponding niobium iminoacyl complexes CpNb(Me)(η^2-CPhCPh)(η^2-CH$_3$CNR), **8a** (R = benzyl) and **8b** (R = *tert*-butyl).

Introduction

Early transition metal complexes are known to be efficient catalysts for the oligomerization and polymerization of internal alkynes.[1] The two major mechanisms generally accepted for metal-catalyzed alkyne polymerization are the alkylidene[2,3] and the alkenyl pathways.[4] According to the alkylidene mechanism, cleavage of both π bonds of the monomer occurs and a polymer of general formula $=(C-C=)_n$ is produced. In the alkenyl mechanism, the polymer formed from insertion of the alkyne into a metal–alkyl bond has the general formula $-(C=C-)_n$.[4b] In either mechanism, the nature of the true catalyst as opposed to the catalyst precursor is often not known, especially when the "catalyst" does not have metal–alkylidene or metal–alkyl bonds.

In alkyne complexes of the type Cp^{R}M(η^2-ArCCAr)X$_2$ (Ar = alkyl or aryl, Cp^R = C$_5$H$_5$, C$_5$H$_4$Me, or Cp* (Cp* = C$_5$Me$_5$); M = Ta, Nb; X = Cl, Me), there is significant multiple bond character between the metal and the alkyne carbon atoms, and the alkyne carbon–carbon bond is long. These piano stool complexes may be considered as metallacyclopropenes.[5] We have also shown that the alkynes in these complexes may couple with other alkynes, with CO, or with isonitriles to form metal–alkylidene bonds.[6] Thus there are two potential sites for coupling reactions with added alkyne. As part of our investigation of alkyne coupling reactions initiated by early transition metal complexes, we have investigated reactions of the more soluble Cp* containing Ta complexes. In this paper we report new members of the now recognized metallacyclopenta*triene* complexes[6] along with some related Ta and Nb compounds.

Experimental Section

General Considerations. All manipulations and reactions in this work were performed under a dinitrogen atmosphere with standard Schlenk techniques or in a glove box. Elemental analyses were performed by University of Michigan microanalytical service located in the Department of Chemistry, by Galbraith Laboratories, Inc. (Knoxville, TN) or by Oneida Research Services, Inc. (Whitesboro, NY). In several instances, satisfactory carbon analyses could not be obtained, even when vanadium pentoxide was used as combustion catalyst and all the spectral evidence indicated the compounds were pure. We assume metal carbide formation was the reason for the low carbon values. NMR spectra were recorded on a Bruker AM-300 (operating at 300 MHz for ^{1}H and at 75.5 MHz for ^{13}C). All spectra, except variable temperature ones, were taken at a probe temperature of ca. 22 °C for ^{1}H and ca. 30 °C for ^{13}C. Infrared measurements were made on a Nicolet 5DXB spectrometer. Mass spectra were obtained on Finnigan Model 4021 GC-MS or VG 70-250s spectrometers.

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Reagents and Solvents. Solvents and common reagents were purchased from different chemical suppliers and purified according to standard procedures.[7] Diethyl ether, toluene, and tetrahydrofuran were distilled from purple sodium benzophenone ketyl. Hexanes, dichloromethane, and acetonitrile were stored over calcium hydride, redistilled from P_4O_{10}, and saturated with dinitrogen prior to use. Di-*p*-tolylacetylene was prepared according to the literature.[8] Diphenylacetylene, $HN(CH_3)_2$, $TaCl_5$, $NbCl_5$, Bu_3SnCp, and methyllithium were purchased from Aldrich. Methyllithium was titrated before use according to a literature method.[9] Deuterated solvents used to obtain NMR spectra of very air/moisture-sensitive samples were stored over sodium (toluene-d_8, benzene-d_6) or over 4-Å Davison molecular sieves (dichloromethane-d_2) in the inert atmosphere box. For moderately air/moisture-stable samples, however, deuterated solvents in vials of 0.5 mL capacity were directly used with minimum or no exposure to air. $Cp^*Ta(ArC_2Ar)Cl_2$[10] (Ar = Ph, or *p*-tolyl) and $CpNb(PhC_2Ph)Cl_2$[5b] was prepared as reported earlier.

$Cp^*Ta(\eta^2\text{-}PhC_2Ph)(CH_3)_2$ (1). A suspension of 2.15 g (3.8 mmol) of $Cp^*Ta(PhC_2Ph)Cl_2$ in 20 mL of diethyl ether was prepared in a 100-mL Schlenk flask. Methyllithium, 7.6 mmol, was added to the suspension drop by drop at −78 °C with stirring. The reaction mixture which was initially orange-yellow turned pale yellow and a colorless precipitate formed. Stirring was continued for 1 h. After filtration through Celite, volatiles were pumped off to give a brown-yellow oil which, when treated with 10 mL of hexane, gave a pale yellow solid. The solid was isolated by carefully removing the supernatant liquid with a syringe. Yield: 1.83 g, 92%. ^1H NMR (300 MHz, C_6D_6): δ 7.38, 7.23, 7.03 (d, t, t, 10H, C_6H_5); 1.71 (s, 15H, $C_5(CH_3)_5$); 0.22 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 239 (C_{alkyne}); 147 (C_{ipso}), 128.5, 127.9, 126.8 (C_6H_5); 115 ($C_5(CH_3)_5$); 50.9 (Ta-CH_3): 10.8 ($C_5(CH_3)_5$). Anal. Calcd for $C_{26}H_{31}Ta$: C, 59.50; H, 5.96. Found: C, 59.11; H, 6.17.

$Cp^*Ta(CH_3)(\eta^2\text{-}C(Me)N(R))(\eta^2\text{-}PhC_2Ph)$, R = *tert*-butyl (2a) and R = CH_3 (2b). In a 100-mL Schlenk flask, a solution of $Cp^*Ta(PhC_2Ph)(CH_3)_2$ (1.6 g, 3.17 mmol) in 10 mL of toluene was cooled to −78 °C. A solution of *tert*-butyl isocyanide (0.26 g, 3.17 mmol) in 10 mL of toluene was added drop by drop via syringe. The cold bath was removed and the mixture was allowed to gradually warm to room temperature. The initially yellow-brown solution turned orange-yellow. Stirring was continued for 3 h. After pumping off volatiles, the residue was redissolved in 15 mL of hexane which was slowly pumped off to obtain a red yellow solid. Yield: 1.76 g, 91%. ^1H NMR (300 MHz, C_6D_6): δ 7.42, 7.26, 7.00 (d, t, t, $J \approx 7.5$ Hz), m, 10H, C_6H_5); 2.60 (s, 3H, $=CCH_3$); 1.78 (s, 15H, $C_5(CH_3)_5$); 1.03 (s, 9H, $C(CH_3)_3$); 0.91 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 245.4 (CH_3CN); 202.0 (C_{alkyne}); 146.1 (C_{ipso}); 131.9, 128.6 128.2, 127.3 (C_6H_5); 110 $C_5(CH_3)_5$, 62.4 (CH_3C); 30.2 ($C(CH_3)_3$); 21.6, 21.4 (Ta-CH_3/CH_3CN); 11.3 ($C_5(CH_3)_5$). Anal. Calcd for $C_{31}H_{40}NTa$: C, 61.28; H, 6.64; N, 2.30. Found: C, 61.01; H, 6.60; N, 2.21.

In a similar way, R = CH3, **2b** was prepared. Yield: 0.52 g (96%). ^1H NMR (300 MHz, C_6D_6): δ 7.63, 7.30, 7.07 (d, t, t, $J \approx 8$ Hz, 10H, C_6H_5); 2.51 (s, 3H, CH_3); 2.23 (bs, 3H, CH_3); 1.74 (s, 15H, $C_5(CH_3)_5$), 0.84 (s, 3H, CH_3).

$Cp^*Ta(C(Ph)C(Ph)C(Me)N(^tBu))(CH_3)$ (3). A solution of (1.0 g, 1.65 mmol) of $Cp^*Ta(CH_3)(\eta^2\text{-}PhC_2Ph)(\eta^2\text{-}MeCN^tBu)$ (**2a**) in 15 mL of toluene was stirred at 90–95 °C for 20 h. After the volatiles were cooled to room temperature, they were pumped off under vacuum to obtain a red-orange oil. The oil was then redissolved in 15 mL of hexane and concentrated to 5 mL, and the solution was left at room temperature. After 24 h red-orange crystals were obtained. Yield: 0.9 g, 90%. ^1H NMR (300 MHz, C_6D_6): δ 7.12–6.75 (m, 10H, C_6H_5); 2.29 (s, 3H, CCH_3); 1.87 (s, 15H, $C_5(CH_3)_5$); 1.42 (s, 9H, $C(CH_3)_3$); −1.04 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 229, (Ta=C); 149.2, 141.3, 130.3, 126.6, 126.5, 123.8, 122.0 (C_6H_5 and CH_3CN); 113.8 ($C_5(CH_3)_5$); 93.1 (C_β), 61.3 ($(CH_3)_3CNC$); 33.4 ($(CH_3)_3CN$); 27.0, 20.8, (CCH_3/$TaCH_3$); 12.3 ($C_5(CH_3)_5$). Anal. Calcd for $C_{31}H_{40}NTa$: C, 61.28; H, 6.64; N, 2.30. Found: C, 60.19; H, 6.48; N, 2.13.

$Cp^*Ta(C(Ph)C(Ph)C(CH_3)O)(CH_3)$ (4). In a 100-mL Schlenk flask was dissolved $Cp^*Ta(PhC_2Ph)(CH_3)_2$ (0.32 g, 0.61 mmol) in 15 mL of toluene. The solution was cooled to −78 °C and 0.61 mmol of CO was added into the solution. The temperature of the solution was then gradually raised and continuous vigorous stirring maintained. The initially pale yellow solution turned red-orange after warming to room temperature. Stirring was continued for a total of 1.5 h and volatiles were removed to obtain a red-orange solid. The solid was dissolved in THF, filtered, and concentrated under vacuum. The concentrated solution was then left at −10 °C to obtain red-orange crystals. Yield: 0.32 g, 95%. ^1H NMR (300 MHz, C_6D_6): δ 7.47, 7.05, 6.95, 6.88, 6.78 (m, 10H, C_6H_5); 2.45 (s, 3H, CH_3); 1.85 (s, 15H, $C_5(CH_3)_5$); −0.58 (s, 3H, $TaCH_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 224.5 (Ta=C); 146.5, 140.4, 131.0, 130.1, 127.2, 126.7, 124.3, 123.7, 122.3 (C_6H_5 and $OCCH_3$); 115.3 ($C_5(CH_3)_5$); 29.4 ($TaCH_3$); 19.9 ($OCCH_3$), 10.9 ($C_5(CH_3)_5$). Anal. Calcd for $C_{27}H_{31}OTa$: C, 58.70; H, 5.66. Found: C, 58.08; H, 5.46. Mass spec (EI 70 eV) m/z = 552, 537 ($M^+ - CH_3$).

$Cp^*Ta(\eta^2\text{-}PhC_2Ph)(CH_3)Cl$ (5). In a 100-mL Schlenk flask was dissolved $Cp^*Ta(PhC_2Ph)(CH_3)_2$ (0.22 g, 0.42 mmol) in 15 mL of THF and a pinch of $AlCl_3$ was added with a tip of a spatula. An excess amount of isopropyl chloride (predried over 4-Å molecular sieves and degassed) was then added at room temperature and the solution stirred for 8 h. A bright yellow residue was obtained after removal of the volatiles under vacuum. Yield: 0.22 g, 96%. ^1H NMR (300 MHz, C_6D_6): δ 7.60, 7.24, 7.08 (d, t, t, $J \approx 8$ Hz), 10H, C_6H_5), 1.74 (s, 15H, $C_5(CH_3)_5$), 0.83 (s, 3H, CH_3). $^{13}C\{^1H\}$ (75.5 MHz, C_6D_6): δ 225.3 (C_{alkyne}), 143.1 (C_{ipso}), 129.2, 128.6, 127.9 (C_6H_5), 117.7 $C_5(CH_3)_5$, 46.1, CH_3, 11.34, $C_5(CH_3)_5$. Anal. Calcd for $C_{25}H_{28}ClTa$: C, 55.11; H, 5.18. Found: C, 54.30; H, 5.17.

Reaction of $Cp^*Ta(\eta^2\text{-}PhC_2Ph)(CH_3)Cl$ (5) with CO. A similar procedure as for synthesis of 4 above was followed. $Cp^*Ta(\eta^2\text{-}PhC_2Ph)(CH_3)Cl$ (0.25 g, 0.46 mmol) and CO (0.46 mmol) were mixed at −85 °C, and the solution was gradually warmed to room temperature. Solvent was pumped off at room temperature to obtain a red-orange, gummy residue. Attempts to recrystallize the product led to deterioration. ^1H NMR (300 MHz, C_6D_6): δ 7.56, 7.04, 6.85, 6.75 (d, m, m, m, 10H, C_6H_5); 2.53 (s, 3H, CH_3); 1.88 (s, 15H, $C_5(CH_3)_5$). Anal. Calcd for $C_{26}H_{28}ClOTa$: C, 54.51; H, 4.92. Found: C, 52.70; H, 5.03.

$Cp^*Ta(\eta^2\text{-}PhC_2Ph)(Cl)N(CH_3)_2$ (7). To a solution of (0.3 g, 0.53 mmol) of $Cp^*Ta(PhC_2Ph)Cl_2$ in 20 mL of toluene was added lithium dimethylamide (0.05 g, 1.06 mmol). After the mixture was stirred at room temperature for 8 h, the solution was filtered through Celite. The filtrate was then concentrated to ~2 mL and layered with 3 mL of hexane. Bright yellow crystals formed after 24 h. Yield: 0.3 g, 98.7%. ^1H NMR (300 MHz, C_6D_6): δ 7.83, 7.24, 7.08 (d, t, t, $J \approx 7$ Hz, 10H, C_6H_5); 3.00 (s, 6H, $N(CH_3)_2$); 1.82 (15H, $C_5(CH_3)_5$). $^{13}C\{^1H\}$ NMR (75.5 MHz, C_6D_6): δ 209.7 (C_{alkyne}); 140.9, 130.6, 128.6, 128.3 (C_6H_5); 116.7 ($C_5(CH_3)_5$); 48.7 ($N(CH_3)_2$); 11.6 ($C_5(CH_3)_5$). Anal. Calcd for $C_{26}H_{31}ClNTa$: C, 54.41; H, 5.44; N, 2.44. Found: C, 54.24; H, 5.47; N, 2.42. Mass spec (EI, 70 eV): m/z = 573.

$[Cp^*Ta(PhCCPh)Cl]_2$. A solution of $Cp^*Ta(PhCCPh)(CH_3)Cl$ (5) (0.22 g, 0.40 mmol) in 20 mL of THF was transferred to a flask containing Na metal (0.01 g, 0.42 mmol) in 15 mL of Hg. The mixture was stirred for 8 h and filtered through a bed of Celite 2 cm deep. Removal of volatiles under vacuum gave a dark-red, gummy residue which was stirred with hexane. The hexane extract was removed, and the red, hexane-insoluble residue was then redissolved in THF. After concentration of the solution under vacuum, a red microcrystalline product was

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Table 1. Crystal Data for Cp*MeTa(CPhCPhCCH$_3$O) (4)

formula	$C_{27}H_{31}OTa$
color, cryst solv	orange-red, THF
mol wt.	552.49
space group	$P\bar{1}$
a, b, c (Å)	9.010(4), 10.742(5), 12.945(3)
α, β, γ (deg)	98.16(3), 101.79(2), 75.93(3)
Z, V (Å^3)	2, 1184
d, calcd (g/mL)	1.56
temp (K)	296
radiation, λ (Å)	0.71069
monochromator	graphite crystal
abs coef, cm^{-1}	47.73
scan range	Mo Kα1 –0.8 to Mo Kα2 +0.9
background:time ratio	0.8
2θ, (deg)	45
data collected	3096
data > $3\sigma(I)$	2753
R, R_w^{a}	0.0349, 0.0343
goodness of fit	1.89

^{a} $R = (\sum[|F_o| - |F_c|])/(\sum|F_o|)$, $R_w = (\sum[w|F_o| - |F_c|]^2)^{1/2}/(\sum|F_o|^2)^{1/2}$.

obtained. ^{1}H NMR (300 MHz): δ 7.83, 7.36, 7.11 (d, t, t, $J \approx 6$ Hz), m, 10H, C_6H_5); 1.57 (s, 15H, $C_5(CH_3)_5$). Mass spec (EI 70 eV) $m/z = 1058$. These properties identify the compound as [Cp*Ta(PhC$_2$Ph)Cl]$_2$, which was synthesized earlier by reduction of Cp*Ta(PhC$_2$Ph)Cl$_2$.[10]

CpNb(η^2-PhC$_2$Ph)(η^2-RNCCH$_3$)(CH$_3$) R = *tert*-butyl (8a) and R = benzyl (8b). In a 100-mL flask, 0.3 g (0.82 mmol) of CpNb(η^2-PhC$_2$Ph)(CH$_3$)$_2$ were dissolved in 15 mL of toluene and cooled to –40 °C. A toluene solution of *tert*-butyl isocyanide (0.82 mmol) was added to the Nb solution drop by drop. The mixture was then stirred for 3 min and gradually warmed to room temperature and stirred for an additional 1.5 h. Volatiles were pumped off to obtain a red-brown, gummy residue. Yield: 95%. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.63 (d, t, $J \approx 8$ Hz), 7.30 7.13 (m), 7.00 (m), 6.8 (m) (10 H, C_6H_5); 5.30 (s, 5H, C_5H_5), 2.48 (s, 3H, CH_3CN), 1.19 (s, 3H, CH_3Nb), 0.98 (s, 9H, $(CH_3)_3C$). ^{13}C-{^{1}H} (C_6D_6, 75.5 MHz): δ 196 (C_{alkyne}), 144 (C_{ipso}), 130, 129, 128.6 (C_6H_5), 101.8 (C_5H_5), 62.9 ($(CH_3)_3C$), 29.7 ($(CH_3)_3C$), 23.26 ($NbCH_3$), $NC(CH_3)_3$ not observed. Anal. Calcd for $C_{29}H_{28}NNb$: C, 72.04; H, 5.84; N, 2.90. Found: C, 71.94; H, 5.86; N, 3.01.

The benzyl isocyanide derivative **8b** was prepared in the similar way from CpNb(PhC$_2$Ph)(CH$_3$)$_2$ (0.24 g, 0.66 mmol) and 0.66 mmol of benzyl isocyanide (0.66 mmol). Yield: 96%. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.62, 7.30, 7.13, 7.0, 6.78 (d, t, $J \approx 8$ Hz, m, m, m, 15H, C_6H_5), 5.26 (s, 5H, C_5H_5), 4.29, 4.17 (d, d, $J = 13$ Hz, 2H, NCH_2); 2.26 (s, 3H, CH_3CN); 1.14 (s, 3H, $NbCH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz): δ 136.8, 129.3, 128.5, 126.3 (C_6H_5), 101.3 (C_5H_5), 49.1 (NCH_2), 23.8, 21.5 ($NbCH_3$, CCH_3). Alkyne and iminoacyl carbons not observed.

X-ray Crystallographic Analysis. Red-orange crystals of Cp*Ta(CPhCPhCCH$_3$O)(CH$_3$) (4) were grown from THF. A suitable crystal was fitted in a thin-walled glass capillary, flame sealed, and mounted on Syntex P2$_1$ diffractometer. Data were collected by the method of θ–2θ scans at variable rate, dependent on peak intensity, and corrected for Lorentz and polarization effects but not for absorption. Lattice parameters were obtained from least-squares refinement of 15 reflection settings obtained from an automatic centering routine. Standard reflections were measured every 100 reflections. The structures were solved and refined using SHELX[12] package on MTS (Michigan Terminal System). The package includes subroutines for direct methods, Patterson and Fourier maps, least square refinements, distance and angle calculations with esd's, etc. Other programs used include PLUTO and ORTEP plotting programs.[13] The atomic scattering factors were obtained from *International Tables for X-ray Crystallography*.[14]

Table 2. Fractional Atomic Coordinates for Cp*MeTa(CPhCPhCCH$_3$O) (4)

atom	*x*	*y*	*z*	*U*
Ta1	0.2688(0)	0.7006(0)	0.2828(0)	0.037
O1	0.4041(6)	0.6593(5)	0.4190(4)	0.043
C1	0.2020(9)	0.5359(7)	0.2649(6)	0.037
C2	0.3699(9)	0.4763(7)	0.2981(6)	0.040
C3	0.4684(9)	0.5410(7)	0.3711(6)	0.039
C10	0.0301(11)	0.8440(9)	0.2028(7)	0.051
C11	0.1479(11)	0.9153(8)	0.2328(8)	0.056
C12	0.1940(10)	0.9247(8)	0.3443(7)	0.047
C13	0.1040(11)	0.8578(8)	0.3830(7)	0.053
C14	0.0017(10)	0.8098(8)	0.2972(8)	0.053
C15	–0.0641(15)	0.8251(11)	0.0948(9)	0.081
C16	–0.1293(12)	0.7474(10)	0.3051(11)	0.088
C17	0.1164(14)	0.8434(11)	0.5006(8)	0.080
C18	0.3172(14)	0.9914(11)	0.4064(11)	0.087
C19	0.2022(16)	0.9827(11)	0.1538(10)	0.098
C20	0.4133(11)	0.6948(9)	0.1641(7)	0.059
C21	0.6433(10)	0.5100(8)	0.3887(7)	0.049
C31	0.4351(9)	0.3520(7)	0.2383(6)	0.040
C32	0.5229(11)	0.2467(8)	0.2951(7)	0.051
C33	0.5790(11)	0.1293(8)	0.2413(9)	0.061
C34	0.5483(11)	0.1136(9)	0.1316(9)	0.063
C35	0.4629(11)	0.2138(10)	0.0751(8)	0.061
C36	0.4046(11)	0.3331(8)	0.1282(7)	0.052
C41	0.0860(9)	0.4578(7)	0.2325(6)	0.040
C42	–0.0268(12)	0.4784(9)	0.1431(8)	0.062
C43	–0.1401(13)	0.4067(11)	0.1111(9)	0.073
C44	–0.1420(12)	0.3102(11)	0.1710(10)	0.073
C45	–0.0312(13)	0.2862(10)	0.2593(9)	0.072
C46	0.0830(11)	0.3573(8)	0.2917(8)	0.056

Table 3. Selected Bond Distances (Å) and Angles (deg) for Cp*MeTa(CPhCPhCCH$_3$O) (4)

Ta1–O1	1.967(05)	Ta1–C1	1.972(08)
Ta1–C2	2.381(08)	Ta1–C3	2.387(07)
Ta1–C10	2.450(09)	C13–C17	1.530(13)
Ta1–C20	2.194(09)	O1–C3	1.379(09)
C1–C2	1.491(11)	C1–C41	1.456(11)
C2–C3	1.391(11)	C2–C31	1.496(11)
C3–C21	1.505(12)		
O1–Ta1–C1	91.7(3)	Ta1–C1–C2	85.7(5)
O1–Ta1–C2	65.4(2)	Ta1–C2–C1	55.7(4)
C1–Ta1–C2	38.6(3)	O1–Ta1–C3	35.3(2)
O1–Ta1–C20	109.2(3)	C1–Ta1–C20	108.6(3)
C1–Ta1–C3	69.9(3)	Ta1–C2–C3	73.3(4)
C2–Ta1–C20	90.4(3)	C3–Ta1–C20	89.8(3)
C10–Ta1–C20	99.1(3)	C2–Ta1–C3	33.9(3)
C1–C2–C3	121.8(7)	C12–C13–C17	124(1)
C12–Ta1–C20	105.1(3)	C41–C1–Ta1	152.6(6)

The Ta atom position was located by direct methods and the remaining non-hydrogen atom positions were determined by Fourier difference maps. During refinement, the function minimized was $\sum w(|F_o| - |F_c|)^2$ where the weight is given by $w = 1/(\sigma^2 + 0.0001{*}F_o^2)$. After the heavy atom parameters had converged, hydrogen atoms were introduced in calculated positions and assigned isotropic temperature factors of 0.07 Å^2. A summary of crystal data is given in Table 1. Table 2 contains the final atomic coordinates and the equivalent isotropic temperature factors. Selected bond distances and angles are given in Table 3.

Results and Discussion

The dimethyl compound Cp*Ta(PhC$_2$Ph)(CH$_3$)$_2$ (1) was synthesized in high yield by reaction of the dichloro compound with 2 equiv of methyllithium.

The proton NMR spectrum of 1 showed a singlet at δ 0.22 for the CH$_3$ ligands, a singlet at δ 1.71 corresponding

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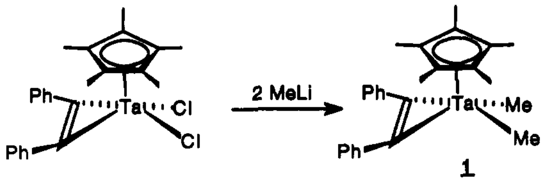
[13] Johnson, C. K. *ORTEP-1- A Fortran Thermal Ellipsoids Plot for Crystal Structure Illustrations*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.

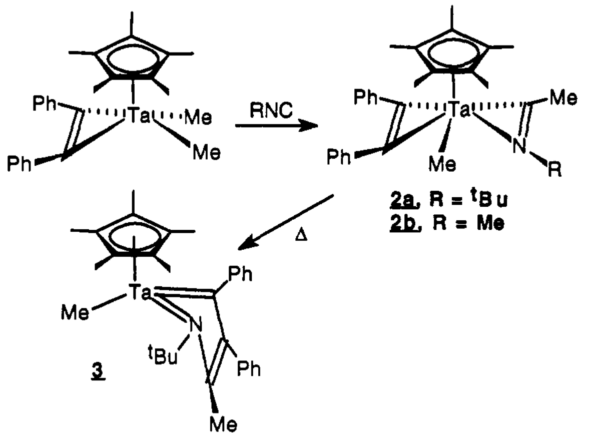
[14] *International Tables for X-ray Crystallography*; Ibers, J. A., Hamilton, W. C., Eds., Kynoch Press, Birmingham, England; Vol. IV, 1974, Tables 2.2 and 2.3.1.



(1)

to the Cp* protons, and resonances at δ 7.38, 7.23, and 7.03 for the phenyl hydrogen atoms, all in the expected ratios. In the ^{13}C-NMR spectrum, the alkyne carbon resonance was observed at δ 239 in agreement with values observed for other similar four-electron donor alkynes.[15] The CH_3 carbon resonance was observed at δ 50.9, and all other carbon peaks were observed in their expected ranges.

Compound 1 reacts with isonitriles to produce high yields of Cp*Ta(η^2-PhC$_2$Ph)(η^2-RNCCH$_3$)(CH$_3$), (R = ^{t}Bu, **2a**; R = CH$_3$, **2b**).

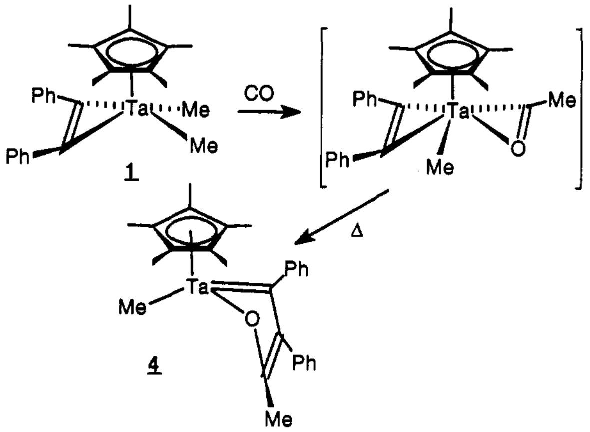


(2)

The proton NMR spectrum of **2a** showed a singlet at δ 0.95 for the CH_3 directly attached to Ta. The signal at δ 2.60 was assigned to the methyl group on the iminoacyl functionality. The *tert*-butyl hydrogen atoms showed a singlet at δ 1.03. In the ^{13}C NMR spectrum, the alkyne carbon resonance appears at δ 202 ppm. The iminoacyl carbon attached to the Ta had the farthest downfield shift at 245.4 ppm, while the CH_3 carbon attached to Ta gave a signal at 21 ppm.

The iminoacyl complex **2a** is stable at room temperature, but in refluxing toluene it was quantitatively converted to the metallacyclopentatriene **3** (eq 2). Spectroscopic properties of the complex **3** are very similar to the Cp analog reported previously.[6c] In the ^{1}H-NMR spectrum, the CH_3 ligand attached to the metal gave a singlet at δ −1.04. The phenyl proton region was more complex than that of **2a** because phenyl rings are inequivalent in **3**. The alkylidene Cα carbon gave rise to a line at 229 ppm in the ^{13}C-NMR spectrum. The Cβ resonance occurred at δ 93.1; while Cγ, initially attached to Ta in **2a** but now part of the metallacyclic ring, displayed a resonance shifted upfield from δ 245 to 61.3 ppm.

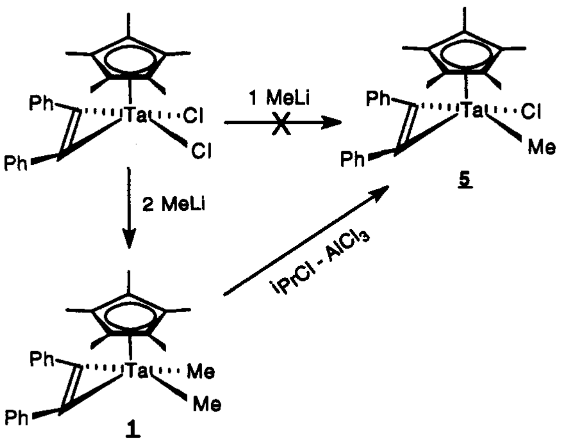
Reaction of the dimethyl compound **1** with 1 equiv of CO led to the oxotantalacyclopentatriene **4** in high yield. An η^2-acyl analogous to **2a** was not observed but is believed to be an unstable intermediate in the reaction. It was necessary to add exactly 1 equiv of CO at low temperature (−78 °C) and gradually warm the solution to room temperature for the success of this reaction. The use of less CO left some of the dimethyl compound unreacted, and the mixture was difficult to separate because **1** and **4** have similar solubilities. When excess CO was employed, extremely complex mixtures resulted that appeared to form from multiple CO insertions and degredation of the Cp*Ta core. In spite of several attempts, we were unable to characterize these intractable mixtures.



(3)

The spectroscopic properties of the oxametallacyclic compound **4** are basically similar to those of the corresponding azametallacycle, complex **3**. The CH_3 peak is observed at δ −0.58 ppm and the phenyl protons show a set of complex multiplets. In the ^{13}C NMR spectrum, the alkylidene Cα carbon is observed at δ 224.5, while the TaCH$_3$ carbon resonates at 29.4.

Although **4** reacts with additional CO or isonitriles, the reactions are complex and pure products could not be isolated. We surmised that the complexity of the reaction was caused by competition between the Ta–CH$_3$ and the alkylidene carbon–metal bonds for an incoming ligand. To solve this problem, we attempted to prepare an analogous oxometallacyclopentatriene that contained no Ta–CH$_3$ bond. Reaction of Cp*Ta(PhC$_2$Ph)Cl$_2$ with 1 equiv of CH$_3$Li does *not* lead to Cp*Ta(PhC$_2$Ph)(CH$_3$)Cl (**5**) but rather to a mixture of the dimethyl compound **1** and the starting material. It appears that once the monomethyl Ta complex is formed it reacts with an additional 1 equiv of CH$_3$Li faster than does the dichloride. However, high yields of Cp*Ta(PhC$_2$Ph)(CH$_3$)Cl (**5**) could be prepared by the reaction of the Ta(CH$_3$)$_2$ complex **1** with isopropyl chloride in the presence of a catalytic amount of AlCl$_3$ (a controlled source of HCl) (eq 4). Thus, electrophilic cleavage of the Ta–Me bond in **1** is faster than in **5** as expected.



(4)

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[15] Templeton, J., Stone, F. G. A., West, R., Eds. *Advances in Organic Chemistry*; Academic Press: San Diego, 1989; pp 1–100.

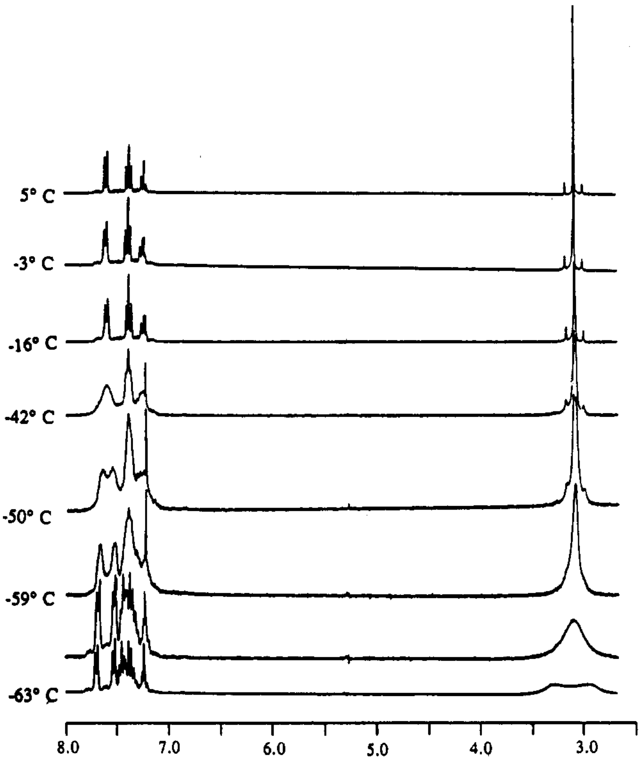
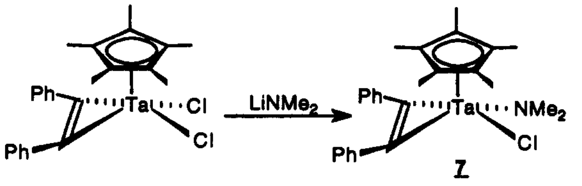


Figure 1. Variable-temperature proton NMR spectra (phenyl and methyl region) of Cp*Ta(η^2-PhCCPh)(Cl)(NMe$_2$) (7).

Reaction of 5 with 1 equiv of CO led to the corresponding metallacycle as deduced from the proton NMR spectrum, but the reaction was not as clean as that of the dimethyl compound. The proton NMR spectrum of the product was similar to that of 4 except that the upfield resonance due to TaCH$_3$ protons in 4 is absent in the chloro compound. The peak due to the ring methyl hydrogen atoms was observed at δ 2.53 (cf. δ 2.45 in 4). The instability of the product in solution prevented the acquisition of a decent ^{13}C-NMR spectrum.

In hopes of obtaining a more stable compound, the dimethylamino derivative Cp*Ta(PhC$_2$Ph)N(CH$_3$)$_2$Cl (7) was made from the reaction of Cp*Ta(PhC$_2$Ph)Cl$_2$ with 2 equiv of lithium dimethylamide (eq 5). No disubstituted product was formed. Compound 7 showed a singlet in the ^{1}H-NMR spectrum at δ 3.00 ppm (6H) assigned to the dimethylamido ligand and a singlet at δ 1.82 for Cp*. The phenyl protons showed the usual splittings observed for the other alkyne complexes, 1 and 5. In the ^{13}C-NMR spectrum, the alkyne carbon atoms resonate at δ 209.7 and the NCH$_3$ carbons were observed at δ 48.7.



(5)

A variable-temperature NMR of 7 showed that the rotation of the alkyne ligand was frozen below *ca.* −50 °C at which temperature the two phenyl rings were inequivalent (see Figure 1). As the temperature was raised, the two sets of ring signals coalesced at ca. −33 °C. The barrier to rotation was estimated to be 11.7 kcal/mol, a value in agreement with those reported for a related compound.[5a]

Table 4. Selected ^{13}C NMR Values of Cp*Ta(ArCCAr)XY Complexes

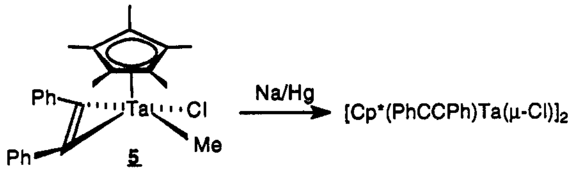
complex	C_{alkyne}	$C_5(CH_3)_5$	ref
X = Y = CH$_3$, Ar = Ph	239	115	this work
X = CH$_3$, Y = Cl, Ar = Ph	225	118	this work
X = Y = Cl, Ar = Ph	222	122[a]	5a
X = Y = Cl, Ar = *p*-tolyl	222	121	11
X = Cl, Y = N(CH$_3$)$_2$, Ar = *p*-tolyl	210	117	this work

[a] In CD$_2$Cl$_2$ solvent. All other values were obtained in C$_6$D$_6$ solvent.

The two methyl groups of the dimethylamido ligand are also equivalent on the NMR time scale at room temperature due to fast rotation around the Ta–N axis. The coalescence temperature of the dimethylamido ligand is *ca.* −63 °C. The barrier to rotation was estimated to be *ca.* 9.8 kcal/mol. It appears that the alkyne and the amido ligands rotate independently of each other.

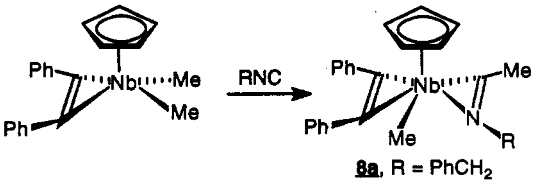
The ^{13}C-NMR resonances of the alkyne carbons for the Cp*Ta(ArCCAr)XY complexes vary with the π-donating abilities of X and Y ligands. When X and Y are better π-donors, these resonances shift upfield (see Table 4), but there is no monotonic correlation of the shift with any of the usual Hammett type σ-constants.

We attempted the preparation of a low-valent Ta alkyl dimer by reduction of Cp*Ta(PhC$_2$Ph)(CH$_3$)Cl (5) with sodium amalgam. The previously reported[11] dimeric compound, [Cp*Ta(PhC$_2$Ph)Cl]$_2$, was the only isolable compound (eq 6). It is unclear why the loss of methyl takes precedence over loss of chloride upon reduction.



(6)

Niobium Complexes. In attempts to extend the synthesis of the metallacyclopentatrienes to niobium, CpNb(PhC$_2$Ph)(CH$_3$)$_2$[5b] was treated with isonitriles to obtain the corresponding iminoacyl complexes 8a and 8b (eq 7). The ^{1}H-NMR spectrum of 8a showed a singlet at δ 1.14 assigned to NbCH$_3$ hydrogen atoms, a singlet at δ 2.26 for (CH$_3$C), and two doublets at δ 4.17 and 4.29 (J = 13 Hz) for the diastereotopic benzylic hydrogen atoms. The Cp protons showed a singlet at δ 5.26. Compound 8b also showed a spectrum consistent with the structure shown in eq 6. The ^{13}C-NMR spectrum showed a line at δ 196 assigned to the alkyne carbons. The iminoacyl carbon bonded to Nb was not observed. The NbCH$_3$ carbon resonated at δ 23.3. Attempts to thermally rearrange 8a or 8b led to intractable mixtures of products. No metallacyclic products were isolated or detected.



(7)

8a, R = PhCH$_2$
8b, R = ^{t}Bu

In an NMR tube experiment, CpNb(PhCCPh)(CH$_3$)$_2$ was treated with less than 1 equiv of CO to give a mixture of starting material and a new compound in which a singlet

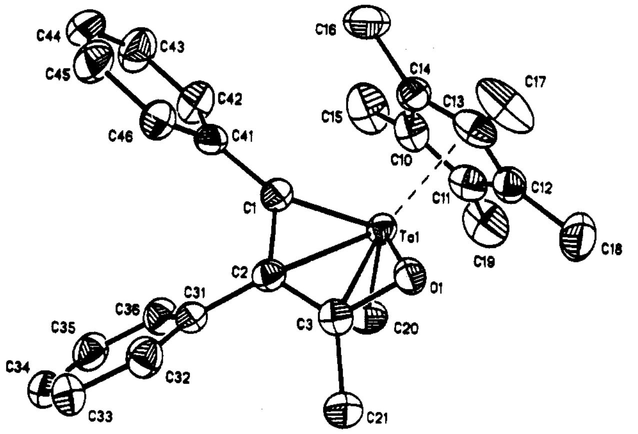


Figure 2. ORTEP plot of Cp*MeTa(CPhCPhCCH$_3$O) (4) with the atom numbering scheme.

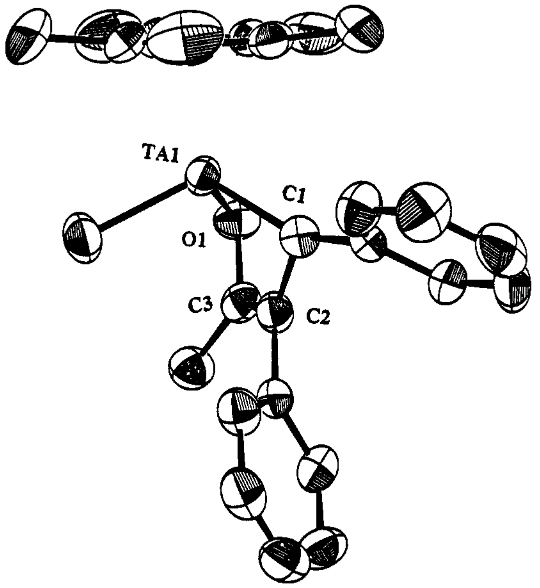
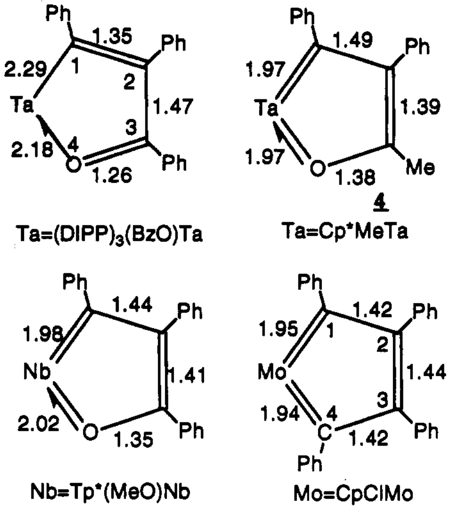


Figure 3. ORTEP plot of Cp*MeTa(CPhCPhCCH$_3$O) (4) that shows the folding of the metallacycle.

at δ −0.45 was observed. This resonance, in comparison with the Ta metallacyclopentatrienes 3 and 4 discussed above, is characteristic of the Nb*CH$_3$* group in three-legged piano-stool metallacyclopentatrienes. A similar reaction with 1 equiv of CO failed to give a clean product. It seems that once the Nb cyclopentatriene is formed, it consumes the incoming CO faster than the starting complex. Recently, a Tp*Nb oxacyclopentatriene complex was synthesized and characterized by X-ray diffraction (Tp* = hydridotris(3,5-dimethylpyrazolyl)borate).[16]

Chart 1



Molecular Structure of Cp*Ta(C(Ph)C(Ph)C(CH$_3$)O)(CH$_3$) (4). An ORTEP plot of 4 with the numbering scheme is shown in Figure 2. Another view that emphasizes the folding of the metallacycle is given in Figure 3. The Ta=C1 bond distance of 1.972(8) Å is in the range observed for Ta alkylidene bonds[17,6c] and is much shorter than the Ta–C20 single bond of 2.194(9) Å. With bond distances of 1.49(1) (C1–C2), 1.39 (1) (C$_2$–C$_3$), and 1.38(1) Å (C3–O1), there is a pronounced single-double-single bond alternation in the metallacyclic ring. The C3–O1 bond distance is about 0.1 Å longer than that observed in a planar oxatungstacyclopentadiene[18] in which the oxygen atom forms a dative bond to the metal. A value of 1.97 Å for the Ta–O bond is about 0.2 Å shorter than that in the Ta(IV) oxacyclopentadiene[19] (see comparison given in Chart 1, DIPP = 2,6-diisopropylphenoxide), and slightly shorter than the Nb-O distance in a folded niobacyclopentatriene.[16] Hence 4 is clearly best represented as an oxotantalacyclopenta*tri*ene similar to the azametallacyclopentatrienes reported earlier.[6a–c] As with the rings in these previous examples, the ring in complex 4 is folded along the C1–O axis by 124°.

The ring folding in metallacyclopenta*trienes* has been traced to the relief of antibonding interactions between the C2,C3 π-bond and one of the d-orbitals on Ta.[6a,20] The metal accepts electrons from the HOMO of the ring fragment and donates electrons into the LUMO of the ring fragment. Thus the metal mediates a flow of electrons from π_2 to π_3* of the C$_3$O- or C$_4$-butadiene-like molecular orbitals. This synergistic back-donation results in enhancement of multiple bond character between the terminal atoms of the C$_3$O- or C$_4$-ligand and the metal. In the extreme of complete transfer of electrons from π_2 to π_3*, the C2–C3 bond order approaches 2 and the C1–C2 and C3–O bond orders approach unity. If the transfer of electrons from π_2 to π_3* is minimal, however, the C1–C2 and the C3–O bonds are double and the C2–C3 bond order approaches 1. In actual compounds, the bonding lies between the two extremes. The "C$_3$O" ring in 4 is more electronegative than the "C$_4$" ring in isoelectronic CpMoCl(C$_4$Ph$_4$),[6a,b] and the Cp*TaMe fragment is probably less electronegative than CpMoCl. Both of these effects would enhance electron transfer from π_2 to π_3* in 4. Thus a more significant single-double-single bond alternation is observed in 4 than in its molybdenum containing counterpart, CpClMo(C$_4$Ph$_4$) (see Chart 1).[6a,b] Also, the data summarized in Chart 1 suggests that there is more electron transfer in 4 than in the Tp*(Me)Nb metallacycle made by Etienne, White, and Templeton.[16]

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[16] Etienne, M.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 4010.

[17] (a) Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793. (b) Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578. (c) Churchill, M. R.; Hollander, F. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1978**, *100*, 647. (d) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am Chem. Soc.* **1982**, *104*, 7338.

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In conclusion, we compare the coupling of alkynes and other isoelectronic groups with the first steps of alkyne polymerization. The alkylidene pathway forms a polyene backbone with double bonds introduced between the starting monomer units. The structure of the Cp*Ta(C(Ph)C(Ph)C(CH_3)O)(CH_3) (4) reveals two coupled ligands, diphenyl acetylene and CO, with a double bond introduced between them along with the formation of a metal–alkylidene bond. This compound and the other metallacyclopentatrienes discussed in this paper can be considered as analogous to an arrested first polymerization step. We believe that a close scrutiny of these compounds as possible alkyne polymerization initiators is worthwhile.

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Supplementary Material Available: Tables of hydrogen atom positions, complete bond distances, angles, and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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