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1,3-Dimetallacyclobutadiene Derivatives of Niobium and Tantalum Supported by Carbazole Ligation: Reactivity with Organic Isocyanides

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The alkylidyne-bridged substrates [$(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2$] (M = Nb, **1a**; M = Ta, **1b**) react over days at 100 °C in hydrocarbon solution with an excess of carbazole reagents (N′H = carbazole (cbH) tetrahydrocarbazole (thcbH), or 3-tert-butylcarbazole (cbH-3Bu^t)) to produce the corresponding derivatives [$(N')_2M(\mu\text{-}CSiMe_3)_2M(N')_2$] (N′ = cb (**2**), thcb (**3**), cbh-3Bu^t (**4**)) as dark-red (M = Nb, **a**) and orange (M = Ta, **b**) solids. Solutions of the niobium and tantalum complexes in hydrocarbon solvents are deep-blue and deep-red, respectively. Only compound **4b** was sufficiently soluble for detection of the bridging alkylidyne carbon resonance at δ 412 ppm in the ^{13}C NMR spectrum. The solid-state structure of **2a** and isomorphous **2b** shows the central 1,3-dimetallacyclobutadiene core supported by the four N-donor carbazole ligands with M−M distances of 2.9015(4) Å (M = Nb) and 2.8801(4) Å (M = Ta). Compounds **2a**,**2b** react rapidly with 1 equiv of 2,6-dimethylphenyl isocyanide to form much more soluble organometallic products **5a**,**5b**, respectively. The solid-state structures of **5a** and isomorphous **5b** show that coupling of the isocyanide molecule has occurred with one of the alkylidyne bridges to produce a new bridging ligand that can be described as an amido−alkyne. The amido nitrogen of this functionality is bonded to one metal center while the alkyne unit is strongly bound to the other metal center in a metallacyclopropene ring. The remaining alkylidyne group is nonsymmetrically bound to the two metal centers with distances of 1.937(8), 2.069(8) Å (M = Nb) and 1.95(1), 2.05(1) Å (M = Ta).

Introduction

The dialkylamido ligand, NR_2, has played an important role in the development of inorganic chemistry.[1] In transition metal chemistry, studies of the homoleptic dialkylamido complexes (a valuable class of starting materials) has contributed greatly to our understanding of the electronic structure and bonding in both mononuclear and binuclear species.[2,3] More recently, bulky dialkylamido ligands as well as chelating and tripodal amido ligands have been utilized to support novel inorganic and organometallic chemistry at early d-block metal centers.[4−9]

A dominant feature in transition metal dialkylamido chemistry is the role that nitrogen-p to metal-d π-bonding plays in determining the structure and controlling the reactivity of derivatives of this ligand. Due to its π-facial nature, the orientation of the dialkylamido ligand controls which metal-based orbitals the ligand can π-donate into. Hence, the conformation adopted by dialkylamido ligands in the solid state can help probe the underlying molecular bonding, while spectroscopic

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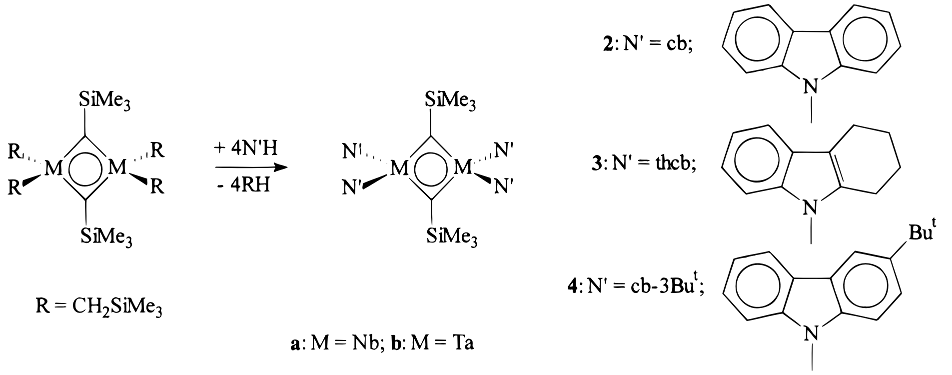
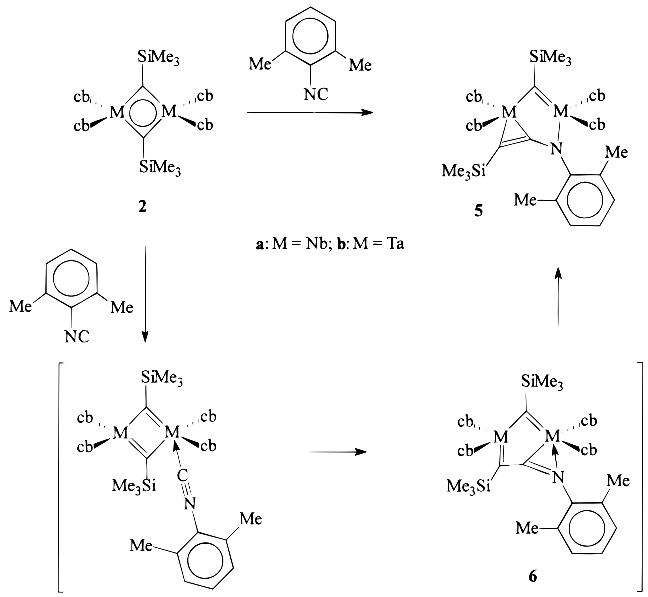
S0276-7333(96)00437-2 CCC: $12.00

Scheme 1



Scheme 2



studies of dialkylamido ligand rotation can sometimes allow estimates of the strength of the metal−ligand π-bonding.[10] In organometallic chemistry, the π-donating ability of dialkylamido ligands has been utilized to suppress fundamental processes such as β-hydrogen abstraction.[11]

In the context of this background we have begun to explore the inorganic and in particular organometallic chemistry of ligands derived from the carbazole nucleus.[12] This is a class of ligands that have so far been underutilized.[13,14] The choice of the carbazole ligand was stimulated by an expectation that the presence of the two coplanar aryl rings would decrease nitrogen-p to metal-d π-donation possibly leading to derivatives that exhibit different chemistry than found with more strongly π-donating dialkylamido ligation. We wish to report here on the formation of a series of 1,3-dimetallacyclobutadiene derivatives of niobium and tantalum supported by carbazole derived ligation and their reactivity toward organic isocyanide reagents. Some aspects of this work have been communicated.[12a]

Results and Discussion

Synthesis and Spectroscopic Characterization. The 1,3-dimetallacyclobutadiene compounds $[(Me_3SiCH_2)_2M(\mu\text{-}CSiMe_3)_2M(CH_2SiMe_3)_2]$ (M = Nb (**1a**), Ta (**1b**))[15] show two distinct reactivity patterns toward protic reagents. With bulky phenols, stepwise substitution of the alkyl groups has been shown to take place leading to a variety of terminally substituted 1,3-dimetallacyclobutadienes.[16] Recently, the addition of HCl to **1b** has been shown to lead to $[(Me_3SiCH_2)_2(Cl)Ta(\mu\text{-}CHSiMe_3)_2Ta(Cl)(CH_2SiMe_3)_2]$ by protonation of the alkylidyne bridging groups.[17] Compounds **1** react slowly in hydrocarbon solvents at 100 °C with an excess of carbazole reagents to produce the tetrasubstituted-derivatives **2**−**4** in moderate to high yield (Scheme 1). Although monitoring the reaction in C_6D_6 solvent by ^1H NMR spectroscopy showed the formation of intermediate substitution species, no attempt was made to try to isolate these intermediates. The niobium compounds **2a**, **3a**, or **4a** are obtained as deep-blue crystalline materials, while the corresponding tantalum complexes are deep red. The carbazole and tetrahydrocarbazole complexes **2** and **3** are only sparingly soluble in cold aromatic solvents while the 3-*tert*-butylcarbazole derivatives **4** are much more soluble. In the ^1H NMR spectra of **2**−**4** the expected ligand signals are resolved along with a characteristic singlet for the μ-CSi*Me*3 protons. This singlet is shifted upfield of TMS for compounds **2** and **4** but remains close to zero ppm in the tetrahydrocarbazole complex **3**. We attribute the upfield shifting of the Si*Me*3 protons in **2** and **4** as being due to the diamagnetic shielding generated by the aromatic wedges of the carbazole ligands. A similar effect is observed in the 2,6-diphenylphenoxide (OAr) complex $[(ArO)_2Ta(\mu\text{-}CSiMe_3)_2Ta(OAr)_2]$.[16] The lack of solubility of **2** and **3** precluded their characterization by ^{13}C NMR spectroscopy, but C_6D_6 solutions of **4b** are

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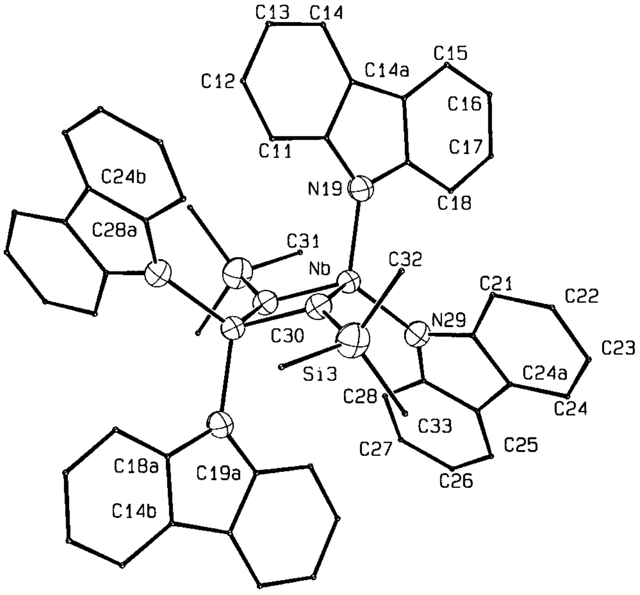

Figure 1. Molecular structure of [(cb)$_2$Nb(μ-CSiMe$_3$)$_2$Nb(cb)$_2$] (**2a**). An identical numbering scheme is used for isomorphous tantalum compound **2b**.

sufficiently concentrated for the alkylidyne bridge carbon to be detected at $\delta = 412$ ppm.

The addition of 2,6-dimethylphenyl isocyanide (xyNC) to benzene suspensions of compounds **2** results in the rapid formation of much more soluble organometallic products. Addition of hexane to these solutions leads to isolation of the derivatives [(cb)$_2$M(μ-CSiMe$_3$)(μ-(xyNCCSiMe$_3$)M(cb)$_2$] (Scheme 2; **5a**, M = Nb; **5b**, M = Ta). Monitoring (^{1}H NMR) the reaction of **2** with xyNC in C_6D_6 solvent shows the buildup of two *Me*$_3$Si signals as expected for compound **5**. The positions of these two singlets was, however, found to vary slightly depending upon the presence of excess xyNC in solution. It was concluded that compounds **5** will form a weak adduct with xyNC. This adduct was not isolable from mixtures of **5** and xyNC but gave rise in the ^{1}H NMR spectrum to a shifting and broadening of the ligand signals.

Structural Studies. The carbazole derivatives **2a**,**b** as well as the isocyanide insertion products **5a**,**b** were subjected to single-crystal X-ray diffraction analysis. In both cases the niobium and tantalum compounds were found to be isomorphous. The molecular structures of **2a** and **5b** are shown in Figures 1 and **2**, respectively. Some selected structural parameters are contained in Tables 1 and 2. As with other isomorphous derivatives of these metals, there is a slight (0.01−0.03 Å) but consistent shortening of the bonds to tantalum (lanthanide contraction) when compared to the corresponding distances to niobium. In compounds **2** there is a crystallographically imposed center of inversion. It can be seen (Figure 1) that one of the carbazole "wedge"-shaped ligands, bound through N(19), at each end of the molecule is oriented almost coplanar with the M−M and M−N(29) axes. The remaining ligand, bound through (N29), is oriented 70° away from the M−M and M−N(19) axes.

The most important structural feature for compounds **2** involves the M−M distance within the 1,3-dimetallacyclobutadiene core. Table 3 highlights this parameter for a selection of 1,3-dimetallacyclobutadiene compounds. The Nb−Nb distance in **2a** can be seen to be slightly elongated over that reported for the alkyl precursor **1a**, while the M−M distances for **2a**,**b** are comparable to those reported for aryloxide derivatives that lack formal metal−metal bonds.

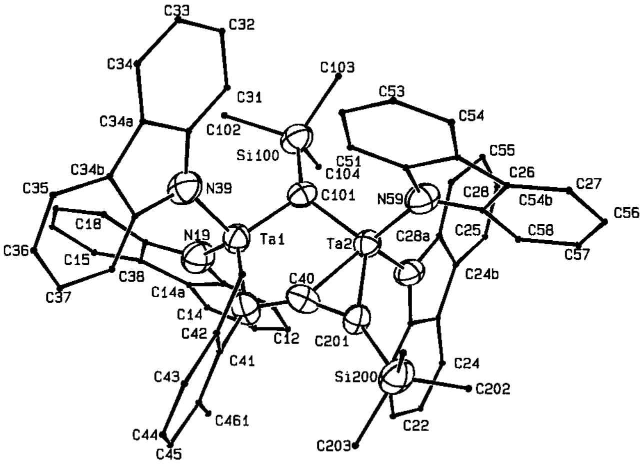

Figure 2. Molecular structure of [(cb)$_2$Ta(μ-CSiMe$_3$)(μ-ArNCCSiMe$_3$)Ta(cb)$_2$] (**5b**). An identical numbering scheme is used for isomorphous niobium compound **5a**.

Table 1. Selected Bond Distances (Å) and Angles (deg) for [(cb)$_2$M(μ-CSiMe$_3$)$_2$M(cb)$_2$] (M = Nb (2a), Ta (2b))

	2a	**2a**
M−M	2.9015(4)	2.8801(4)
M−N(19)	2.065(2)	2.035(4)
M−N(29)	2.049(3)	2.021(4)
M−C(30)	1.971(3)	1.957(5)
M−C(30)	1.968(3)	1.948(4)
M−C(30)−M	94.9(1)	95.0(2)
N(19)−M−N(29)	115.6(1)	115.2(2)
C(30)−M−C(30)	85.1(1)	85.0(2)
N(19)−M−C(30)	112.6(1)	113.6(2)
N(19)−M−C(30)	108.9(1)	109.4(2)
N(29)−M−C(30)	114.3(1)	113.6(2)
N(29)−M−C(30)	116.5(1)	116.5(2)

There are some similarities in the orientations of the carbazole ligands in **5** when compared to those discussed above for **2**. One pair of ligands, bound through N(19) and N(59), is oriented approximately coplanar with the metal−metal axis while the remaining pair of carbazole "wedges" are twisted away from this axis. A number of structural parameters for compounds **5** (Table 2) are of interest. The alkylidyne bridge in **5** has a definite asymmetry with the bond to M(1) being 0.132 Å (**5a**) and 0.10 Å (**5b**) shorter than the distance to M(2). In the case of **2** the distances to the symmetrically bridging alkylidyne group are intermediate between these values. This, combined with the other structural parameters,

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Table 2. Selected Bond Distances (Å) and Angles (deg) for [(cb)$_2$M(μ-CSiMe$_3$)(μ-ArNCCSiMe$_3$)M(cb)$_2$] (M = Nb (5a), Ta (5b))

	5a	5b
M(1)−M(2)	3.115(1)	3.0742(6)
M(1)−N(19)	2.044(8)	2.04(1)
M(1)−N(39)	2.004(8)	2.01(1)
M(1)−N(40)	2.012(7)	2.005(8)
M(1)−C(40)	2.368(9)	2.31(1)
M(1)−C(101)	1.937(8)	1.95(1)
M(2)−N(29)	2.022(7)	2.021(9)
M(2)−N(59)	2.044(7)	2.024(9)
M(2)−C(40)	2.157(9)	2.15(1)
M(2)−C(101)	2.069(8)	2.05(1)
M(2)−C(201)	2.043(8)	2.06(1)
N(40)−C(40)	1.32(1)	1.34(1)
C(40)−C(201)	1.33(1)	1.33(1)
N(39)−M(1)−N(19)	110.5(3)	110.1(4)
N(29)−M(2)−N(59)	111.8(3)	110.1(4)
M(1)−C(101)−M(2)	102.0(4)	100.4(4)
N(19)−M(1)−C(101)	104.7(3)	104.6(4)
N(39)−M(1)−C(101)	108.2(4)	108.1(4)
N(29)−M(2)−C(101)	108.4(3)	108.5(4)
N(59)−M(2)−C(101)	112.3(3)	111.8(4)
N(19)−M(1)−N(40)	113.9(3)	112.6(4)
N(39)−M(1)−N(40)	101.8(3)	101.1(4)
N(40)−M(1)−C(101)	117.8(3)	120.2(4)
N(29)−M(2)−C(40)	116.2(3)	117.9(4)
N(59)−M(2)−C(40)	118.3(3)	118.7(4)
N(29)−M(2)−C(201)	100.7(3)	100.9(4)
N(59)−M(2)−C(201)	99.2(3)	100.6(4)
C(101)−M(2)−C(40)	84.2(3)	85.1(4)
C(101)−M(2)−C(201)	123.6(3)	124.0(4)

is consistent with a formulation for **5** as shown in Scheme 2. The two Ta(V) metal centers are bridged by the alkylidyne unit, double bond to M(1) and single bond to M(2), and an amido−alkyne ligand which is bound to M(1) via the amido nitrogen atom while the alkyne unit is strongly η^2-bound to M(2) resulting in a metallacyclopropene ring. The molecular geometry of the amido−alkyne ligand dictates a close approach of C(40) to M(1). This distance is certainly short for a nonbonded contact but 0.1 Å longer than typically found for alkyl derivatives of these metals, and this is discussed in more detail below.

Mechanistic Discussion. The migratory insertion of organic isocyanides into transition metal alkyl, hydride, silyl, and related bonds has been extensively studied.[24] In the case of early d-block metal alkyl bonds the reaction typically produces an η^2-iminoacyl functionality that can exhibit a range of interesting reactivity. By analogy one might expect addition of RNC to alkylidyne-bridged **2** to produce an η^2-iminoacyl ligand that contains an alkylidene group adjacent to the iminoacyl carbon (**6**, Scheme 2). A minor rearrangement then leads from **6** to product **5**. The structural parameters for **5a**,**b** (Table 2) are inconsistent with an iminoacyl formulation for these compounds. In particular the N(40)−C(40) distances are significantly longer than present in η^2-iminoacyl derivatives of these metals while the M(1)−N(40) distance is comparable to the M−N(carbazole) distances. As discussed above, the M(1)−C(40) distances are at the fringes of what may be considered bonding.

The reactivity of **2** toward 2,6-dimethylphenyl isocyanide contrasts markedly with that reported by Chisholm and Heppert for the 1,3-ditungstacyclobutadiene compound [(i-PrO)$_2$W(μ-CSiMe$_3$)$_2$W(OPr-i)$_2$] (**A**, Scheme 3).[20a,25] The extra pair of electrons initially present in the tungsten−tungsten bond results in cleavage of the C−N bond yielding terminal imido and bridging alkynyl ligands (**B**, Scheme 3). This compound contains a nonsymmetrical arrangement of alkoxide ligands (the alkynyl group π-bound to the metal center that contains the imido group). If this reaction initially proceeds to produce a compound analogous to **5** (**C**, Scheme 3), it would be expected to lead to a product (**D**, Scheme 3) that contains the imido and π-bound alkynyl ligands attached to different tungsten metal centers. The formation of **B** would then require an imido/alkoxide exchange reaction, although there are no compelling reasons to propose such an isomerization. On the basis of extensive studies of the reactivity of 1,3-ditungstacyclobutadiene compounds, Chisholm and Heppert propose a reaction sequence for the formation of **B** from **A** in which coupling of the alkylidyne and isocyanide units produces a 1,3-dimetalated-azaallyl ligand bound to a single metal center which then undergoes C−N bond cleavage.[25]

Experimental Section

All operations were carried out under a dry nitrogen atmosphere or *in vacuo* either in a Vacuum Atmosphere Dri-Lab or by standard Schlenk techniques. Hydrocarbon solvents were dried by distillation from sodium/benzophenone and stored under dry nitrogen. 9-*H* carbazole and 1,2,3,4-tetrahydrocarbazole were purchased from Aldrich Chemical Co. 2,6-Dimethylphenyl isocyanide was purchased from Fluka Chemical Co. The compounds 3-*tert*-butylcarbazole,[26] [(Me$_3$SiCH$_2$)$_2$Nb(μ-CSiMe$_3$)$_2$Nb(CH$_2$SiMe$_3$)$_2$] **(1a)**, and [(Me$_3$SiCH$_2$)$_2$Ta(μ-CSiMe$_3$)$_2$Ta(CH$_2$SiMe$_3$)$_2$] **(1b)** were prepared by reported procedures.[15] The ^{1}H and ^{13}C NMR spectra were recorded on Varian Associates Gemini 200 and General Electric QE-300 spectrometers. Microanalyses were obtained in-house at Purdue University. Considerable difficulties were encountered in obtaining accurate microanalytical data for some of these compounds. In particular, the values for the percentage of carbon were consistently found to be low, a fact we ascribe to the possible formation of metal carbides on combustion.

[(cb)$_2$Nb(μ-CSiMe$_3$)$_2$Nb(cb)$_2$], 2a. To a toluene (10 mL) solution of [(Me$_3$SiCH$_2$)$_2$Nb(μ-CSiMe$_3$)$_2$Nb(CH$_2$SiMe$_3$)$_2$] (0.24 g, 0.34 mmol) was added 4 equiv of 9-*H*-carbazole (0.23 g, 1.35 mmol). The solution was heated at 110 °C for 18 h during which time dark red crystals of product precipitated out of solution. The crystals were washed with toluene and hexane and dried *in vacuo*. Yield: 0.16 g (46%). Anal. Calcd for $C_{56}H_{50}N_4Si_2Nb_2$: C, 65.88; H, 4.94; N, 5.49. Found: C, 65.63; H, 4.84; N, 5.52. ^{1}H NMR (C_6D_6, 30 °C): δ −0.38 (s, μ-CSi*Me$_3$*); 8.00 (d, *cb ortho*); 6.80−7.40 (m, aromatics).

[(cb)$_2$Ta(μ-CSiMe$_3$)$_2$Ta(cb)$_2$], 2b. To a toluene (10 mL) solution of [(Me$_3$SiCH$_2$)$_2$Ta(μ-CSiMe$_3$)$_2$Ta(CH$_2$SiMe$_3$)$_2$] (1.08 g, 1.23 mmol) was added 4 equiv of 9-*H*-carbazole (0.82 g, 4.90 mmol). The solution was heated at 110 °C for 36 h, during which time bright red crystals precipitated out of solution. The crystals were washed with toluene and hexane and dried *in vacuo*. Yield: 0.70 g (49%). Anal. Calcd for $C_{56}H_{50}N_4Si_2Ta_2$: C, 56.19; H, 4.21; N, 5.85. Found: C, 55.49; H, 4.16; N, 4.22. ^{1}H NMR (C_6D_6, 30 °C): δ −0.42 (s, μ-CSi*Me$_3$*); 8.16 (d, *cb ortho*); 6.80−7.40 (m, aromatics).

[(thcb)$_2$Nb(μ-CSiMe$_3$)$_2$Nb(thcb)$_2$], 3a. To a hexane (20 mL) solution of [(Me$_3$SiCH$_2$)$_2$Nb(μ-CSiMe$_3$)$_2$Nb(CH$_2$SiMe$_3$)$_2$]

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[24] Rothwell, I. P.; Durfee, L. D. *Chem. Rev.* **1988**, *88*, 1059.

[25] Chisholm, M. H.; Heppert, J. A.; Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1985**, 1771.

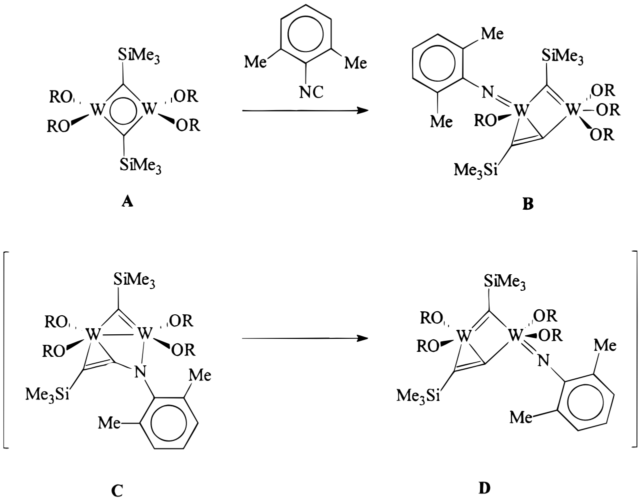
[26] Robinson, B. *The Fisher Indole Synthesis*; Wiley-Interscience: New York, 1982; p 74.

Table 3. Metal−Metal Bond Distances for 1,3-Dimetallacyclobutadiene Compounds

compd	M−M, Å	ref
$[(Me_3SiCH_2)_2Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)_2]$	2.897(2)	15
anti-$[(ArO)(Me_3SiCH_2)Nb(\mu\text{-}CSiMe_3)_2Nb(CH_2SiMe_3)(OAr)]$	2.9082(8)	18
$[(ArO)(Me_3SiCH_2)Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$	2.8825(6)	16
$[(ArO)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$	2.9071(4)	16
$[(cb)_2Nb(\mu\text{-}CSiMe_3)_2Nb(cb)_2]$ (**2a**)	2.9015(4)	*a*
$[(cb)_2Ta(\mu\text{-}CSiMe_3)_2Ta(cb)_2]$ (**2b**)	2.8801(4)	*a*
$[(Me_3SiCH_2)_2(Cl)W(\mu\text{-}CSiMe_3)_2W(Cl)(CH_2SiMe_3)_2]$	2.760(1)	19
$[(Me_3SiCH_2)_2(Br)W(\mu\text{-}CSiMe_3)_2W(Br)(CH_2SiMe_3)_2]$	2.757(1)	19
$[(Me_3SiCH_2)_2W(\mu\text{-}CSiMe_3)_2W(CH_2SiMe_3)_2]$	2.521(2), 2.549(2)	20
$[(i\text{-}PrO)_2W(\mu\text{-}CSiMe_3)_2W(OPr\text{-}i)_2]$	2.618(2)	21
$[(t\text{-}BuO)_2W(\mu\text{-}CPh)_2W(OBu\text{-}t)_2]$	2.665(1)	22
$[(Me_3SiCH_2)_2Re(\mu\text{-}CSiMe_3)_2Re(CH_2SiMe_3)_2]$	2.557(1)	23

[a] This work.

Scheme 3



(0.50 g, 0.73 mmol) was added 4.5 equiv of 1,2,3,4-tetrahydrocarbazole (0.56 g, 3.3 mmol). The solution was heated at 110 °C for 24 h, during which time dark blue crystals of product precipitated out of solution. The crystals were washed with hexane and dried *in vacuo*. Yield: 0.52 g (69%). Anal. Calcd for $C_{56}H_{66}N_4Si_2Nb_2$: C, 64.85; H, 6.41; N 5.40. Found: C, 64.46; H, 6.79; N, 5.12. ^{1}H NMR (C_6D_6, 30 °C): δ −0.06 (s, μ-CSiMe_3); 1.59 (br), 2.66 (br), 2.91 (br), 7.0−7.6 (m), 7.88 (d).

$[(thcb)_2Ta(\mu\text{-}CSiMe_3)_2Ta(thcb)_2]$, 3b. To a hexane (20 mL) solution of $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$ (0.50 g, 0.57 mmol) was added 4.5 equiv of 1,2,3,4-tetrahydrocarbazole (0.44 g, 2.6 mmol). The solution was heated at 110 °C for 72 h, during which time red crystals precipitated out of solution. The crystals were washed with hexane and dried *in vacuo*. Yield: 0.49 g (72%). Anal. Calcd for $C_{56}H_{66}N_4Si_2Ta_2$: C, 55.44; H, 5.48; N, 4.62. Found: C, 55.21; H, 5.60; N, 4.46. ^{1}H NMR (C_6D_6, 30 °C): δ −0.07 (s, μ-CSiMe_3); 1.59 (br), 2.67 (br), 3.02 (br), 6.9−7.6 (m), 7.93 (d).

$[(cb\text{-}3Bu^t)_2Ta(\mu\text{-}CSiMe_3)_2Ta(cb\text{-}3Bu^t)_2]$, 4b. To a hexane (20 mL) solution of $[(Me_3SiCH_2)_2Ta(\mu\text{-}CSiMe_3)_2Ta(CH_2SiMe_3)_2]$ (0.50 g, 0.57 mmol) was added 4.5 equiv of 3-*tert*-butylcarbazole (0.57 g, 2.6 mmol). The solution was heated at 110 °C for 72 h, during which a red solid precipitated out of solution. The solid was washed with hexane and dried *in vacuo*. Yield: 0.50 g (62%). Anal. Calcd for $C_{72}H_{82}N_4Si_2Ta_2$: C, 60.8; H, 5.81; N, 3.94. Found: C, 57.02; H, 5.63; N, 3.96. ^{1}H NMR (C_6D_6, 30 °C): δ −0.45 (s, μ-CSiMe_3); 1.26 (s, CCMe_3); 6.8−8.4 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 4.63 (μ-CSiMe_3); 32.3 (CCMe_3); 35.3 (*C*CMe$_3$); 412 (μ-*C*SiMe$_3$).

$[(cb)_2Nb(\mu\text{-}CSiMe_3)(\mu\text{-}(xyNCCSiMe_3)Nb(cb)_2]$, 5a. To a hexane (20 mL) solution of $[(cb)_2Nb(\mu\text{-}CSiMe_3)_2Nb(cb)_2]$ (0.40 g, 0.36 mmol) was added 1 equiv of 2,6-dimethylphenyl isocyanide (xyNC, 0.03 g, 0.36 mmol). The solution was allowed to stir at room temperature for 1 h. The solvent was removed under vacuum. The resulting dark orange solid was washed thoroughly with hexane and dried *in vacuo*. The solid was dissolved in toluene and filtered. The filtrate was concentrated and layered with hexane. After several hours, large orange crystals of product precipitated out of solution. Yield: 0.15 g (33%). Anal. Calcd for $C_{65}H_{59}N_5Si_2Nb_2$: C, 67.76; H, 5.16; N, 6.08. Found: C, 64.29; H, 5.01; N, 5.81. ^{1}H NMR (C_6D_6, 30 °C): δ −0.20, 0.20 (s, SiMe_3), 1.29 (s, Me_2C$_6$H$_3$); 6.4−8.2 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 0.4 (CSiMe_3); 3.6 (Nb-μCSiMe_3-Nb); 18.3 (xy-*Me*).

$[(cb)_2Ta(\mu\text{-}CSiMe_3)(\mu\text{-}(xyNCCSiMe_3)Ta(cb)_2]$, 5b. To a hexane (20 mL) solution of $[(cb)_2Ta(\mu\text{-}CSiMe_3)_2Ta(cb)_2]$ (0.38 g, 0.32 mmol) was added an excess of 2,6-dimethylphenyl isocyanide (0.09 g, 0.68 mmol). The solution was allowed to stir at room temperature for 1 h. The solvent was removed under vacuum. The resulting orange solid was washed thoroughly with hexane and dried under vacuum. The washed solid was dissolved in toluene and filtered. The filtrate was concentrated and layered with hexane. After several hours, large pale orange crystals precipitated out of solution. Yield: 0.17 g (40%). Anal. Calcd for $C_{65}H_{59}N_5Si_2Ta_2$: C, 58.78; H, 4.48; N, 5.27. Found: C, 58.36; H, 4.57; N, 4.95. ^{1}H NMR (C_6D_6, 30 °C): δ −0.27, 0.50 (SiMe_3); 1.24 (Me_2C$_6$H$_3$); 6.4−8.2 (aromatics). ^{13}C NMR (C_6D_6, 30 °C): δ 0.9 (CSiMe_3); 4.9 (Ta-μCSiMe_3-Ta); 18.2 (xy-*Me*).

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Supporting Information Available: Text describing X-ray procedures and tables of experimental details associated with data collection and crystal structure refinement, final atomic coordinates, thermal parameters, and complete bond distances and angles for complexes **2a**,**b**, and **5a**,**b** (90 pages). Ordering information is given on any current masthead page.

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