

# Insertion and Alkyne Coupling Reactions on Early-Transition-Metal Centers. Structures of CpTa(Me)( $\eta^2$ -ArCCAr)( $\eta^2$ -MeCN<sup>t</sup>Bu), CpMeTaC(Ph)C(Ph)C(Me)N<sup>t</sup>Bu, and CpClMo(CPh)<sub>4</sub> (Ar = *p*-Tolyl)

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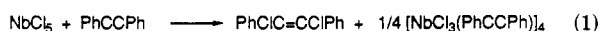
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CpTaCl<sub>2</sub>( $\eta^2$ -ArCCAr) (Ar = phenyl, *p*-tolyl) reacts with MeLi to give CpTaMe<sub>2</sub>( $\eta^2$ -ArCCAr) (1) in high yield. Compound 1 reacts with <sup>t</sup>BuNC to give the  $\eta^2$ -acetimidoyl derivatives CpTaMe( $\eta^2$ -ArCCAr)( $\eta^2$ -MeCN<sup>t</sup>Bu) (4) from the insertion of the isocyanide into one of the Ta-Me bonds. Gentle heating causes a quantitative conversion of 4 into metallacyclopentatriene derivatives, CpMeTaC(Ar)C(Ar)C(Me)N(<sup>t</sup>Bu) (5), in which the alkyne has coupled to the acetimidoyl ligand with the formation of a new C-C bond. A similar coupling reaction is observed when CpMoCl(ArCCAr)<sub>2</sub> is heated in toluene; one of the products of this reaction is the metallacyclopentatriene CpClMo(CAr)<sub>4</sub> (7). The metallacyclic ring in 7 features two Mo=C double bonds (*d* = 1.94 Å) and the ring is folded (dihedral angle  $\approx 117^\circ$ ). The crystal structures of 4b (Ar = *p*-tolyl), 5a (Ar = phenyl), and 7a·CH<sub>2</sub>Cl<sub>2</sub> (Ar = phenyl) have been determined: 4b, *a* = 10.518 (3) Å, *b* = 12.782 (3) Å, *c* = 18.816 (6) Å,  $\alpha = \beta = \gamma = 90^\circ$ , *V* = 2530 (1) Å<sup>3</sup>, *Z* = 4,  $\rho_c = 1.48$  g/mL, space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *R* = 0.027, *R*<sub>w</sub> = 0.026; for 5a, *a* = 9.540 (3) Å, *b* = 10.830 (4) Å, *c* = 11.932 (3) Å,  $\alpha = 114.77$  (2)°,  $\beta = 91.47$  (2)°,  $\gamma = 91.68$  (3)°, *V* = 1117.8 (6) Å<sup>3</sup>, *Z* = 2,  $\rho_c = 1.59$  g/mL, space group *P* $\bar{1}$ , *R* = 0.045, *R*<sub>w</sub> = 0.044; 7a·CH<sub>2</sub>Cl<sub>2</sub>, *a* = 10.039 (4) Å, *b* = 11.760 (3) Å, *c* = 12.674 (8) Å,  $\alpha = 92.21$  (4)°,  $\beta = 87.35$  (4)°,  $\gamma = 104.05$  (3)°, *V* = 1449 (1) Å<sup>3</sup>, *Z* = 2,  $\rho_c = 1.46$  g/mL, space group *P* $\bar{1}$ , *R* = 0.038, *R*<sub>w</sub> = 0.038.

## Introduction

Alkyne complexes of early transition metals are of interest for several reasons, among them the fact that compounds of these elements are efficient catalysts for the oligomerization and polymerization of internal alkynes.<sup>1</sup> Many of the catalyst recipes start with NbCl<sub>5</sub> or TaCl<sub>5</sub> plus an alkylating/reducing agent, e.g. R<sub>4</sub>E (R = alkyl, hydride; E = Si, Sn), and the nature of the catalytically active species is obscure. Even diphenylacetylene alone is capable of reducing NbCl<sub>5</sub> to a Nb(III) alkyne adduct (eq 1),<sup>2</sup> so it is almost certain that the actual catalyst is a reduced Nb or Ta complex.



Cotton et al. obtained similar alkyne adducts by the reaction of internal alkynes with M<sub>2</sub>Cl<sub>6</sub>(THT)<sub>3</sub> (M = Nb, Ta; THT = tetrahydrothiophene) and showed these were capable of catalyzing alkyne trimerization and polymerization.<sup>3</sup>

Metal-catalyzed alkyne polymerization reactions are known to follow at least two different mechanisms.<sup>4</sup> Broadly, these are the *alkylidene*<sup>5,6</sup> and *alkenyl*<sup>7</sup> pathways. In the former, alkynes add to a metal alkylidene to form

a metallacyclobutene intermediate, which ring-opens and forms a vinyl alkylidene, etc. This process has much in common with olefin metathesis, and catalysts active for metathesis are also active for alkyne polymerization.<sup>8</sup> In the alkenyl mechanism, the initiation step consists of the insertion of an alkyne into an M-R (R = H, alkyl, etc.) bond to form a metal-alkenyl bond. Propagation then consists of repeated insertions of the alkyne into succeeding M-CR=CRP bonds (P = polymer chain).

If these mechanisms are operative in the early-transition-metal-catalyzed polymerizations of internal alkynes, then there arises the question of how the initial metal alkylidene or alkenyl is formed, especially in systems that contain no cocatalyst, e.g. R<sub>4</sub>Sn. In this paper, we report the synthesis and characterization of some new alkyl/alkyne complexes of Nb and Ta and some new coupling reactions involving alkynes on early transition metals that produce metallacycles with metal-carbon double bonds (i.e. alkylidenes). Such reactions may have some bearing on chain initiation steps in alkyne polymerization reactions. Preliminary communications on this subject have been published.<sup>9,10</sup>

## Experimental Section

All solvents were rigorously dried and distilled under vacuum or under an inert atmosphere by standard methods. All manipulations of solutions and air-sensitive materials were performed in an inert-atmosphere box equipped with a catalytic purifying train or in the usual Schlenk equipment. NMR spectra were recorded on Bruker WM-360 or AM-300 instruments (360 MHz (<sup>1</sup>H), 90.56 MHz (<sup>13</sup>C) and 300 MHz (<sup>1</sup>H), 75.5 MHz (<sup>13</sup>C), respectively). Unless noted otherwise, the probe temperature was ca. 22 °C for <sup>1</sup>H spectra and 30 °C for <sup>13</sup>C spectra. IR spectra were obtained on either a Perkin-Elmer 1330 grating spectrometer or on a Nicolet 60-SX FTIR instrument. Polystyrene films were used to calibrate frequencies. Mass spectra were gathered on a Finnegan 4021 or a VG-70-250-S spectrometer. Elemental analyses

(1) (a) Masude, T.; Isobe, E.; Higashimura, T.; Takada, K. *J. Am. Chem. Soc.* **1983**, *105*, 7473. (b) Masude, T.; Niki, A.; Isobe, E.; Higashimura, T. *Macromolecules* **1985**, *18*, 2109.

(2) (a) Hey, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *514*. (b) Hey, E.; Weller, F.; Dehnicke, K. *Naturwissenschaften* **1983**, *70*.

(3) (a) Cotton, F. A.; Hall, W. T.; Conn, K. J.; Karol, F. J. *Macromolecules* **1981**, *14*, 233. (b) Cotton, F. A.; Roth, W. J. *Inorg. Chim. Acta* **1984**, *85*, 17. (c) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1981**, *10*, 1285; **1980**, *19*, 2352; *J. Am. Chem. Soc.* **1979**, *101*, 5094.

(4) (a) Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 2182. (b) Clarke, T. C.; Yannoni, C. S.; Katz, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 7787.

(5) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

(6) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, England, **1982**; Vol. 8, pp 499-552.

(7) Taqui Kahn, M. M.; Martell, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic Press: New York, **1974**; Vol. II.

(8) Katz, T. J.; Lee, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 422.

(9) Curtis, M. D.; Real, J. *J. Am. Chem. Soc.* **1986**, *108*, 4608.

(10) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218.

were performed by Schwarzkopf Microanalytical Laboratories or Galbraith Laboratories.

The syntheses of  $(\text{Cp} \text{ or } \text{Cp}')\text{MCl}_2(\text{ArCCAr})$  ( $\text{M} = \text{Nb}, \text{Ta}$ ;  $\text{Cp} = \text{C}_5\text{H}_5$ ;  $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$ ;  $\text{Ar} = \text{Ph}, p\text{-tolyl}$ ) have been reported previously.<sup>11,12</sup>

**CpNbMe<sub>2</sub>(ArCCAr)** ( $\text{Ar} = p\text{-Tolyl}$ ). A solution of  $\text{CpNbCl}_2(\text{ArCCAr})$  (0.50 g, 1.15 mmol) in 50 mL of toluene was cooled to  $-8^\circ\text{C}$ , and 16 mL of a 0.144 M MeLi (2.30 mmol) solution in ether was added with vigorous stirring. The solution turned from red to yellow immediately. The mixture was stirred at  $-8^\circ\text{C}$  for 1 h, and the LiCl precipitate was removed by filtration through a 1-cm layer of Celite. The Celite was washed with hexane, and the solvent was removed from the combined filtrate and washings under vacuum. The residue was redissolved in 20 mL of toluene and filtered through Celite again if any cloudiness due to the remaining LiCl was evident. The clear toluene solution was concentrated to a minimal volume (ca. 1 mL), and 2 mL of hexane was added. Scratching the walls of the flask with a spatula induced crystallization of the product, which was collected by filtration, washed with a few milliliters of cold hexane, and dried under vacuum; yield 0.41 g (90%). Alternatively, the oil resulting from the complete removal of solvent from the filtered reaction mixture was held under dynamic vacuum for 2-h until the product solidified. In this case, the yield is quantitative and the product shows no impurities in the  $^1\text{H}$  NMR spectrum. Anal. Found (calcd for  $\text{C}_{23}\text{H}_{25}\text{Nb}$ ): C, 70.18 (70.15); H, 6.52 (6.39).  $^1\text{H}$  NMR (360 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.76 (s, 6 H, NbMe), 2.14 (s, 6 H, ArMe), 5.70 (s, 5 H, Cp), 7.08, 7.52 (dd,  $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz, 8 H, Ar H).  $^{13}\text{C}$  NMR (90.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  21.4 (ArMe), 40.1 (br,  $w_{1/2} = 71$  Hz, NbMe), 107.5 (Cp), 129.6, 137.4, 140.2 (Ar, fourth peak not resolved), 226.8 (br,  $w_{1/2} = 19$  Hz,  $\text{C}\equiv\text{C}$ ). At  $-60^\circ\text{C}$ , the NbMe peak sharpens:  $w_{1/2} = 10$  Hz.

**CpTaMe<sub>2</sub>(ArCCAr)** ( $\text{Ar} = p\text{-Tolyl}$ ). This complex was prepared from 0.52 g (1.00 mmol) of  $\text{CpTaCl}_2(\text{ArCCAr})$  and 13.9 mL of 0.144 M MeLi (2.00 mmol) in ethyl ether by the procedure described above; yield 92–100%. Anal. Found (calcd for  $\text{C}_{23}\text{H}_{25}\text{Ta}$ ): C, 57.39 (57.27); H, 5.47 (5.22).  $^1\text{H}$  NMR (360 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  0.36 (s, 6 H, TaMe), 2.17 (s, 6 H, ArMe), 5.71 (s, 5 H, Cp), 7.11, 7.50 (dd,  $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz, 8 H, Ar H).  $^{13}\text{C}$  NMR (gated  $^1\text{H}$ , 90.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  21.2 (q,  $J = 126$  Hz, ArMe), 46.3 (q,  $J = 120$  Hz, TaMe), 107.5 (d,  $J = 175$  Hz, Cp), 128.3 (d,  $J = 158$  Hz) and 129.5 (d,  $J = 156$  Hz, Ar C<sub>2</sub>, C<sub>3</sub>), 137.2 (s, Ar C<sub>4</sub>), 143.1 (s, Ar C<sub>1</sub>), 239.4 (s,  $\text{C}\equiv\text{C}$ ).

**CpTa(Me)(ArCCAr)( $\eta^2\text{-MeCN}^t\text{Bu}$ )** ( $\text{Ar} = p\text{-Tolyl}, \text{Ph}$ ). The two derivatives with  $\text{Ar} = p\text{-tolyl}, \text{Ph}$  were prepared by identical procedures from the corresponding alkyne complex  $\text{CpTaMe}_2(\text{ArCCAr})$ .

A solution of 0.48 g (0.99 mmol) of  $\text{CpTaMe}_2(\text{ArCCAr})$  ( $\text{Ar} = p\text{-tolyl}$ ) in 30 mL of toluene was cooled to  $-8^\circ\text{C}$ , and 9.90 mL of a 0.10 M stock solution of *tert*-butyl isocyanide (0.99 mmol) was added with stirring. The mixture was stirred several hours at  $-8^\circ\text{C}$ , and then the solvent was evaporated under vacuum. The crystals were washed with 5 mL of hexane and dried under vacuum. A second crop may be obtained by concentrating and cooling the hexane washings; yield 0.55 g (98%) of yellow crystals. Anal. Found (calcd for  $\text{C}_{28}\text{H}_{34}\text{NTa}$ ): C, 59.23 (59.47); H, 5.90 (6.06); N, 2.38 (2.48).  $^1\text{H}$  NMR (300 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  1.01 (s, 9 H, *t*-Bu), 1.09 (s, 3 H, TaMe), 2.21 (s, 6 H, ArMe), 2.58 (s, 3 H, MeCN), 5.35 (s, 5 H, Cp), 7.15, 7.52 (dd,  $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz, 8 H, Ar H). The methyl groups of the *p*-tolyl ligand remained magnetically equivalent at  $-80^\circ\text{C}$ .  $^{13}\text{C}$  NMR (gated  $^1\text{H}$ , 75.5 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  21.16 (q,  $J = 119$  Hz, TaMe), 21.29 (q,  $J = 126$  Hz, ArMe), 23.25 (q,  $J = 128$  Hz, MeCN), 29.70 (q,  $J = 126$  Hz, NCM<sub>3</sub>), 62.43 (s, NCM<sub>3</sub>), 101.76 (d,  $J = 175$  Hz, Cp), 142.42 (s, Ar C<sub>1</sub>), 127.82, 129.07 (d, Ar C<sub>2</sub>, C<sub>3</sub>,  $J$  values obscured by solvent peaks), 135.21 (s, Ar C<sub>4</sub>), 199.68 (s,  $\text{C}\equiv\text{C}$ ). The diphenylacetylene complex shows analogous spectral properties.

**CpMeTaC(Ar)C(Ar)C(Me)N(<sup>t</sup>Bu)** ( $\text{Ar} = p\text{-Tolyl}$  or Ph). Only the synthesis of the *p*-tolyl complex is given. The phenyl derivative was prepared by an exactly analogous procedure.

A solution of 0.20 g (0.35 mmol) of  $\text{CpTaMe}(\text{ArCCAr})(\eta^2\text{-MeCN}^t\text{Bu})$  in 12 mL of toluene was held at  $90^\circ\text{C}$  for 15 h. The solution was then evaporated to dryness under vacuum to give

an orange, microcrystalline product in quantitative yield.  $^1\text{H}$  NMR (360 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  -0.96 (s, 3 H, TaMe), 1.28 (s, 9 H, *t*-Bu), 2.01, 2.04 (s, s, 3 H, 3 H, ArMe), 2.38 (s, 3 H, Me), 5.89 (s, 5 H, Cp), 6.92, 7.10 ( $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz, 4 H, Ar H), 6.97 ( $w_{1/2} = 30$  Hz) and 7.43 ( $w_{1/2} = 50$  Hz) (4 H, Ar H).  $^1\text{H}$  NMR (360 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.34 (s, 3 H, TaMe), 1.44 (s, 9 H, *t*-Bu), 2.20 (s, 3 H, Me), 2.24, 2.25 (s, s, 3 H, 3 H, ArMe), 6.18 (s, 5 H, Cp), 6.78, 6.87 ( $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz), 6.99 ( $w_{1/2} = 40$  Hz).  $^1\text{H}$  NMR (360 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-60^\circ\text{C}$ ):  $\delta$  -1.38 (s, 3 H, TaMe), 1.46 (s, 9 H, *t*-Bu), 2.20, 2.26, 2.27 (3 s, 3  $\times$  3 H, 2 ArMe + CMe), 6.23 (s, 5 H, Cp), 6.81, 6.90 ( $\text{A}_2\text{B}_2$ ,  $J = 8$  Hz, 4 H, Ar H), 6.61, 6.86, 7.21, 7.67 (4 dd,  $^3J = 8$  Hz, 4  $\times$  1 H, Ar H).  $^{13}\text{C}$  NMR (90.5 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $-60^\circ\text{C}$ ):  $\delta$  20.5, 21.1, 21.3, 22.1 (4 Me), 33.4 (CMe<sub>3</sub>), 61.7 (CMe<sub>3</sub>), 104.2 (Cp), 98.0, 117.6 (2 Cp), 128.3, 128.4, 128.5, 131.1, 132.6, 132.9, 135.9, 137.5, 144.9 (9 aryl C atoms, tenth not resolved), 228.0 (C<sub>2</sub>). Anal. Found (calcd for  $\text{C}_{28}\text{H}_{34}\text{NTa}$ ): C, 59.32 (59.47); H, 5.91 (6.06); N, 2.29 (2.48).

Similar spectral properties were obtained for the  $\text{Ar} = \text{phenyl}$  derivative. MS (Cl, methane,  $m/z$  (relative intensity)): 538 (100,  $\text{M}^+ + 1$ ), 537 (56,  $\text{M}^+$ ), 522 (9,  $\text{M}^+ - \text{Me}$ ), 460 (z,  $\text{M}^+ - \text{Ph}$ ), 292 (71), 280 (41). Anal. Found (calcd for  $\text{C}_{26}\text{H}_{30}\text{NTa}$ ): C, 57.86 (58.10); H, 5.79 (5.63); N, 2.51 (2.61).

**Reaction of CpTaMe<sub>2</sub>(ArCCAr) with CO** ( $\text{Ar} = p\text{-Tolyl}$ ). The reaction of  $\text{CpTaMe}_2(\text{ArCCAr})$  with excess CO at  $-80^\circ\text{C}$  or at ambient temperature gave a variety of products that could not be separated.

The reaction with  $\leq 1$  equiv of CO was followed by NMR spectroscopy. The  $^1\text{H}$  NMR spectrum of the reaction mixture in  $\text{C}_6\text{D}_6$  showed only those peaks that could be attributed to the starting alkyne complex plus those due to a single, new product. The product has peaks at  $\delta$  -0.55 (s, 3 H, TaMe), 1.98, 2.07 (s, s, 2  $\times$  3 H, ArMe), 2.57 (s, 3 H, OCM<sub>2</sub>), 5.77 (s, 5 H, Cp), and 7.42, 7.03, 6.91, 6.89 (2  $\text{A}_2\text{B}_2$  systems,  $J = 8$  Hz, Ar H). The IR spectrum shows a weak peak at  $1510\text{ cm}^{-1}$  due to the C–O stretch. Attempts to separate the product from the starting material failed, but the spectroscopic properties are consistent with the structure  $\text{CpMeTa}(\text{OCMeCarCar})$ .

**CpMoCl(PhC $\equiv$ CPh)<sub>2</sub>**. This bis(alkyne) complex was prepared by a slight modification of the procedure of Davidson et al.<sup>13</sup>  $\text{CpMo}(\text{CO})_3\text{Cl}$  was refluxed with diphenylacetylene (1:3 mole ratio) in hexane for 24 h while the evolved CO was allowed to escape through a Hg bubbler. The yield of product is increased to 85% by venting the CO.

**CpClMo(C<sub>4</sub>Ph<sub>4</sub>) (7)**. In a 100-mL Schlenk flask was placed 0.70 g (1.3 mmol) of  $\text{CpMoCl}(\text{PhCCPh})_2$  and 30 mL of toluene. This solution was heated under  $\text{N}_2$  for 24 h. After the solution was cooled to room temperature, the toluene was stripped under vacuum and the green-yellow residue washed with hexane (3  $\times$  10 mL). The solid was then dissolved in 30 mL of  $\text{CH}_2\text{Cl}_2$ , and this solution was slowly concentrated under vacuum at room temperature until crystallization just began. The mixture was then allowed to stand at room temperature for 24 h to give brown crystals of the product. The green supernatant was carefully syringed away from the crystals and saved for chromatography, which gives  $\text{Cp}(\eta^4\text{-Ph}_4\text{C}_4)\text{MoCl}_2$  (8; 5%) and the biccapped, dimetallatetrahedrane cluster  $[\text{CpClMo}]_2(\mu\text{-}\eta^4\text{-C}_4\text{Ph}_4)$  (9).<sup>10</sup> The brown crystals were washed with hexane (3  $\times$  10 mL) and dried under vacuum; yield 55%. Anal. Found (calcd for  $\text{C}_{33}\text{H}_{25}\text{ClMo}$ ): C, 70.54 (71.68); H, 4.51 (4.56). MS:  $m/z$  554 (parent ion) with correct MoCl isotope pattern.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.3–7.0 (m, 20 H, Ph), 5.71 (s, 5 H, Cp).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  246 (C<sub>2</sub>), 136.8, 132.7, 132.1, 128.5, 128.0, 127.4, 127.0, 126.2 (Ph), 105.6 (C<sub>2</sub>), 99.3 (Cp).

**X-ray Structure Determinations.** Data were collected on a Syntex P2<sub>1</sub> automated diffractometer operated with the Syntex software package. Crystals were sealed in thin-walled glass capillaries in the inert-atmosphere box. Cell constants and orientation matrices were determined from 15 accurately centered reflections scattered in reciprocal space. Intensities of standard reflections were measured after every 50 data reflections. The direct-methods program MULTAN<sup>14</sup> was used to locate the heavy

(13) Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* 1976, 738.

(14) MULTAN-78 by P. Main, Department of Physics, University of York, York, England, 1978.

(11) Curtis, M. D.; Real, J. *Organometallics* 1985, 4, 940.

(12) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* 1989, 8, 1644.

Table I. Crystallographic Statistics for 4b, 5a, and 7•CH<sub>2</sub>Cl<sub>2</sub>

	4b	5a	7•CH <sub>2</sub> Cl <sub>2</sub>
formula, <i>M<sub>r</sub></i>	C <sub>28</sub> H <sub>34</sub> N <sub>2</sub> Ta, 565.5	C <sub>26</sub> H <sub>30</sub> N <sub>2</sub> Ta, 537	C <sub>34</sub> H <sub>27</sub> Cl <sub>3</sub> Mo, 638
color, crystallizn solvent	pale yellow, hexane	pale yellow, toluene/hexane	brown, CH <sub>2</sub> Cl <sub>2</sub> /hexane
<i>a</i> , <i>b</i> , <i>c</i> , Å	10.518 (3), 12.782 (3), 18.816 (6)	9.540 (3), 10.830 (4), 11.932 (3)	10.039 (4), 11.700 (3), 12.674 (8)
α, β, γ, deg	90.0, 90.0, 90.0	114.77 (2), 91.47 (2), 91.68 (3)	92.21 (4), 87.35 (4), 104.05 (3)
<i>Z</i> ; <i>V</i> , Å <sup>3</sup>	4; 2530 (1)	2; 1117.8 (6)	2; 1449 (1)
ρ <sub>c</sub> , g/cm <sup>3</sup>	1.48	1.59	1.46
space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
cryst dimens, mm	0.11 × 0.22 × 0.33	0.23 × 0.23 × 0.27	
radiation; λ, Å	Mo Kα; 0.710 69	Mo Kα; 0.710 69	Mo Kα; 0.710 69
monochromator	graphite cryst	graphite cryst	graphite cryst
μ, cm <sup>-1</sup>	43.1	48.6	7.41
scan speed, deg/min	4–29 (variable)	2–15 (variable)	2–15 (variable)
scan range	Mo Kα ± 1.0	Mo Kα ± 1.0	Mo Kα – 0.8 to Mo Kα + 0.9
bkgd:scan time	1.0	0.8	0.8
std rflns	400, 040, 004	232, 321, 103	341, 051, 022
2θ limit, deg	45	45	50
no. of rflns	1992 (1550 with <i>I</i> > 3σ( <i>I</i> ))	3142 (2577 with <i>I</i> > 3σ( <i>I</i> ))	5450 (4176 with <i>I</i> > 3σ( <i>I</i> ))
<i>N<sub>o</sub></i> / <i>N<sub>v</sub></i>	6.7	10.2	12.2
GOF	1.77	1.85	1.16
<i>R</i> , <i>R<sub>w</sub></i>	0.027, 0.026	0.045, 0.044	0.039, 0.038

atoms, and the structure was solved and refined with the SHELX<sup>15</sup> software package. Scattering factors were taken from ref 16. Computations were performed either on an Amdahl 5860 or on an IBM 3090 computer at the University of Michigan Computing Center. Crystallographic statistics are presented in Table I.

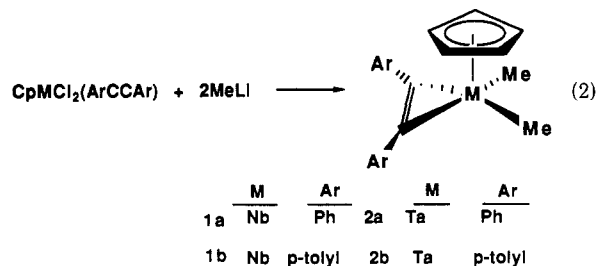
**CpTaMe(ArCCAr)(η<sup>2</sup>-MeC=N<sup>t</sup>Bu) (Ar = *p*-Tolyl).** Crystals suitable for diffraction were grown from a saturated hexane solution cooled to –10 °C. Table I contains relevant statistics. Data were corrected for absorption.<sup>14</sup> The molecule is chiral and crystallized in the polar space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. Refinement with the coordinates inverted from those listed in Table II converged at *R* = *R<sub>w</sub>* = 0.034, thus establishing the structure reported here as the correct enantiomorph.

**CpMeTaC(Ph)C(Ph)C(Me)N<sup>t</sup>Bu.** The *p*-tolyl derivative failed to give high-quality crystals, but excellent crystals of the phenyl analogue were grown from toluene/hexane at –8 °C. All non-hydrogen atoms were refined anisotropically, and H atoms were placed at calculated positions with fixed isotropic temperature factors (*U* = 0.05). The data were corrected for absorption. Table I contains the crystallographic statistics.

**CpMoCl(C<sub>4</sub>Ph<sub>4</sub>)-CH<sub>2</sub>Cl<sub>2</sub>.** Single crystals were grown by allowing hexane to diffuse into a solution of the complex in CH<sub>2</sub>Cl<sub>2</sub>. The X-ray analysis revealed a molecule of CH<sub>2</sub>Cl<sub>2</sub> of solvation, and this was confirmed by the NMR spectrum of the lot of crystals submitted for X-ray analyses. Table I contains the crystallographic statistics. Hydrogen atoms were inserted into calculated positions but not refined. No absorption correction was required.

## Results and Discussion

**Dimethyl Complexes.** The complexes CpMCl<sub>2</sub>(ArC-Ar)<sup>11,12</sup> react smoothly with 2 equiv of MeLi to give the dimethyl derivatives in essentially quantitative yield (eq 2).



Both 1 and 2 are stable indefinitely in the absence of air. Their structures are undoubtedly similar to the

(15) SHELX-76 by G. Sheldrick, University of Cambridge, Cambridge, England, 1976.

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

Table II. Fractional Atomic Coordinates for 4b

atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> , Å <sup>2</sup>
Ta	0.6402 (1)	0.0050 (1)	0.3041 (1)	0.044
C1	0.5491 (12)	0.1429 (9)	0.2488 (7)	0.076
C2	0.7815 (12)	-0.2207 (10)	0.2350 (8)	0.077
C3	0.7124 (12)	-0.1195 (9)	0.2435 (6)	0.055
N1	0.6562 (9)	-0.0603 (7)	0.2008 (5)	0.055
C4	0.6368 (26)	-0.0670 (15)	0.1214 (10)	0.122
C5	0.6727 (23)	0.0256 (22)	0.0907 (9)	0.207
C6	0.4969 (25)	-0.0795 (21)	0.1141 (11)	0.228
C7	0.6970 (47)	-0.1523 (22)	0.0854 (12)	0.355
C60	0.7814 (10)	0.1172 (8)	0.3280 (6)	0.047
C61	0.8225 (10)	0.2281 (8)	0.3279 (6)	0.048
C62	0.8397 (11)	0.2815 (9)	0.2630 (6)	0.057
C63	0.8789 (12)	0.3839 (9)	0.2645 (7)	0.065
C64	0.8966 (14)	0.4356 (10)	0.3279 (10)	0.064
C65	0.8826 (12)	0.3832 (9)	0.3893 (8)	0.070
C66	0.8430 (13)	0.2807 (8)	0.3912 (7)	0.068
C67	0.9471 (16)	0.5487 (10)	0.3263 (11)	0.089
C70	0.8191 (9)	0.0262 (8)	0.3503 (5)	0.041
C71	0.9299 (9)	-0.0175 (9)	0.3851 (5)	0.042
C72	0.9346 (10)	-0.1245 (8)	0.4018 (6)	0.052
C73	1.0367 (11)	-0.1672 (9)	0.4379 (6)	0.056
C74	1.1376 (13)	-0.1102 (10)	0.4570 (6)	0.064
C75	1.1377 (9)	-0.0004 (12)	0.4395 (5)	0.054
C76	1.0363 (10)	0.0426 (8)	0.4053 (6)	0.048
C77	1.2513 (10)	-0.1560 (11)	0.4952 (7)	0.078
C51	0.4326 (14)	0.0148 (13)	0.3613 (9)	0.082
C52	0.4410 (12)	-0.0855 (13)	0.3349 (8)	0.079
C53	0.5408 (12)	-0.1348 (10)	0.3717 (7)	0.067
C54	0.5926 (12)	-0.0609 (13)	0.4205 (7)	0.068
C55	0.5236 (14)	0.0322 (10)	0.4124 (8)	0.070

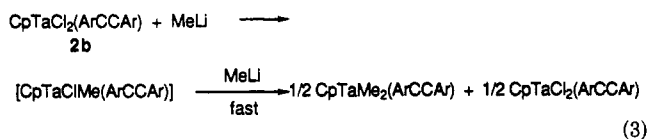
three-legged piano-stool geometry found for the parent dichlorides<sup>11,12</sup> and the related complex Cp\*TaMe<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>),<sup>17</sup> which contains the unusual benzyne ligand.

Compounds 1 and 2 have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Sharp singlets are observed in the <sup>1</sup>H NMR spectrum at δ 0.76 and 0.36 for the methyl groups in 1b and 2b, respectively. The methyl carbon in 2b gives rise to a sharp signal at δ 46.3 (*J*<sub>CH</sub> = 120 Hz). In the Nb compound 1b, a broad (*w*<sub>1/2</sub> = 70 Hz) signal is observed at δ 40.1 at 30 °C, which sharpens somewhat (*w*<sub>1/2</sub> = 10 Hz) at –60 °C. The broadness of the signal is due to unresolved coupling with the Nb nucleus (*I* = 9/2, 100% abundance). At lower temperatures, the relaxation of the quadrupolar nucleus is faster and the metal nucleus is decoupled more effectively.

(17) (a) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* 1979, 101, 263. (b) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* 1979, 18, 1697.

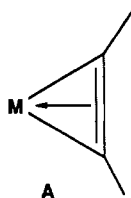
The  $^{13}\text{C}$  NMR chemical shifts of the alkyne carbons appear at low field, ca. 227 and 240 ppm for **1** and **2**, respectively, in the range characteristic of 4e-donor alkyne ligands.<sup>18</sup> Complexes **1** and **2** thus have a 16e count. At first glance, it may seem surprising that a seemingly electronically and coordinatively unsaturated complex with an alkyne cis to an alkyl group would not undergo some type of insertion reaction. However, EHMO calculations<sup>12</sup> have shown that there is a large HOMO-LUMO gap in complexes of the type  $\text{CpM}(\text{alkyne})\text{X}_2$  due to the interaction of the metal orbitals with the unique array of  $\pi_{||}$ ,  $\pi_{\perp}$ , and  $\pi_{||}^*$  orbitals of the alkyne ligand and the complexes are in fact electronically saturated. Any type of insertion reaction would destroy the array of  $\pi_{||}$ ,  $\pi_{\perp}$ , and  $\pi_{||}^*$  orbitals and result in a high-energy, 14e intermediate. A steep ascent along any reaction coordinate to this high-energy intermediate prevents internal insertion reactions.

An attempt to prepare the monomethyl complex by the reaction of 1 equiv of MeLi with the dichloride led to a 50:50 mixture of unreacted starting material and the dimethyl complex according to eq 3. Apparently, when one



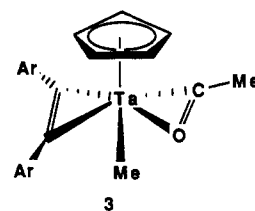
$\pi$ -donor chloride is displaced by a methyl group, the metal atom in the monochloride is more electrophilic and reacts faster with MeLi. Support for this hypothesis is seen in the fact that the alkyne carbons of the methyl derivatives are 10–20 ppm downfield from those in the corresponding dichloro complexes.

**Insertion Reactions.** The structures of  $\text{CpMX}_2(\text{alkyne})$  complexes, and an EHMO analysis of  $\text{CpNbCl}_2(\text{HCCH})$ ,<sup>12</sup> suggest that the bonding between the metal and the coordinated alkyne is best represented as a metallacyclopentene with additional electron donation to the metal from  $\pi_{\perp}$  (structure A). It was therefore of interest



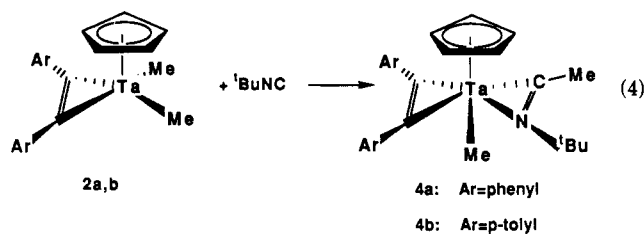
to determine whether or not the metal-carbon bond of the metallacyclopentene would undergo insertion reactions typical of  $\sigma$ -bonds with small molecules, e.g.  $\text{H}_2$ , CO, and isocyanides and, if so, how the Ta-Me bond would compete in these insertion reactions.

Complex **2b** did not react with  $\text{H}_2$  (50 psi) at room temperature. The reactions of **2b** with CO and *tert*-butyl isocyanide were facile, however. With excess CO, a complex mixture of products is formed, but with  $\leq 1$  equiv of CO only one product other than unreacted starting material was shown by NMR spectroscopy to be present in the reaction mixture. The spectroscopic properties of this product were fully consistent with a *static*  $\eta^2$ -acyl complex (**3**). Thus, a resonance at  $\delta -0.55$  could be assigned to the Ta-Me peak and another at  $\delta 2.57$  to the acetyl methyl. The aryl groups were magnetically nonequivalent. A  $\nu_{\text{CO}}$  stretch at  $1510 \text{ cm}^{-1}$  is in the range associated with  $\eta^2$ -acyl complexes.<sup>19</sup> However, **3** is *not* the correct structure as



was shown by the behavior of **2** with isocyanides (see below).

The reaction of **2** with 1 equiv of *tert*-butyl isocyanide in toluene at  $-8^\circ\text{C}$  gives a quantitative conversion to the  $\eta^2$ -acetimidoyl complexes **4** (eq 4). Unlike the NMR



spectrum of the putative compound **3**, the Ta-Me signal is found more downfield at  $\delta 1.09$  and the aryl groups are magnetically equivalent. Magnetically equivalent Ar groups for structure **4** are possible only if there is rapid end-over-end rotation of the coordinated alkyne. The aryl groups of **4** remained magnetically equivalent even at  $-80^\circ\text{C}$ . The fact that the alkyne in **4** appears to rotate freely, whereas the alkyne was static in the CO adduct, strongly suggested that one of the assigned structures was incorrect. An X-ray structure study confirmed the structure shown above for **4**, and EHMO calculations predicted a low barrier for alkyne rotation (see below) in analogous model complexes. Similar low rotation barriers have been observed previously for coordinated alkynes and  $\eta^2$ -alkaneimidoyl complexes,<sup>20–22</sup> and EHMO calculations also predict low barriers for alkyne rotation in similar compounds.<sup>23</sup>

Some of the  $^1\text{H}$  NMR chemical shifts in **4b** differ substantially from those of the precursor, **2b**. The peak corresponding to the Cp protons shifts upfield from  $\delta 5.68$  in **2b** to  $\delta 5.35$  in **4b**, while the methyl resonance moves downfield from  $\delta 0.36$  to  $\delta 1.09$ .

In the  $^{13}\text{C}$  NMR spectrum of **4b**, the resonance of the carbon in the  $\eta^2$ -acetimidoyl group is found at  $\delta 241$  in the range observed previously for acetimidoyl carbons in the early-transition-metal complexes.<sup>24</sup> The alkyne carbon atoms resonate at  $\delta 200$ , and the Ta-Me carbon resonance is found at  $\delta 21$ , 25 ppm upfield from the corresponding resonance in the precursor, **2b**.

At room temperature, we observed no evidence for isocyanide insertion into the Ta-alkyne bonds,<sup>25</sup> nor was any double insertion into the Ta-Me bonds observed. Double insertion, i.e. the migration of two alkyl groups to another ligand, has been found in the reaction of CO with  $\text{Cp}^*\text{TaMe}_4$  ( $\text{Cp}^* = \text{C}_5\text{Me}_5$ ), which gives an  $\eta^2$ -acetone

(20) Adams, R. D.; Chodos, D. F. *Inorg. Chem.* **1978**, *178*, 41.

(21) Alt, H. G. *J. Organomet. Chem.* **1977**, *127*, 349.

(22) Allen, S. R.; Baker, P. K.; Barnes, S. G.; Green, M.; Trollope, L.; Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1981**, 873.

(23) (a) Kreissel, F. R.; Sieber, W. J.; Hofmann, P.; Riedle, J.; Wolfgruber, M. *Organometallics* **1985**, *4*, 788. (b) Schilling, B. E. R.; Hoffmann, R.; Faller, J. W. *J. Am. Chem. Soc.* **1979**, *101*, 592.

(24) McMullen, A. K.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 1072.

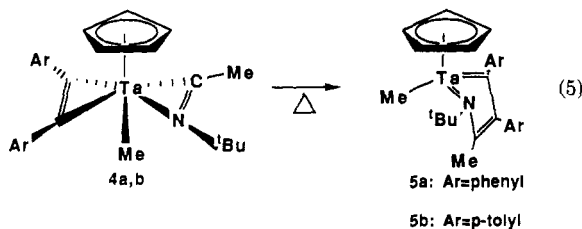
(25) Yamajaki, H. J.; Aoki, K.; Yamamoto, Y.; Wakatsuki, Y. *J. Am. Chem. Soc.* **1975**, *97*, 3546.

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

(19) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550.

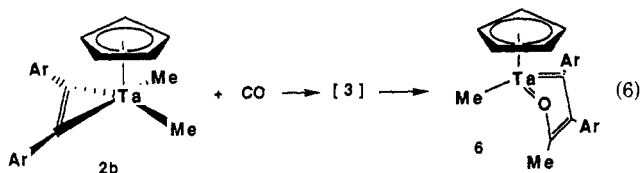
complex,  $\text{Cp}^*\text{TaMe}_2(\eta^2\text{-OCMe}_2)$ .<sup>26</sup>

**Coupling Reactions.** The acetimidoyl complex **4** is stable as a solid at room temperature but slowly undergoes reaction in solution. Heating a solution of **4** results in its rapid and quantitative conversion to an azatantalacyclopentatriene complex, **5** (eq 5).



The structure of **5a** has been confirmed by X-ray diffraction (see below). The Cp resonance in the  $^1\text{H}$  NMR spectrum of **5b** is found at  $\delta$  5.89 (0.54 ppm downfield from the corresponding resonance in **4b**), while the resonance of the methyl bonded to Ta shifts (from  $\delta$  1.09 in **4**) to  $\delta$  -0.96. The peak corresponding to the ring-methyl group is found at  $\delta$  2.38, and the aryl groups are nonequivalent as expected.

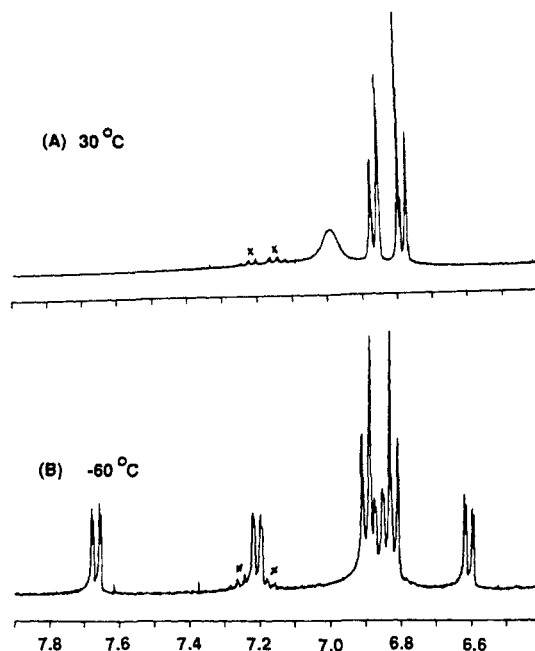
These spectral properties are very similar to those for the product from the reaction of  $\leq 1$  equiv of CO with **2b**. Hence, we are confident that the latter reaction proceeds according to eq 6; i.e., an oxatantalacyclopentatriene (**6**) is formed, probably through the  $\eta^2$ -acetyl complex **3**.



The  $^{13}\text{C}$  NMR spectrum of **5b** shows the expected features, the most interesting being those due to the atoms in the ring. The  $\beta$ -carbons give rise to peaks at  $\delta$  98.0 and 117.6, while the  $\alpha$ -carbon (Ta=C) resonance is found at  $\delta$  228.0. The latter resonance is in the range observed for alkylidene complexes.<sup>27</sup>

Curiously, one of the *p*-tolyl groups (presumably the one attached to  $\text{C}_\alpha$ ) shows restricted rotation about the  $\text{C}_\alpha$ -Ar bond ( $\Delta G^\ddagger = 14 \pm 1$  kcal/mol at 30 °C). Figure 1 shows the aryl region of the  $^1\text{H}$  NMR spectrum of **5b** at room temperature and at -60 °C. At room temperature, one *p*-tolyl group gives rise to the expected  $\text{A}_2\text{B}_2$  quartet, but the other *p*-tolyl proton signals appear as a broad hump. At -60 °C, the  $\text{A}_2\text{B}_2$  pattern remains unchanged, but the hump resolves into four doublets of doublets (ABCD pattern). Similar behavior is seen in the  $^{13}\text{C}$  NMR spectra of **5b**; at room temperature, four peaks are observed for the aryl carbons of the *p*-tolyl attached to  $\text{C}_\alpha$ , whereas at -60 °C six peaks are observed.

In the solid-state structure of **5a**, the phenyl ring bonded to  $\text{C}_\alpha$  adopts a rotational conformation such that the  $\pi$ -system of the phenyl group is conjugated with the Ta-C $_\alpha$  double bond (cf. Figure 3). The partial double-bond character of the  $\text{C}_\alpha$ -Ph bond imparted by the conjugation is most likely responsible for the rotational barrier. The barrier to aryl ring rotation in **6** must be slightly greater than that in **5b**, since the ABCD pattern for one phenyl

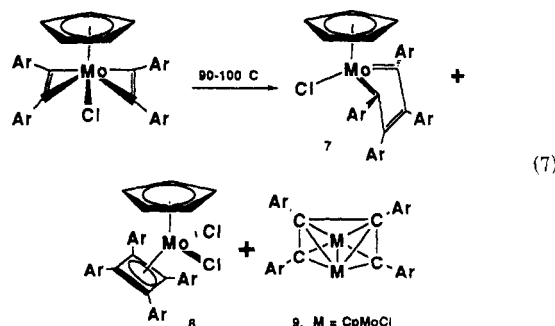


**Figure 1.** Variable-temperature  $^1\text{H}$  NMR (360 MHz) spectra (aryl region only) of  $\text{CpMeTaC}(\text{Ar})\text{C}(\text{Ar})\text{C}(\text{Me})\text{N}(\text{t-Bu})$  (**5b**). The small peaks marked with an "x" arise from a trace impurity (Ar = *p*-tolyl).

is observed even at room temperature.

The structural features of **5a** (see below) showed this compound to be a derivative of a new type of metallacycle, viz. a folded metallacyclopentatriene. It was desirable, therefore, to determine whether or not the parent  $\text{M}(\text{C}_4\text{R}_4)$  ring structure could be produced. The isoelectronic, isolobal  $\text{M}(\text{C}_4\text{R}_4)$  counterpart to **4** is a group 6 complex,  $\text{CpM}(\text{X})(\text{C}_4\text{R}_4)$ , where X is a uninegative ligand. We therefore explored the coupling of two alkyne ligands in complexes of the type  $\text{CpMo}(\text{X})(\text{RCCR})_2$ .<sup>10</sup>

Heating a toluene solution of  $\text{CpMoCl}(\text{PhCCPh})_2$  for 24 h gives a 55% yield of the brown, crystalline metallacycle **7**, along with a 5% yield of the paramagnetic,  $\eta^4$ -cyclobutadiene complex **8** and the bicapped, dimetallate-tetrahedrane cluster **9** (eq 7).<sup>10</sup> Details of the isolation and structures of the last two complexes will be given elsewhere.<sup>28,29</sup>



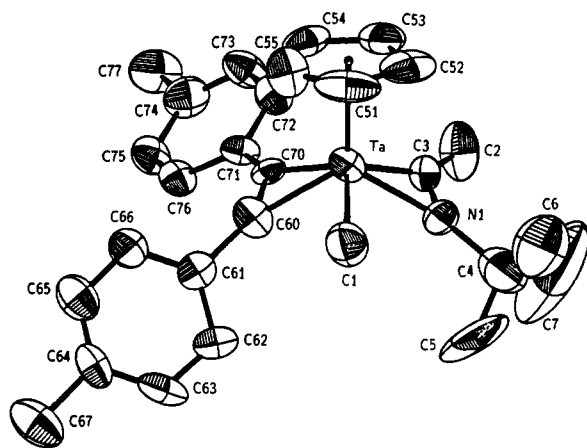
The NMR parameters of **7** are consistent with its solid-state structure (see below). The Cp protons resonate at  $\delta$  5.71, and the phenyl protons give rise to a complex, overlapping set of multiplets in the range  $\delta$  7.3-7.0. The  $\text{C}_\alpha$  resonance is found at  $\delta$  246, and a peak at  $\delta$  105.6 is tentatively assigned to  $\text{C}_\beta$  of the metallacycle. The phenyl carbons give rise to eight peaks in the  $\delta$  137-126 region.

(26) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

(27) (a) van Assalt, A.; Burger, B. J.; Gibson, V. C.; Bercau, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347. (b) Chamberlain, L.; Rothwell, I. P.; Huffman, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 7338. (c) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148.

(28) Curnow, O.; Hirpo, W.; Curtis, M. D. To be submitted for publication.

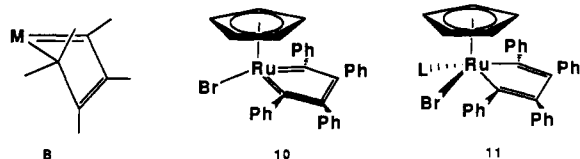
(29) Hirpo, W.; Curtis, M. D. To be submitted for publication.



**Figure 2.** ORTEP plot (50% thermal ellipsoids) of CpTaMe-(ArCCAr)(MeCN<sup>t</sup>Bu) (**4b**).

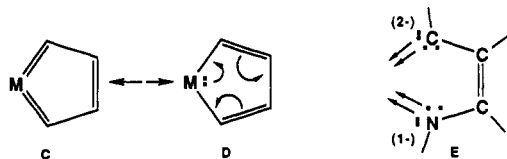
Thus, the phenyl groups appear to be freely rotating on the <sup>13</sup>C NMR time scale at room temperature. In the solid state, the phenyl group attached to C4 is conjugated with the Mo-C4 bond, but the phenyl bonded to C1 is rotated ~90° and is not conjugated with the metallacyclic π-system. The remaining phenyl groups bonded to the C<sub>β</sub> carbons are at intermediate angles.

Related coupling reactions of η<sup>2</sup>-alkaneimidoyls and η<sup>2</sup>-acyls have been observed to give enediamido and enamidolate ligands, respectively.<sup>30</sup> Protonations of bis-(alkyne) complexes have led to folded 1-metalla-1,3-cyclopentadiene structures (B).<sup>31</sup> The most closely related



coupling reaction seems to be that observed by Singleton et al.,<sup>32</sup> in which two alkynes couple to give a planar metallacyclopentatriene (**10**). Addition of a ligand to **10** gives a metallacyclopentadiene structure, e.g. **11**.

At this point, we might note that, for d<sup>n</sup> (n ≥ 2) metal configurations, metallacyclopentatrienes and -dienes are actually resonance extremes, C ↔ D, and that the metal in structure C is formally oxidized 2 units with respect to the metal in structure D. The (formally) C<sub>4</sub>R<sub>4</sub><sup>4-</sup> ligand in C donates eight electrons to the metal, while the C<sub>4</sub>R<sub>4</sub><sup>2-</sup> ligand in D donates four. The C<sub>3</sub>NR<sub>4</sub><sup>3-</sup> ligand in **5** also donates eight electrons to the metal (see E).



Thus, in compound **5** Ta has a formal oxidation state of +5 and has a 16e count; the Mo in **7** is +6 and also has a 16e count. Were **5** and **7** to have the alternate metallacyclopentadiene structure D, each metal would achieve

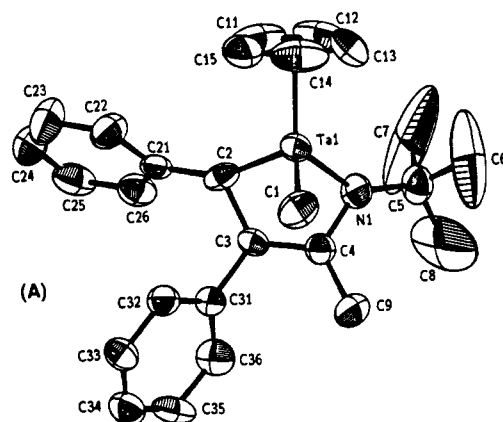
(30) Chamberlain, L. R.; Durfee, L. D.; Fanwick, P. E.; Koberger, L. M.; Latesky, S. L.; McMullen, A. K.; Steffy, B. D.; Rothwell, I. P.; Foltz, K.; Huffman, J. C. *J. Am. Chem. Soc.* 1987, 109, 6068.

(31) Morrow, J. R.; Tonker, J. L.; Templeton, J. L. *J. Am. Chem. Soc.* 1985, 107, 5004.

(32) Albers, M. O.; deWaal, P. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* 1986, 1680.

**Table III.** Bond Distances (Å) and Angles (deg) for **4b**

Distances			
Ta-C1	2.26 (1)	N1-C4	1.51 (2)
Ta-N1	2.12 (1)	C2-C3	1.49 (2)
Ta-C3	2.10 (1)	C4-Me	1.43 [6] (av)
Ta-C60	2.11 (1)	C-C (Cp)	1.40 [2] (av)
Ta-C70	2.09 (1)	C60-C61	1.48 (1)
N1-C3	1.25 (1)	C-C (aryl)	1.38 [3] (av)
C60-C70	1.30 (1)	Ar-Me	1.52 [2] (av)
Angles			
Ta-N1-C3	71.8 (7)	C60-C70-C71	138 (1)
Ta-N1-C4	157.1 (1)	C70-C60-C61	140 (1)
Ta-C3-N1	73.7 (7)	C2-C3-N1	133 (1)
Ta-C3-C2	153 (1)	C4-N1-C3	132 (1)
Ta-C60-C70	71.1 (6)	C1-Ta-N1	85.4 (4)
Ta-C60-C61	148.6 (8)	C1-Ta-C3	119.6 (5)
Ta-C70-C60	72.9 (6)	C1-Ta-C60	82.4 (4)
Ta-C70-C71	149.5 (8)	C1-Ta-C70	118.2 (4)



**Figure 3.** (A) ORTEP plot (50% thermal ellipsoids) of CpMe-TaC(Ph)C(Ph)C(Me)NN<sup>t</sup>Bu (**5a**) that shows the numbering scheme. (B) Side view with the methyl groups of <sup>t</sup>Bu omitted for clarity.

only a 14e count with formal oxidation states of Ta(III) and Mo(IV), respectively.

**Molecular Structures.** CpTa(Me)(η<sup>2</sup>-ArC-CAr)(η<sup>2</sup>-MeCN<sup>t</sup>Bu) (**4b**). Figure 2 shows the molecular structure and numbering scheme. Atomic coordinates are listed in Table II, and derived bond distances and angles are in Table III.

The overall structure is very similar to that of isoelectronic group 6 bis(alkyne) complexes, CpMoX(η<sup>2</sup>-



Table IV. Atomic Coordinates for CpMeTaC(Ph)C(Ph)C(Me)N(<sup>t</sup>Bu) (5a)

atom	x	y	z	U, Å <sup>2</sup>
Ta	0.3737 (1)	0.0927 (1)	0.7735 (1)	0.0368
C11	0.5830 (18)	0.0751 (23)	0.8768 (25)	0.1012
C12	0.5331 (18)	0.1973 (30)	0.9495 (14)	0.0861
C13	0.5390 (20)	0.2776 (16)	0.8882 (24)	0.0823
C14	0.5990 (17)	0.2041 (25)	0.7769 (19)	0.0890
C15	0.6251 (15)	0.0795 (21)	0.7680 (19)	0.0738
C1	0.3319 (14)	0.1136 (15)	0.5970 (13)	0.0662
C2	0.3347 (12)	-0.0995 (13)	0.7420 (10)	0.0430
C3	0.1907 (12)	-0.0808 (12)	0.7046 (10)	0.0344
C4	0.1260 (12)	0.0427 (12)	0.7607 (10)	0.0402
N1	0.1980 (10)	0.1440 (10)	0.8630 (9)	0.0451
C5	0.1329 (15)	0.2416 (14)	0.9734 (12)	0.0535
C6	0.1716 (39)	0.3794 (25)	0.9968 (29)	0.2033
C7	0.1791 (45)	0.2272 (44)	1.0760 (24)	0.3227
C8	-0.0162 (27)	0.2412 (34)	0.9707 (21)	0.1612
C9	0.0095 (14)	0.0801 (14)	0.6946 (12)	0.0580
C21	0.3834 (12)	-0.2333 (11)	0.7222 (10)	0.0376
C22	0.5130 (13)	-0.2782 (14)	0.6695 (14)	0.0613
C23	0.5595 (17)	-0.4050 (17)	0.6524 (17)	0.0818
C24	0.4814 (18)	-0.4886 (15)	0.6870 (15)	0.0733
C25	0.3563 (16)	-0.4491 (14)	0.7398 (14)	0.0660
C26	0.3069 (14)	-0.3214 (14)	0.7575 (12)	0.0542
C31	0.1257 (11)	-0.1931 (11)	0.5879 (10)	0.0381
C32	0.2036 (12)	-0.2518 (12)	0.4830 (11)	0.0437
C33	0.1464 (14)	-0.3597 (13)	0.3763 (11)	0.0483
C34	0.0106 (15)	-0.4081 (14)	0.3758 (12)	0.0555
C35	-0.0675 (14)	-0.3500 (15)	0.4793 (14)	0.0603
C36	-0.0125 (14)	-0.2434 (14)	0.5853 (12)	0.0562
CT <sup>a</sup>	0.5758	0.1667	0.8519	

<sup>a</sup>CT = calculated position of the Cp-ring centroid.

RCCR)<sub>2</sub>.<sup>33</sup> The coordinated atoms of the η<sup>2</sup>-alkyne and η<sup>2</sup>-acetimidoyl ligands are essentially coplanar (deviations ~0.003 Å), and the Ta lies 1.12 Å above this plane. The C60–C70 (1.30 Å) and N1–C3 (1.25 Å) distances are each consistent with bond orders of ca. 2.2. The Ta–C60, Ta–C70, and Ta–C3 distances (2.10 [1] Å average) are considerably shorter than the Ta–Me bond (2.26 Å), indicative of multiple-bond character in the former.

**CpMeTaC(Ph)C(Ph)C(Me)N(<sup>t</sup>Bu) (5a).** Figure 3A shows a view of the molecule along the direction of the Ta–Me bond and shows the numbering scheme. Figure 3B shows the side view, which emphasizes the folding of the metallacyclic ring. Crystallographic statistics are collected in Table I, fractional atomic coordinates are in Table IV, and bond distances and angles are in Table V.

The Ta–C2 distance (1.98 Å) indicates a Ta=C double bond. In tantalum alkylidene complexes, the Ta=C bonds range from 1.98 to 2.07 Å (2.00 [8] Å average).<sup>27b,34</sup> The Ta–N length (1.98 Å) is consistent with an amido linkage with substantial double-bond character. In simple Ta–NMe<sub>2</sub> complexes, the Ta–N bond lengths are found in the range 1.95–1.99 Å, while the Ta–N bonds in dimethylamino complexes, Ta–NHMe<sub>2</sub>, are longer, 2.36–2.38 Å.<sup>35</sup>

Except for Ta, each of the atoms in the metallacyclic ring are planar or sp<sup>2</sup> hybridized. However, these planes are not all parallel. The deviations (Å) of the atoms in the plane (P1) defined by C2, Ta, C3, and C21 are -0.07, +0.02, +0.02, and +0.03, respectively. Plane P2, around C3, forms a dihedral angle of 40° with P1 due to the folding of the metallacyclic (see below). Since P1 and P2 are not copla-

Table V. Bond Distances (Å) and Angles (deg) for 5a

Distances			
Ta–N1	1.98 (1)	C2–C21	1.46 (2)
Ta–C2	1.98 (1)	C3–C31	1.52 (2)
Ta–C1	2.24 (1)	C4–C9	1.51 (2)
C2–C3	1.48 (2)	N1–C5	1.47 (2)
C3–C4	1.39 (2)	C5–Me	1.40 [4] (av)
C4–N1	1.40 (1)	C–C (Cp)	1.36 [2] (av)
Ta···C3	2.39 (1)	C–C (phenyl)	1.39 [2] (av)
Ta···C4	2.40 (1)		
Angles			
Ta–N1–C4	88.7 (6)	C1–Ta–N1	104.8 (4)
Ta–C2–C3	86.1 (7)	C3–C2–C21	122 (1)
C2–C3–C4	122 (1)	C2–C3–C31	117 (1)
C3–C4–N1	117 (1)	C3–C4–C9	121 (1)
Ta–C2–C21	150.6 (9)	C4–N1–C5	126 (1)
Ta–N1–C5	145.5 (9)	N1–C4–C9	120 (1)
C1–Ta–C2	108.1 (5)		

nar, π-overlap between C2 and C3 is diminished. The double-bond character is thus partially destroyed, and the bond is relatively long (1.48 Å).

Similarly, the deviations from plane P3 around N, defined by N, Ta, C5, and C4 are -0.04, +0.01, +0.02, and +0.01 Å. This plane also forms an angle of about 40° with the plane around C4, so substantial N=C4 double bond character is precluded. On the other hand, the planes around C3 and C4 are nearly coincident (the distortions seem to be sterically caused—see Figure 3B) and the C3–C4 bond is short (1.39 Å).

The ring is folded substantially about the C2–N axis. Atoms C2, Ta, and N1 define a plane, P4. Plane P5, formed by the atoms (deviations in Å) C2 (+0.01), C3 (-0.03), C4 (+0.03), and N1 (-0.01), forms a dihedral angle of 120° with P4. Thus, we have the highly unusual situation of a five-membered ring containing three double bonds, yet the ring is nowhere near to being planar!

The folding of the ring brings C3 and C4 within bonding distance of Ta: Ta–C3 = 2.39 Å, Ta–C4 = 2.40 Å (cf. Ta–Cp carbon atoms distances of 2.37–2.41 Å). However, EHMO calculations, to be presented in detail elsewhere, suggest that the primary reason for the ring folding is the relief of antibonding interactions between Ta and C3, C4. Electrons are back-donated from Ta to a C<sub>3</sub>N fragment orbital (π<sub>3</sub><sup>\*</sup>), with the nodal properties shown in F. There



is bonding overlap with the atoms directly bonded to Ta but negative overlap with p orbitals on C3, C4 in the planar conformation. The folding of the ring places one lobe of the d orbital in the nodal plane of the p orbitals (see G), and the Ta–C3, C4 overlap population approaches zero. The Mulliken overlap population between Ta and C3 or Ta and C4 is computed to be ca. -0.1 in the planar ring and 0.0 in the folded ring.

**CpClMo(CPh)<sub>3</sub>·CH<sub>2</sub>Cl<sub>2</sub> (7·CH<sub>2</sub>Cl<sub>2</sub>).** Figure 4A presents an ORTEP plot of the molecular structure with the numbering scheme, and Figure 4B shows the folding of the metallacyclic ring. Crystallographic statistics are in Table I, atomic coordinates are in Table VI, and selected bond distances and angles are collected in Table VII.

The overall molecular structure of 7 is very similar to that of 5. The metallacyclic ring is folded 117° (cf. 120° for 5). The Mo–C1 and Mo–C4 bond lengths are 1.95 and

(33) Mead, K. A.; Morgan, H.; Woodward, P. J. *J. Chem. Soc., Dalton Trans.* 1983, 271.

(34) (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.

(35) Chisholm, M. H.; Huffman, J. C.; Tan, L.-S. *Inorg. Chem.* 1981, 20, 1859.

Table VI. Fractional Atomic Coordinates for  $\text{CpClMo}(\text{CPh})_4 \cdot \text{CH}_2\text{Cl}_2$  ( $7 \cdot \text{CH}_2\text{Cl}_2$ )

atom	x	y	z	U, Å <sup>2</sup>
Mo	0.2037 (0)	-0.0629 (0)	-0.1974 (0)	0.031
Cl1	0.1490 (1)	-0.1186 (1)	-0.0201 (1)	0.060
C1	0.3860 (4)	-0.0753 (3)	-0.2462 (3)	0.032
C2	0.3438 (4)	-0.1963 (3)	-0.2243 (3)	0.030
C3	0.2056 (4)	-0.2557 (3)	-0.2488 (3)	0.030
C4	0.1222 (4)	-0.1896 (3)	-0.2937 (3)	0.032
C11	0.5230 (4)	-0.0028 (3)	-0.2735 (3)	0.034
C12	0.5974 (5)	0.0763 (4)	-0.2016 (3)	0.049
C13	0.7243 (5)	0.1470 (4)	-0.2324 (4)	0.063
C14	0.7767 (5)	0.1404 (5)	-0.3331 (5)	0.066
C15	0.7048 (5)	0.0633 (5)	-0.4050 (4)	0.063
C16	0.5781 (5)	-0.0096 (4)	-0.3749 (3)	0.047
C21	0.4325 (4)	-0.2478 (3)	-0.1581 (3)	0.036
C22	0.5636 (5)	-0.2502 (4)	-0.1966 (4)	0.060
C23	0.6502 (5)	-0.2961 (5)	-0.1366 (5)	0.081
C24	0.6060 (6)	-0.3404 (5)	-0.0405 (5)	0.078
C25	0.4760 (6)	-0.3393 (4)	-0.0004 (4)	0.063
C26	0.3897 (5)	-0.2927 (4)	-0.0594 (3)	0.048
C31	0.1424 (4)	-0.3768 (3)	-0.2126 (3)	0.034
C32	0.2106 (4)	-0.4659 (3)	-0.2321 (3)	0.041
C33	0.1516 (6)	-0.5789 (3)	-0.1991 (4)	0.056
C34	0.0248 (6)	-0.6045 (4)	-0.1480 (4)	0.061
C35	-0.0452 (4)	-0.5183 (5)	-0.1304 (4)	0.065
C36	0.0132 (4)	-0.4039 (4)	-0.1620 (4)	0.049
C41	0.0163 (4)	-0.2352 (3)	-0.3706 (3)	0.034
C42	-0.1045 (4)	-0.1953 (4)	-0.3728 (3)	0.043
C43	-0.1998 (4)	-0.2373 (4)	-0.4489 (4)	0.054
C44	-0.1778 (5)	-0.3198 (4)	-0.5238 (4)	0.051
C45	-0.0606 (5)	-0.3616 (4)	-0.5226 (3)	0.049
C46	0.0360 (4)	-0.3190 (3)	-0.4464 (3)	0.042
C51	0.1525 (5)	0.1138 (4)	-0.1420 (4)	0.054
C52	0.0534 (5)	0.0604 (4)	-0.2147 (4)	0.053
C53	0.1219 (5)	0.0533 (3)	-0.3130 (4)	0.050
C54	0.2639 (5)	0.1038 (3)	-0.3011 (4)	0.048
C55	0.2819 (5)	0.1421 (3)	-0.1945 (4)	0.050
C70	0.3438 (8)	-0.4127 (8)	-0.6170 (6)	0.128
Cl71	0.4151 (2)	-0.3462 (2)	-0.4975 (2)	0.125
Cl72	0.4719 (3)	-0.4173 (3)	-0.7080 (2)	0.164

Table VII. Bond Distances (Å) and Angles (deg) for  $7 \cdot \text{CH}_2\text{Cl}_2$ 

Distances			
Mo-C1	1.946 (4)	C1-C2	1.418 (5)
Mo-C4	1.941 (4)	C2-C3	1.436 (5)
Mo...C2	2.364 (3)	C3-C4	1.422 (5)
Mo...C3	2.350 (3)	Mo-C (Cp)	2.34 [1] (av)
Mo-Cl	2.370 (1)	C-C (Ph)	1.38 [1] (av)
Angles			
Mo-C1-C2	87.8 (2)	Cl-Mo-C4	110.1 (1)
Mo-C4-C3	87.2 (2)	C2-C1-C11	129.9 (3)
C1-C2-C3	116.9 (3)	C1-C2-C21	118.5 (3)
C2-C3-C4	118.0 (3)	C2-C3-C31	121.4 (3)
Mo-C1-C11	141.2 (3)	C4-C3-C31	119.8 (3)
Mo-C4-C41	147.1 (3)	C3-C4-C41	125.2 (3)
Cl-Mo-C1	113.1 (1)		

1.94 Å, respectively. These distances are consistent with Mo=C double-bond distances in acyclic Mo-alkylidene complexes.<sup>19</sup>

The C-C bond distance alternations in **7** are not as pronounced as in **5**. The C1-C2 and C3-C4 lengths are 1.42 Å, and the C2-C3 distance is only slightly longer, 1.44 Å (cf. for **5** C3-C4 = 1.39 Å, C2-C3 = 1.48 Å). The degree of bond localization depends on the net transfer of electrons from  $\pi_2$  to  $\pi_3^*$ :

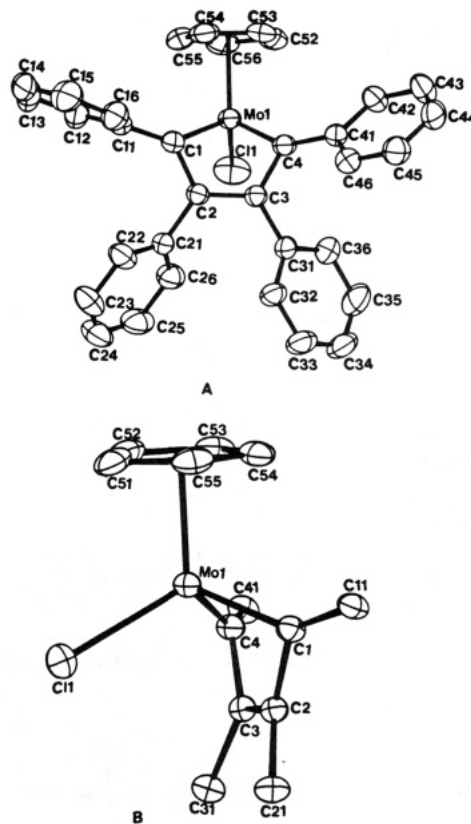
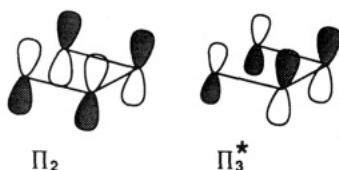


Figure 4. (A) ORTEP plot (50% thermal ellipsoids) of  $\text{CpClMo}(\text{CPh})_4$  (**7**) that shows the numbering scheme. (B) Side view with the ipso carbon atoms only of the phenyl rings retained for clarity.

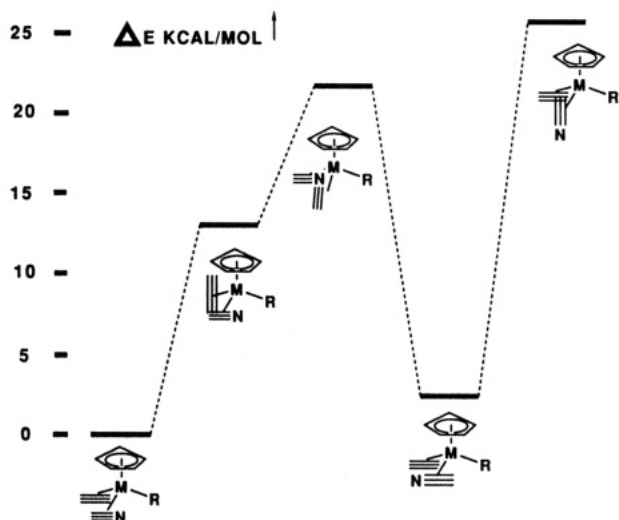
The metal fragment accepts electrons from  $\pi_2$ ; this decreases the bonding population between  $C_\alpha$  and  $C_\beta$  and decreases the antibonding population between the  $\beta$ -carbons. The metal fragment back-donates electrons into  $\pi_3^*$  (normally empty), which increases the antibonding population between  $C_\alpha$  and  $C_\beta$  and increases the bonding population between the  $\beta$ -carbons. The net result of electron flow from  $\pi_2$  to  $\pi_3^*$  is synergetic decrease of the  $C_\alpha$ - $C_\beta$  bond order. The bond lengths change accordingly;  $C_\alpha$ - $C_\beta$  increases, and  $C_\beta$ - $C_\beta$  decreases.

The  $\text{NC}_3$  ring of **5** is undoubtedly more electronegative than the  $\text{C}_4$  ring of **7** and the  $\text{Cp}(\text{Me})\text{Ta}$  fragment less electronegative than the  $\text{CpClMo}$  fragment. Both effects would favor more electron donation into  $\pi_3^*$  in **5** relative to **7** and hence explain the increased bond length alternation in the former.

**EHMO Calculations.**<sup>36</sup> The bonding properties of alkynes to early transition metals have been detailed elsewhere,<sup>12,23</sup> and the same features were seen in the calculations on the model  $\eta^2$ -formimidoyl structure  $\text{CpNb}(\text{Me})(\eta^2\text{-HNCH})(\eta^2\text{-HCCH})$  described here. In compounds of the type  $\text{CpML}_2(\eta^2\text{-HCCH})$ ,  $\pi_1^*$  of the alkyne is found to be a strong acceptor of electrons, the calculated C-C bond order is ca. 2.3, and low barriers (6–10 kcal/mol) for alkyne rotation are computed. The calculations described here were undertaken to assess the effect of the  $\eta^2$ -formimidoyl ligand on the barrier to alkyne rotations, to determine the barrier to formimidoyl group rotation, and to compare the bonding properties of the alkyne and alkaneimidoyl ligands.

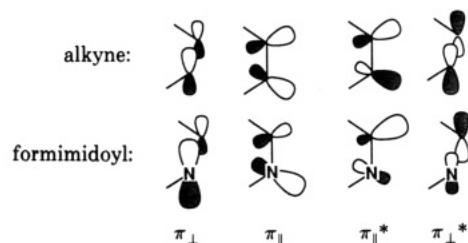
(36) EHMO calculations were performed with Hoffman's program ICONS with the weighted  $H_{ij}$  option: Ammeter, J. H.; Burgi, H.-B.; Thibault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* 1978, 100, 3686.





**Figure 5.** Diagram of the relative energies of  $\eta^2$ -alkyne and  $\eta^2$ -formimidoyl rotamers as calculated by the EHMO method in the model compound  $\text{CpNbMe}(\eta^2\text{-HCCH})(\eta^2\text{-HCNH})$ .

The  $\eta^2$ -formimidoyl ligand is isolobal with an alkyne as shown by the figures



Hence, the overall bonding of the  $\eta^2$ -formimidoyl group to the CpM fragment is very similar to that of alkynes, and the structures of the two ligands are nearly identical (see Figure 2). The Mulliken overlap populations (MOP's) are also very similar. For a +1 charge on the formimidoyl group (i.e. both  $\pi_{\parallel}$  and  $\pi_{\perp}$  filled and, hence, isoelectronic with RCCR),  $\pi_{\parallel}$  donates 0.18e to the metal and  $\pi_{\perp}$  0.21e, and  $\pi_{\parallel}^*$  accepts 1.10e from the metal. For comparison, the corresponding numbers for the  $\eta^2$ -alkyne ligand are  $\pi_{\parallel}$  (0.26),  $\pi_{\perp}$  (0.32), and  $\pi_{\parallel}^*$  (0.81). The C-N bond order calculated from the orbital occupations is 2.2, a number in good agreement with the bond-distance-bond-order correlations.

The relative energies of various rotations are shown in Figure 5. The rotamer with the calculated lowest total energy is the one observed in the solid state, i.e. C-N and C-C vectors parallel and N cis to methyl. The next lowest energy rotamer has the  $\eta^2$ -formimidoyl ligand rotated 180°. This conformation is calculated to be ca. 3 kcal/mol less stable than the observed structure, but a barrier to rotation of 21–26 kcal/mol is computed. The barrier to alkyne group rotation is lower, 13 kcal/mol. These energy barriers are probably upper limits, since no attempt was made to minimize the energies by allowing distortions in the rest of the molecule. Thus, the  $\eta^2$ -formimidoyl group raises slightly the barrier to alkyne rotation (by spreading the energies to the  $t_{2g}$  set of orbitals on the metal), and the activation energy for formimidoyl group rotation is about double that of the alkyne.

### Conclusions

A new class of metallacycles of the type  $\text{MC}_4\text{R}_4$  is now recognized, the metallacyclopentatrienes—these may be folded or flat depending on the electron count. These metallacycles are electronic isomers of the more familiar metallacyclopentadienes and may be formed by coupling of alkyne ligands on early-transition-metal centers. The resulting alkylidene structures may play a role in initiating alkyne polymerization. Aspects of this possibility are currently under investigation.

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### Appendix

The EHMO parameters for C, H, and N were the standard ones contained in the program ICONS. The Nb parameters are listed in ref 12. The molecular geometry was idealized from the observed structures by setting all Nb-C(Cp) distances to 2.34 Å, Nb-C(alkyne or acyl) = 2.10 Å = Nb-N, and C-H = N-H = 1.0 Å. Bond angles were averaged from the observed structure.

**Supplementary Material Available:** Tables IS–IIIS (thermal parameters for 4b, 5a, and 7-CH<sub>2</sub>Cl<sub>2</sub>) and Tables IVS–VIS (bond distances and angles for 4b, 5a, and 7-CH<sub>2</sub>Cl<sub>2</sub>) (6 pages); Tables VIIS–IXS ( $F_o$  vs  $F_c$  for 4b, 5a, and 7-CH<sub>2</sub>Cl<sub>2</sub>) (34 pages). Ordering information is given on any current masthead page.