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Reactions of 1,4- and 2,3-Diazadienes with Titanocene and Zirconocene Complexes of Bis(trimethylsilyl)acetylene: Acetylene Coupling or Substitution Including Subsequent C−H Activation, C−C Coupling, and N−N Cleavage to Heterobimetallic Complexes

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The reaction of 1,4-diazadienes RN═CHCH═NR with the titanocene and zirconocene complexes of bis(trimethylsilyl)acetylene $Cp_2M(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (M = Ti, without L (**1**); M = Zr, L = THF (**2**), pyridine (**3**)) is a general and new method to obtain 1-metalla-2,5-diazacyclopent-3-ene complexes $Cp_2M(\eta^2\text{-}1{:}4\text{-}RNCH{=}CHNR)$ (M = Zr, R = 2,6-$^i Pr_2C_6H_3$ (**4a**), 4-Me-C_6H_4 (**4b**), Cy (**4c**); M = Ti, R = 2,6-$^i Pr_2C_6H_3$ (**5a**), 4-Me-C_6H_4 (**5b**), Cy (**5c**)). In the analogous reaction with differently substituted azines RR′C═NN═CRR′ the products depend strongly on the metals used, Zr and Ti, as well as on the substituents R and R′. With R = R′ = Me and M = Ti, a substitution of the alkyne by the azine and a subsequent CH activation to the 1-titana-2,3-diazacyclopent-3-ene species **6** was observed. Using R = Ph and R′ = H the acetylene was also substituted and, by a reductive coupling of two azine molecules, the paramagnetic binuclear Ti(III) complex $(Cp_2Ti)_2[\mu\text{-}(\eta^4\text{-}2{:}3,6{:}7\text{-}PhHC{=}NNCHPhCHPhNN{=}CHPh)$ (**7**) was formed. With M = Zr and R = Ph and R′ = H no substitution of the acetylene was observed, but one of the C═N double bonds of the azine inserts into the Zr−C bond of the zirconacyclopropene moiety of the starting acetylene complex to yield the 1-zircona-2-azacyclopent-4-ene species **8**, which is additionally stabilized by N-coordination of the second imino group as a substituent in α position to the metal. Using R = R′ = Ph, the central N−N single bond of the azine is cleaved by both of the metals and the bis(imido) complexes $Cp_2M(-N{=}CPh_2)_2$ (M = Zr (**9**), Ti (**10**)) were isolated. The central C−C bond of **7** is cleaved in a subsequent reaction with $CpCo(C_2H_4)_2$ and, after an activation of the N−N bond of the azine, the heterobimetallic complex $(Cp_2Ti)(\mu\text{-}N{=}CHPh)_2(CpCo)$ (**11**) was formed. In the reaction of benzaldehyde azine with $CpCo(C_2H_4)_2$ the isoelectronic homobimetallic bis(alkylideneamido) complex $(CpCo)(\mu\text{-}N{=}CHPh)_2(CpCo)$ (**12**) was prepared. In reactions of **9** and **10** with $CpCo(C_2H_4)_2$ heterobimetallic complexes of this type analogous to complex **11** were not obtained. All new complexes have been characterized by spectroscopic methods, and additionally, **4a**, **7**, **8**, **10**, **11**, and **12** were characterized by single-crystal X-ray structure analysis.

Introduction

Reactions of organic substrates containing multiple bonds with transition-metal complexes are of general interest in organometallic chemistry from the theoretical and the synthetic point of view, respectively.[1] In a series of investigations concerning the reactions of group 4 metallocene acetylene complexes [2a−c] with acetylenes and with substituted butadiynes as well as with ketones, aldehydes, and imines we could often illustrate unexpected results, which also lead to an interesting chemistry.[2d] Reactions of titanocene and zirconocene complexes with C═N double bonds are well-known.[3] We

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Table 1. Crystallographic Data of 4a, 7, 8, 10, 11, and 12

	4a	**7**	**8**	**10**	**11**	**12**
cryst color, habit	yellow-orange, prism	brown-black, prism	yellow, prism	dark red, prism	red-brown, prism	brown, prism
cryst system	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic	orthorhombic
space group	$P2_1/c$	Pn	$P2_12_12_1$	$P2_12_12_1$	Pc	$Pca2_1$
lattice constants						
a (Å)	13.789(3)	12.007(2)	7.900(2)	13.698(3)	17.962(4)	21.602(4)
b (Å)	15.397(3)	15.337(2)	14.012(3)	13.784(3)	15.293(3)	10.129(2)
c (Å)	15.188(3)	22.660(4)	28.718(6)	15.102(3)	8.796(2)	9.660(2)
α (deg)						
β (deg)	102.70 (3)	103.99 (2)			98.35(3)	
γ (deg)						
Z	4	4	4	4	4	4
cell vol (Å^3)	3145.7(11)	4049.1(11)	3178.9(12)	2851.5(10)	2390.6(9)	2113.7(7)
density (g cm^{-3})	1.263	1.267	1.254	1.254	1.418	1.434
temp (K)	293 (2)	293(2)	293(2)	293(2)	293(2)	293(2)
μ(Mo Kα) (mm^{-1})	0.375	0.432	0.443	0.327	1.047	1.580
θ range (deg)	1.91−24.34	1.85−24.34	2.03−24.36	2.00−24.31	1.76−24.33	1.89−24.22
no. of rflns (measd)	9267	10793	9477	8593	7014	6010
no. of rflns (indep)	5035	5982	4859	4593	3759	3224
no. of rflns (obsd)	3746	3181	3501	3038	2633	2761
no. of params	352	973	334	352	596	261
R1 ($I > 2\sigma$(I))	0.036	0.048	0.041	0.037	0.062	0.027
wR2 (all data)	0.095	0.126	0.108	0.075	0.173	0.073

have studied reactions of bis(trimethylsilyl)acetylene titanocene and zirconocene complexes with isolated C=N double-bond-containing compounds, e.g. for aldimines, ketimines,[4a] oxazoles, isoxazoles, thiazoles,[4b] and siloximes.[4c] In addition, lactams (keto-amine hydroxy-imine tautomerization)[4d] and 2-vinylpyridine, [4e] containing special C=N double bonds, were investigated. Herein we offer a full report on reactions of zirconocene and titanocene complexes of bis(trimethylsilyl)acetylene with 1,4- and 2,3-diazadienes under substitution or coupling of the acetylene as well as subsequent C−H activation, C−C coupling, N−N cleavage, and preparation of “early−late” heterobimetallic complexes.[2e]

Experimental Part

General Considerations. All operations were carried out under an inert atmosphere (argon) using standard Schlenk techniques. Solvents were freshly distilled from sodium tetraethylaluminate under argon prior to use. Deuterated solvents were treated with sodium or sodium tetraethylaluminate, distilled, and stored under argon. The following spectrometers were used: NMR, Bruker ARX 400 at 9.4 T (chemical shifts are given in δ (ppm) referenced to the signals of the solvents used: benzene-d_6, δ_H 7.16, δ_C = 128.0; toluene-d_8, δ_H = 2.03, δ_C = 20.4; THF-d_8, δ_H = 1.73, δ_C = 25.2); IR, Nicolet Magna 550 (Nujol mulls using KBr plates); MS, AMD 402. Melting points were measured in sealed capillaries on a Büchi 535 apparatus. Elemental analyses were carried out on a Leco CHNS-932 elemental analyzer.

X-ray Crystallographic Study of Complexes 4a, 7, 8, 10, 11, and 12. Data were collected with a STOE-IPDS diffractometer using graphite-monochromated Mo Kα radiation. The structures were solved by direct methods (SHELXS-86)[5] and refined by full-matrix least-squares techniques against F^2 (SHELXL-93).[6] The hydrogen atoms were included at calculated positions. All other non-hydrogen atoms were refined anisotropically. Cell constants and other experimental details were collected and recorded in Table 1. XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Preparation of Complexes. $Cp_2Zr[\eta^2$-1:4-(2,6-^{i}PrC$_6$H$_3$N-CH=CHN-2,6-^{i}PrC$_6$H$_3$)] (4a). To a solution of 480 mg (1.02 mmol) of $Cp_2Zr(Py)(\eta^2-Me_3SiC_2SiMe_3)$ (**3**) in 10 mL of THF was added a solution of 385 mg (1.02 mmol) of glyoxalbis[(2,6-diisopropylphenyl)imine] in 10 mL of THF, and the mixture was stirred at room temperature for 5.5 h. The color changed from green to red-orange within this time. After the solvent was removed in vacuo, the oily residue was redissolved in Et_2O and the solution filtered. The red filtrate was then dried in vacuo and the obtained yellow foam was crystallized from n-pentane at −40 °C. After 4 days the mother liquor was decanted, and the yellow-orange crystals were washed with cold n-pentane and dried in vacuo. Yield: 285 mg (47%). Mp: 127−129 °C. MS: m/z 597 (M$^+$), 532 (M − Cp$^+$), 221 (Cp$_2$Zr$^+$). ^{1}H NMR (benzene-d_6, 297 K): δ 1.22, 1.29, 1.31, 1.34 (d, $^3J_{HH}$ = 6.7 Hz, 4 × 6H, Me), 3.05, (m, 2H, CH, ^{i}Pr), 3.92 (septet, 2H, CH, ^{i}Pr), 5.54 (s, 2H, CH=CH), 5.77, 5.83 (s, 2 × 5H, Cp), 7.11−7.21 (m, 6H, Ar). ^{13}C{^{1}H} NMR (benzene-d_6, 297 K): δ 24.2, 24.8, 26.5, 27.0, 27.1, 27.7 (4 × Me, 2 × CH, ^{i}Pr), 106.7, 110.0 (Cp), 114.3 (C=C), 124.1, 124.7, 124.9 (C3−5, Ar), 142.2, 145.7 (C2, C6, Ar), 148.4 (C1, Ar). Anal. Calcd for $C_{36}H_{46}N_2Zr$ (597.99): C, 72.31; H, 7.75; N, 4.68. Found: C, 72.32; H, 7.59; N, 4.75.

$Cp_2Zr[\eta^2$-1:4-(4-Me-C$_6$H$_4$NCH=CHN-4-MeC$_6$H$_4$)] (4b). A solution of 200 mg (862 μmol) of glyoxalbis(p-tolylimine) in 10 mL of THF was added to 400 mg (862 μmol) of $Cp_2Zr(THF)(\eta^2-Me_3SiC_2SiMe_3)$ (**2**) in 10 mL of THF, and the mixture was stirred at room temperature for 4 h. The solvent was removed in vacuo, and the remaining oil was dissolved in the minimum volume of Et_2O. After addition of 15 mL of n-pentane, the claret-colored solution was passed through a frit. Cooling to −40 °C for 7 days induced the formation of orange-red needles, which were separated from the mother liquor, washed with cold n-hexane, and dried in vacuo. Yield: 295 mg (75%) of **4b**. Mp: 85−87 °C dec. MS: m/z 457 (M$^+$), 392 (M − Cp$^+$), 221 (Cp$_2$Zr$^+$). IR (Nujol mull): 1569, 1606 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (THF-d_8, 220 K): δ 2.29 (s, 6H, Me), 5.81 (s, 2H, CH=CH), 5.88, 6.14 (s, 2 × 5H, Cp), 6.77 (d, J = 8.3 Hz, 4H, Ar), 7.05 (d, J = 8.3 Hz, 4H, Ar). ^{1}H NMR (THF-d_8, 297 K): δ 2.29 (br s, 6H, Me), 5.80 (br s, 2H, CH=CH), 5.98 (br s, 10H, Cp), 6.57, 7.03 (d, 2 × 4H, J = 8.3 Hz, Ar).^{13}C{^{1}H} NMR (THF-d_8, 220 K): δ 20.8 (Me), 105.3, 109.3 (Cp), 113.0 (C=C), 121.0,

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129.8 (C2/6, C3/5, Ar), 130.5 (C4, Ar), 151.4 (C1, Ar). Anal. Calcd for $C_{26}H_{26}N_2Zr$ (457.73): C, 68.23; H, 5.73; N, 6.12. Found: C, 68.13; H, 6.09; N, 5.56.

$Cp_2Zr[\eta^2$-1:4-(CyNCH=CHNCy)] (4c). A solution of 200 mg (908 μmol) of glyoxalbis(cyclohexylimine) in 10 mL of THF was added to 430 mg (913 μmol) of $Cp_2Zr(Py)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**3**) in 15 mL of THF via syringe, and the mixture was stirred at 60 °C for 5 h. After 15 min the color of the solution changed from violet to dark green. The solvent was removed in vacuo, and the resulting oil was washed with cold *n*-hexane. The residue was crystallized from *n*-pentane at −40 °C. After 3 days the solution afforded bright, orange crystals, which were isolated by filtration, washed with *n*-hexane, and dried in vacuo. Yield: 274 mg (68%) of **4c**. Mp: 108−110 °C dec. MS: *m/z* 440 (M^+), 330 ($M - CyNC^+$), 221 (Cp_2Zr^+). IR (Nujol mull): 1786, 1679 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (benzene-d_6, 297 K): δ 1.00−1.40 (m, 12H, CH_2, Cy), 1.58−1.89 (m, 8H, CH_2, Cy), 2.95−3.03 (m, 2H, CH, Cy), 5.32 (br s, 2H, CH=CH), 5.45, 5.85 (br s, 2 × 5H, Cp). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 19.7, 30.6, 31.6 (CH_2, Cy), 61.6 (CH, Cy), 101.7, 107.7 (br s, Cp), 110.3 (C=C). Anal. Calcd for $C_{24}H_{34}N_2Zr$ (441.47): C, 65.25; H, 7.76; N, 6.34. Found: C, 65.07; H, 7.92; N, 6.12.

$Cp_2Ti[\eta^2$-1:4-(2,6-$^iPrC_6H_3NCH=CHN$-2,6-$^iPrC_6H_3$)] (5a). A 360 mg (0.96 mmol) amount of glyoxalbis[(2,6-diisopropylphenyl)imine] in 10 mL of THF was added to a yellowish brown solution of 330 mg (0.95 mmol) of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 10 mL of THF. The color changed to dark brown within 20 min. After the mixture was stirred at 20 °C for 2.5 h, the solvent was removed in vacuo and the residue crystallized from *n*-hexane. After 1 week at −40 °C the solution afforded brown crystals, which were separated from the mother liquid, washed with cold *n*-hexane, and dried in vacuo. Yield: 400 mg (75%). Mp: 145−147 °C. MS: *m/z* 554 (M^+), 489 ($M - Cp^+$), 333 ($C_{26}H_{36}N_2 - {}^iPr^+$), 178 ($Cp_2Ti^+$). ^{1}H NMR (THF-$d_8$, 230 K): δ 1.08, 1.14, 1.30, 1.36 (d, 4 × 3H, Me), 2.80, 3.75 (septet, 2 × 1H, CH, ^{i}Pr), 5.68, 5.76 (s, 2 × 5H, Cp), 6.29 (s, 2H, CH=CH), 7.06−7.17 (m, 6H, CH, Ar). ^{1}H NMR (benzene-d_6, 297 K): δ 1.18, 1.34 (d, 2 × 12H, Me), 3.4 (br s, 2H, CH, ^{i}Pr), 5.65 (br s, 10H, Cp), 6.21 (s, 2H, CH=CH), 7.12−7.18 (m, 6H, Ar). $^{13}C\{^1H\}$ NMR (THF-d_8, 230 K): δ 23.4, 23.8, 25.7, 26.4, 27.9, 28.4 (4 × Me, 2 × CH, ^{i}Pr), 106.0, 111.3 (br, Cp), 124.3, 124.7, 125.7, 125.8 (C3−C5, Ar, 1 × C=C), 142.1, 146.6 (C2/6, Ar), 151.6 (C1, Ar). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 23.7 (Me), 27.1 (br, CH, ^{i}Pr), 27.7 (Me), 108.3 (br, Cp), 124.3, 124.4, 125.8 (C3−5, Ar), 144.2 (br, C2/6, Ar), 151.0 (C1, Ar). Anal. Calcd for $C_{36}H_{46}N_2Ti$ (554.65): C, 77.96; H, 8.36; N, 5.05. Found: C, 77.68; H, 8.66; N, 5.13.

$Cp_2Ti[\eta^2$-1:4-(4-Me-$C_6H_4NCH=CHN$-4-MeC_6H_4)] (5b). To a solution of 430 mg (1.23 mmol) of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 10 mL of THF was added 290 mg (1.23 mmol) of glyoxalbis(*p*-tolylimine) in 10 mL of THF. As the red-brown reaction mixture was stirred at room temperature for 4.5 h, the color changed to dark brown. The solvent was removed under reduced pressure, affording a brown oil. The oil was dissolved in a minimum amount of Et_2O and then covered by *n*-pentane. A brown product crystallized, which was separated from the mother liquid, washed with cold *n*-pentane, and dried in vacuo. Yield: 240 mg (58%) of **5b**. Mp: 144−146 °C dec. MS: *m/z* 414 (M^+), 349 ($M - Cp^+$), 178 (Cp_2Ti^+). IR (Nujol mull): 1608 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (benzene-d_6, 297 K): δ 2.26 (s, 6H, Me), 5.60 (br s, 10H, Cp), 6.29 (s, 2H, CH=CH), 6.70 (d, *J* = 8.0 Hz, 4H, CH, Ar), 7.04 (d, *J* = 7.7 Hz, 4H, CH, Ar). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 20.8 (Me), 107.0 (Cp), 121.7 (C=C), 123.9, 129.4 (C2/6, C3/5, Ar), 132.0 (C4, Ar); 152.5 (C1, Ar). Anal. Calcd for $C_{26}H_{26}N_2Ti$ (414.39): C, 75.36; H, 6.32; N, 6.76. Found: C, 75.19; H, 6.39; N, 3.83.

$Cp_2Ti[\eta^2$-1:4-(CyNCH=CHNCy)] (5c). To a solution of 520 mg (1.49 mmol) of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 20 mL of toluene was added 330 mg (1.50 mmol) of crystalline glyoxalbis(cyclohexylimine). As the yellowish brown reaction mixture was stirred for 20 h at 100 °C, the color changed to dark green. The solvent was evaporated in vacuo, and the residue was crystallized at −78 °C from *n*-hexane. After 5 days the solution afforded dark green crystals, which were washed with *n*-hexane and dried in vacuo. Yield: 520 mg (88%) of **5c**. Mp: 106 °C dec. MS: *m/z* 398 (M^+), 333 ($M - Cp^+$), 178 (Cp_2Ti^+). IR (Nujol mull): 1491 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (benzene-d_6, 297 K): δ 0.95−1.06 (m, 2H, CH_2, Cy), 1.13−1.32 (m, 8H, CH_2, Cy), 1.53−1.57 (m, 2H, CH_2, Cy), 1.67−1.73 (m, 8H, Cy), 3.20 (tt, $^3J_{HH'}$ = 11.3 Hz, $^3J_{HH}$ = 3.37 Hz, 2H, CH, Cy), 5.50 (s, 10H, Cp); 6.16 (br, 2H, CH=CH). ^{1}H NMR (THF-d_8, 220 K): δ 1.19−1.45 (m, 10H, CH_2, Cy), 1.60−1.85 (m, 10H, CH_2, Cy), 2.95 (m, 2H, CH, Cy), 5.40 (s, 2H, CH=CH), 5.50, 5.87 (s, 2 × 5H, Cp). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 26.4, 26.8, 35.9 (CH_2, Cy), 66.2 (CH, Cy), 104.7 (Cp), 121.1 (C=C). $^{13}C\{^1H\}$ NMR (THF-d_8, 220 K): δ 26.8, 26.9, 27.4, 37.2, 38.0 (CH_2, Cy), 66.2 (CH, Cy), 101.8, 108.1 (Cp), 110.8 (C=C). Anal. Calcd for $C_{24}H_{34}N_2Ti$ (398.43): C, 72.35; H, 8.60; N, 7.03. Found: C, 72.57; H, 8.62; N, 7.02.

$Cp_2Ti[N(CHMe_2)N=C(Me)CH_2]$ (6). To a solution of 275 mg (789 μmol) of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 15 mL of THF was added 105 μL (793 μmol) of acetone azine. As the yellowish brown reaction mixture was stirred at 60 °C for 15 h, the color changed to dark green within 15 min. After removal of the solvent in vacuo, dissolution of the residue in a THF/*n*-hexane mixture, filtration, and repeated removal of the solvent, the turquoise complex **6** was dried in vacuo. Yield: 153 mg (67%) of **6**. MS: *m/z* 290 (M^+). IR (Nujol mull): 1603 cm^{-1} (νC=N). ^{1}H NMR (toluene-d_8, 330 K): δ 1.12 (d, 6H, Me), 1.36 (s, 2H, CH_2), 2.24 (s, 3H, Me), 3.82 (septet, 1H, CH), 5.21 (s, 10H, Cp). ^{1}H NMR (toluene-*d*8, 297 K): δ 1.14 (d, ^{3}*J*HH = 6.3 Hz, 6H, Me), 1.36 (br, 2H, CH_2), 2.28 (s, 3H, Me), 3.82 (septet, ^{3}JHH = 6.3 Hz, 1H, $CHMe_2$), 5.17 (s, 10H, Cp). ^{1}H NMR (toluene-d_8, 220 K): δ 0.65 (s, 1H, CH_2), 1.23, 1.36 (br, 2 × 3H, Me), 2.16 (s, 1H, CH_2), 2.35 (s, 3H, Me), 3.73 (br, 1H, $CHMe_2$), 5.06, 5.21 (s, 2 × 5H, Cp), $^{13}C\{^1H\}$ NMR (toluene-d_8, 297 K): δ 24.5, 25.7 (Me), 55.9 (CH_2), 60.2 (CH), 105.2 (Cp), 151.7 (C=N). $^{13}C\{^1H\}$ NMR (toluene-d_8, 220 K): δ 24.0, 25.0, 25.9 (Me), 55.0 (CH_2), 59.8 (CH), 102.7, 107.3 (Cp), 151.8 (C=N). Anal. Calcd for $C_{16}H_{22}N_2Ti$ (290.24): C, 66.21; H, 7.64; N, 9.65. Found: C, 66.35; H, 7.58; N, 9.70.

$(Cp_2Ti)_2[\mu\text{-}(\eta^4$-2:3,6:7-PhHC=NNCHPhCHPhNN=CHPh) (7). To a solution of 550 mg (1.58 mmol) of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 10 mL of toluene was added a solution of 330 mg (1.58 mmol) of *trans*,*trans*-benzaldehyde azine in 10 mL of toluene, and the mixture was stirred at 60 °C for 20 h. The color of the solution changed from yellowish brown to dark brown within 15 min. The solvent was removed in vacuo, and the residue was dissolved in 2 mL of THF. After addition of 15 mL of cold *n*-hexane (−78 °C), the crude product precipitated, which was washed with a further 10 mL of *n*-hexane and dried in vacuo. Yield: 530 mg (87%). The brown powder was redissolved in a THF/*n*-hexane (1:3) solution at 60 °C and filtered. The filtrate was then allowed to crystallize at −78 °C. The obtained brown crystals were washed with cold *n*-hexane and dried in vacuo. Yield: 485 mg (80%) of **7**. Mp: 192 °C dec. MS: *m/z* 387 ($M/2^+$). IR (Nujol mull): 1594, 1576 cm^{-1} ($\nu_{C=N}$). NMR: no spectra, since complex **7** is paramagnetic. Anal. Calcd for $C_{48}H_{44}N_4Ti_2$ (772.67): C, 74.62; H, 5.74; N, 7.25. Found: C, 74.71; H, 5.87; N, 7.28.

$Cp_2Zr[C(SiMe_3)=C(SiMe_3)CHPhNN=CHPh]$ (8). A solution of 195 mg (936 μmol) of *trans*,*trans*-benzaldehyde azine in 5 mL of THF was added to a stirred solution of 435 mg (938 μmol) of $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) in 15 mL of THF. After 15 h at 20 °C the solvent and eliminated bis(trimethylsilyl)acetylene were removed from the green solution in vacuo. The residue was redissolved in Et_2O, filtered and dried in vacuo to yield 255 mg (44%) of analytically pure **8**. Alternatively, crystallization of the crude material from 15 mL of *n*-pentane at −40 °C yielded the pure crystalline orange complex **8** in 41% yield. Mp: 102−103 °C dec. MS: *m*/*z* 209 ($(PhCH{=}N)_2^+$), 171 ($(Me_3SiC)_2^+$). IR (Nujol mull): 1543 cm^{-1} (νC=N). ^{1}H NMR (benzene-d_6, 297 K): δ 0.18, 0.51 (s, 2 × 9H, $SiMe_3$), 5.42 (br, 1H, CH), 5.72, 5.87 (s, 2 × 5H, Cp), 7.05 (m, 2H, Ph), 7.21 (m, 4H, Ph), 7.36 (s, 1H, N=CH), 7.42 (m, 4H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 3.7, 6.0 (SiMe3), 91.6 (CH), 109.2, 109.9 (Cp), 124.2, 124.5, 126.9, 127.6, 128.5, 129.1, 129.6 (C2−6, Ph, 1 × CH), 136.5, 141.1 (C1, Ph), 167.6 (C_β-$SiMe_3$), 218.7 (C_α-$SiMe_3$). Anal. Calcd for $C_{32}H_{40}N_2Si_2Zr$ (600.07): C, 64.05; H, 6.72; N, 4.67. Found: C, 64.54; H, 6.74; N, 4.77.

$Cp_2Zr(-N{=}CPh_2)_2$ (9). A 420 mg (1.17 mmol) amount of benzophenone azine was added to a yellowish brown solution of 540 mg (1.16 mmol) of $Cp_2Zr(THF)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**2**) in 20 mL of THF. The solution was stirred at 60 °C for 14 h. Under reduced pressure the reaction volume was decreased to a volume of about 2 mL, and 15 mL of cold *n*-hexane was added to precipitate the product. Filtering followed by washing with cold *n*-hexane (2 × 5 mL) and drying in vacuo yields 580 mg (86%) of **9**. The red powder crystallized by diffusion of *n*-pentane into a THF solution. After standing for 2 days at room temperature red crystals separated, which were decanted, washed with *n*-hexane, and dried in vacuo. Yield: 510 mg (75%). Mp: 157 °C dec. MS: *m*/*z* 581 (M^+), 401 ($M - Ph_2C{=}N^+$), 221 (Cp_2Zr^+), 180 ($Ph_2C{=}N^+$), 77 (Ph^+). IR (Nujol mull): 1632, 1655 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (benzene-d_6, 297 K): δ 5.77 (s, 10H, Cp), 7.17−7.24 (m, 12H, CH, Ph), 7.61−7.64 (m, 8H, CH, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 108.8 (Cp), 128.2, 128.6 (C2/6, C3/5, Ph), 128.5 (C4, Ph), 141.8 (C1, Ph), 170.3 (C=N). Anal. Calcd for $C_{36}H_{30}N_2Zr$ (581.87): C, 74.31; H, 5.20; N, 4.81. Found: C, 74.28; H, 5.21; N, 4.78.

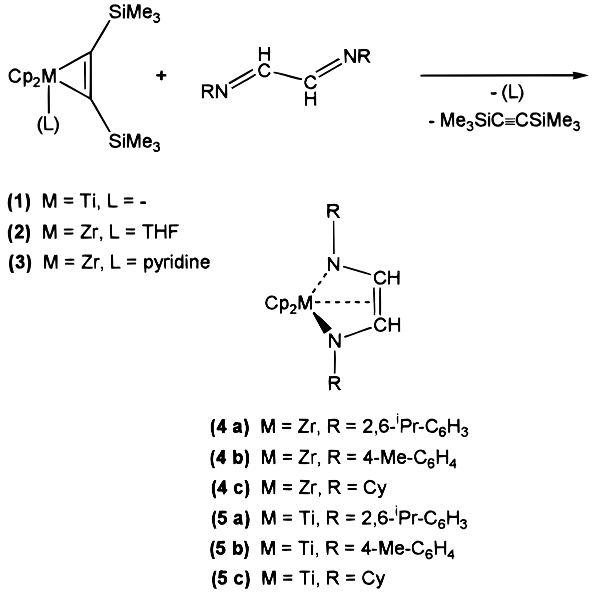
$Cp_2Ti(-N{=}CPh_2)_2$ (10). An amount of 440 mg (1.22 mmol) of benzophenone azine was added to a stirred solution of 430 mg (1.23 mmol) of $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**) in 20 mL of toluene, and the mixture was stirred at 60 °C while the yellowish brown reaction mixture became dark brown within 5 min. After 1 day the solvent was evaporated under reduced pressure. The residue was dissolved in *n*-hexane (60 °C), the solution was filtered, and dark red crystals were obtained by crystallization at room temperature. Yield: 580 mg (85%) of **10**. Mp: 145 °C dec. MS: *m*/*z* 538 (M^+), 473 ($M - Cp^+$), 358 ($M - N{=}CPh_2^+$), 77 (Ph^+). IR (Nujol mull): 1622 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (benzene-d_6): δ 5.57 (s, 10H, Cp), 7.17−7.22 (m, 12H, Ph), 7.51−7.54 (m, 8H, Ph). $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 109.4 (Cp), 141.7 (C1, Ph), 129.1, 129.4, 129.7 (C2−6, Ph), 165.8 (C=N). Anal. Calcd for $C_{36}H_{30}N_2Ti$ (538.53): C, 80.29; H, 5.61; N, 5.20. Found: C, 80.10; H, 5.60; N, 5.20.

$(Cp_2Ti)(\mu\text{-}N{=}CHPh)_2(CpCo)$ (11). A solution of 40 mg (222 μmol) of $CpCo(C_2H_4)_2$ in 10 mL of THF was added to 85 mg (110 μmol) of complex **7** in 10 mL of THF. The orange-brown solution changed to dark violet within 10 min. After 6 h the solvent was evaporated in vacuo and the residue crystallized from THF/*n*-hexane at −78 °C. After 4 days the solution afforded brown, well-formed prismatic crystals, which were washed with *n*-hexane and dried in vacuo. Yield: 94 mg (83%) of **7**. Mp: 187 °C dec. MS: *m*/*z* 510 (M^+), 124 ($CpCo^+$), 104 ($N{=}CHPh^+$), 77 (Ph^+). IR (Nujol mull): 1592 cm^{-1} ($\nu_{C=N}$). ^{1}H NMR (benzene-d_6, 297 K): δ 4.51 (s, 5H, Cp), 5.44 (s, 10H, Cp), 7.28−7.35 (m, 6H, *m*-, *p*-Ph), 7.77 (m, 4H, *o*-Ph), 10.70 (s, 2H, N=CH). $^{13}C\{^1H\}$ NMR (benzene-d_6, 297 K): δ 90.2 (Co−Cp), 108.6 (Ti−Cp), 125.3, 126.2, 129.4 (C2−6, Ph), 138.5 (C1, Ph), 170.5 (C=N). Anal. Calcd for $C_{29}H_{27}N_2CoTi$ (510.36): C, 68.25; H, 5.33; N, 5.49. Found: C, 67.98; H, 5.50; N, 5.58.

$(CpCo)(\mu\text{-}N{=}CHPh)_2(CpCo)$ (12). To a solution of 210 mg (1.17 mmol) of $CpCo(C_2H_4)_2$ in 10 mL of THF was added a solution of 120 mg (0.58 mmol) of *trans*,*trans*-benzaldehyde azine in 10 mL of THF. After 14 h at 60 °C the solvent was removed in vacuo and the yellowish brown residue crystallized from *n*-hexane at 20 °C. Yield: 450 mg (80%) $C_s + C_2$. Mp: 159 °C dec. MS: 456 (M^+), 351 ($M - N{=}CHPh^+$), 189 (Cp_2Co^+), 124 ($CpCo^+$), 77 (Ph^+), 59 (Co^+). IR (Nujol mull): 1565, 1573, 1583 cm^{-1} ($\nu_{C=N}$). C_s-symmetric product: ^{1}H NMR (THF-d_8, 297 K) δ 4.71, 4.86 (s, 2 × 5H, Cp), 7.27 (m, 2H, Ph), 7.40 (t, J = 7.6 Hz, 4H, Ph), 8.04 (m, 4H, Ph), 9.20 (s, 2H, N=CH). C_2-symmetric product: ^{1}H NMR (THF-d_8, 297 K): δ 4.82 (s, 10H, Cp), 7.23 (m, 2H, Ph), 7.36 (t, J = 7.6 Hz, 4H, Ph), 7.89 (m, 4H, Ph), 9.30 (s, 2H, N=CH). $^{13}C\{^1H\}$ NMR (THF-d_8, 297 K): C_s, δ 79.7, 80.6 (Cp); C_2, δ 80.2 (Cp); $C_s + C_2$, 126.7, 126.8, 128.6 (2), 128.7 (2) (C2−6, Ph), 137.4, 137.6 (C1, Ph), 173.6, 174.1 (N=CH). Anal. Calcd for $C_{24}H_{22}N_2Co_2$ (456.32): C, 63.17; H, 4.86; N, 6.14. Found: C, 63.35; H, 4.87; N, 6.02.

Results and Discussion

Preparation of Complexes. Since the bis(trimethylsilyl)acetylene titanocene $Cp_2Ti(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (**1**)[2a] and zirconocene complexes $Cp_2Zr(L)(\eta^2\text{-}Me_3SiC_2SiMe_3)$ (L = THF (**2**),[2b] pyridine (**3**))[2c] are excellent starting materials for the generation of the reactive Cp_2Ti and Cp_2Zr fragments,[2d] the reactions with 1,4-diazadienes RN=CHCH=NR were carried out with **1**−**3** as metallocene precursors. These complexes react via substitution of the acetylene (and, in the case of zirconium, of ligands L) to give the corresponding 1-metalla-2,5-diazacyclopent-3-ene (diazadiene) complexes $Cp_2M(\eta^2\text{-}1{:}4\text{-}RNCH{=}CHNR)$ (M = Zr, R = 2,6-$^i Pr_2C_6H_3$ (**4a**), 4-MeC_6H_4 (**4b**), Cy (**4c**); M = Ti, R = 2,6-$^i Pr_2C_6H_3$ (**5a**), 4-MeC_6H_4 (**5b**), Cy (**5c**)) (eq 1).



(1) M = Ti, L = -
(2) M = Zr, L = THF
(3) M = Zr, L = pyridine

(4 a) M = Zr, R = 2,6-^{i}Pr-C_6H_3
(4 b) M = Zr, R = 4-Me-C_6H_4
(4 c) M = Zr, R = Cy
(5 a) M = Ti, R = 2,6-^{i}Pr-C_6H_3
(5 b) M = Ti, R = 4-Me-C_6H_4
(5 c) M = Ti, R = Cy

(1)

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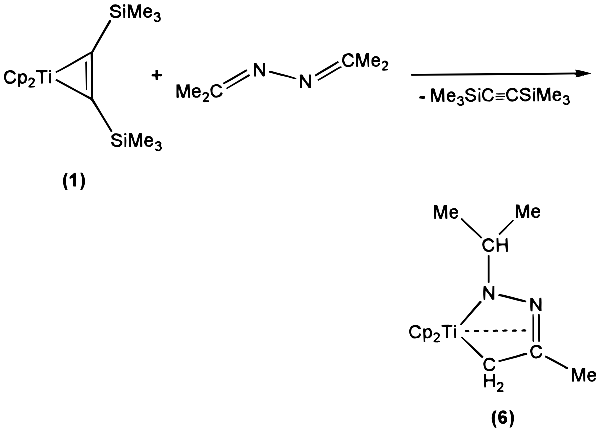
Titanium and zirconium complexes with 1,4-diazadienes are well-known and were described before.[7] The substitution of an acetylene by the 1,4-diazadiene is a new method for preparing a series of such complexes. In most of those complexes the β-positions are substituted.[7]

Complexes without substituents in these positions are very rare,[7h,j] and complexes **4a**−**c** and **5a**−**c** are new examples of such ethanediimine (ethylenediamide) ligands.

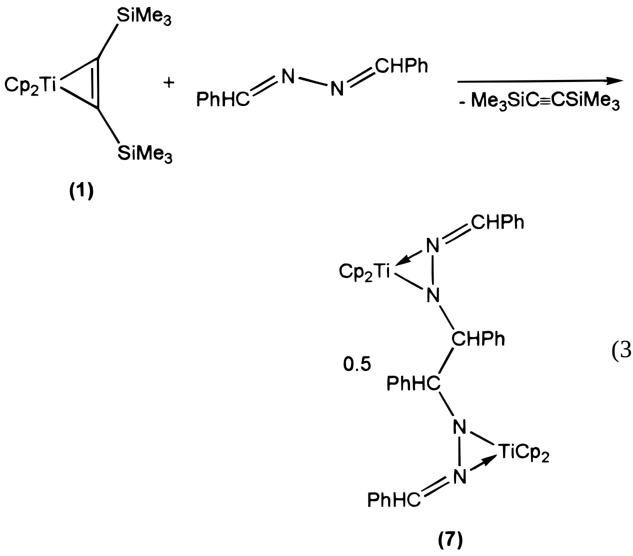
In the analogous reaction with azines RR′C=NN=CRR′ the products depend strongly on the metals used, Zr and Ti, as well as the substituents R and R′. With R = R′ = Me and M = Ti, the reaction of **1** with acetone azine leads after substitution of the alkyne with the azine to an unexpected activation of the methyl C−H bond. In the resulting green complex **6** a hydrogen atom is shifted from one methyl group to the carbon atom of the second C=N moiety and the five-membered 1-titana-2,3-diazacyclopent-3-ene metallacycle **6** is obtained (eq 2).



(2)

The course of the reaction of acetone azine and titanocene with the activation of a strong sp^3 C−H bond in **6** is rather surprising in view of the ease of oxidative addition and cleavage of the N−N bond of $Ph_2C{=}NN{=}CPh_2$ to $Cp_2Zr(C_4H_6)$[8b] and $CpCo(C_2H_4)$,[9] where mononuclear $Cp_2Zr(N{=}CPh_2)_2$ or dinuclear species (CpCo)-(μ-$(N{=}CPh_2)_2$(CpCo) were obtained (see also below).

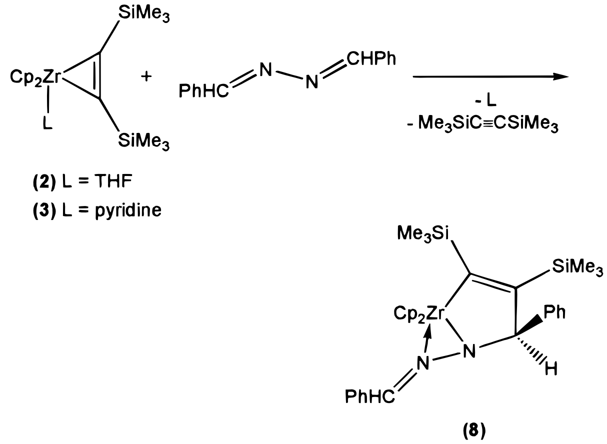
A completely different result compared to that for R = R′ = Me was obtained in the reaction of **1** with benzaldehyde azine using R = Ph and R′ = H. In this case the paramagnetic binuclear Ti(III) complex $(Cp_2Ti)_2[\mu\text{-}(\eta^4\text{-}2{:}3,6{:}7\text{-}PhHC{=}NNCHPhCHPhNN{=}CHPh)]$ (**7**) was formed (eq 3).



(3)

In this reaction the acetylene was also substituted by the azine and, by a reductive coupling of two azine molecules, **7** was formed. The reaction path shows some similarities to the coupling of ketones $R_2C{=}O$ between two titanium(II) centers in the McMurry reaction.[10] This type of reaction has been verified also for heterocarbonyl compounds such as $R_2C{=}NR$.[11]

In the analogous reaction with M = Zr, no substitution of the acetylene was observed, but one of the C=N double bonds of the azine inserts into the Zr−C bond of the zirconacyclopropene structure of the starting acetylene complex to yield the five-membered 1-zircona-2-azacyclopent-4-ene species **8**, which is additionally stabilized by N-coordination of the second imino group as substituent in a position α to the metal (eq 4).



(4)

Such a coupling of acetylenes with C=N double bonds is not unusual,[3] but this is the first example found for azines.

Using R = R′ = Ph the central N−N single bond of the azine is cleaved by both of the metals and the bis(imido) complexes $Cp_2M(-N{=}CPh_2)_2$ (M = Zr (**9**),[8b] M = Ti (**10**)) were isolated (eq 5).

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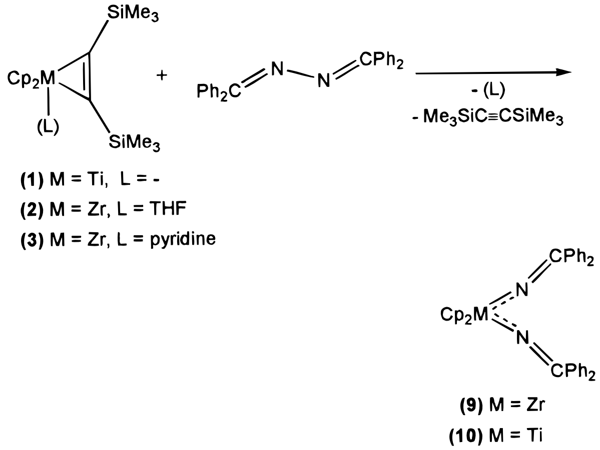


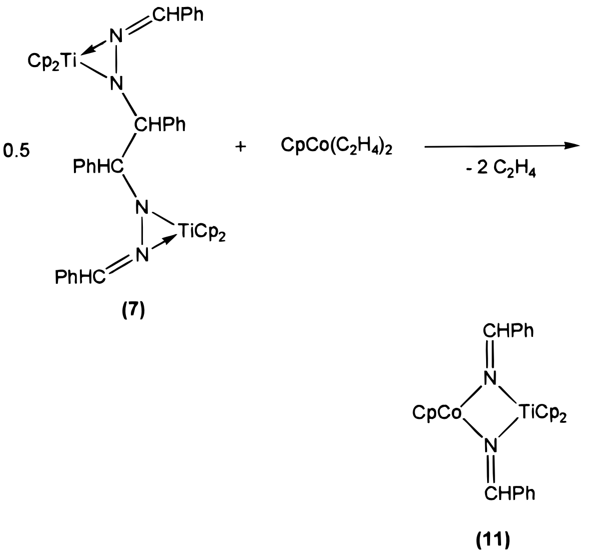
(1) M = Ti, L = -
(2) M = Zr, L = THF
(3) M = Zr, L = pyridine

(9) M = Zr
(10) M = Ti

(6)

Complex **9** has been prepared before by using the $Cp_2Zr(C_4H_6)$ [8b] as zirconocene precursor.

The reaction of **7** and $CpCo(C_2H_4)_2$[12] yields almost quantitatively the heterobimetallic product (Cp_2Ti)-μ-$(N{=}CHPh)_2(CpCo)$ (**11**) (eq 6).



(7)

(11)

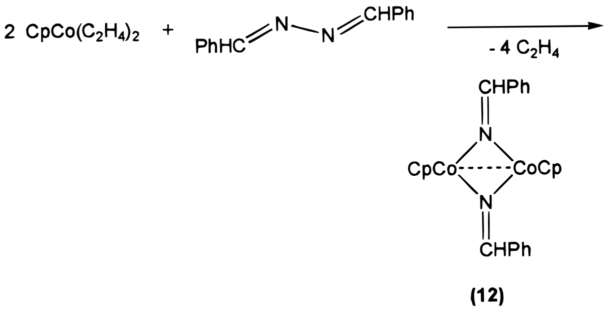
(6)

The interaction of the bis(titanocene) species **7** with an additional Co(I) center causes the activation of the central C–C bond as well as the cleavage of the azine N–N bonds, leading to the bridged heterobimetallic bis(alkylideneamido) complex **11**.

In the reaction of complex **7** with $CpRh(C_2H_4)_2$ by using thermal or photochemical activation no analogous heterobimetallic compound was observed.

For comparison and preparation of the homobimetallic bis(alkylideneamido) complex the reaction of benzaldehyde azine with $CpCo(C_2H_4)_2$ was investigated. The reaction product $(CpCo)(\mu$-$N{=}CHPh)_2(CpCo)$ (**12**) (eq 7) is analogous to the well-known complex $(CpCo)(\mu$-$N{=}CPh_2)(CpCo)$.[9]

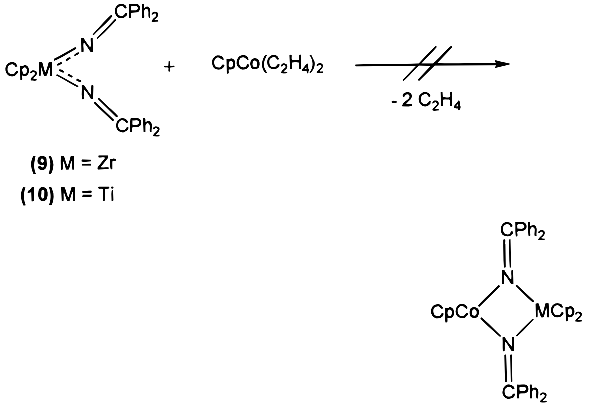
Complex **12** consists of a mixture of C_s- and C_2-symmetric products, as shown by NMR spectra. For X-ray crystal structure analysis a single crystal of the C_2-symmetric product was used (see below).



(12)

(7)

In reactions of **9** and **10** with $CpCo(C_2H_4)_2$ heterobimetallic complexes of the type $(Cp_2Ti)(\mu$-$N{=}CPh_2)_2(CpCo)$, being analogous to complex **11**, were not obtained (eq 8).



(9) M = Zr
(10) M = Ti

(8)

All new complexes have been characterized by spectroscopic methods and, for **4a, 7**, **8**, **10**, **11**, and **12**, by single-crystal X-ray analysis.

NMR Spectroscopic Investigations. The ^1H and ^{13}C NMR spectra of the complexes **4a**–**c** as well as **5a**–**c** behave like those of the previously investigated complexes $Cp_2M(\eta^2$-1:4-$R^1NCR^2{=}CR^2NR^1)$ (M = Zr, Ti; $R^1 = R^2 =$ Ph or $R^1 =$ Ph, $R^2 =$ Me)[7f] and exhibited at room temperature only one signal for the Cp_2M moiety. The ^{13}C resonances of the internal C atoms of the complexed heterodiene shifted to high field in a range which is characteristic for C=C double bonds. The ^1H NMR spectra show also a great temperature dependence; indeed at lower temperatures (225 K) the singlet of the Cp ligands split into two signals, which were assigned to two diastereotopic Cp units. This dynamic behavior (in solution) of zirconocene and titanocene complexes with 1,4-diazadienes has been discussed in detail.[7f]

The NMR spectra of **6** confirm the C–H activation by signals of a CH_2 group at 1.36 ppm (very broad, becomes a sharp singlet at 330 K) and 55.9 ppm in ^1H and ^{13}C NMR, respectively. In addition, there are two different methyl signals at 1.14/ 2.28 ppm and 24.5/25.7 ppm in the ratio of 2:1. In the ^1H NMR spectrum the isopropyl methyl groups appear as a doublet (1.14 ppm, $^3J_{HH} = 6.3$ Hz, 6H) and, consequently, the signal of the methine proton is a septet at 3.82 ppm ($^3J_{HH} = 6.3$ Hz, 1H). Very broad methylene and cyclopentadienyl resonances at ambient temperatures result from dynamic behavior due to a folded ground-state conformation typical for such azametallacycles.[7l] Indeed, at higher temperatures (330 K) the NMR spectra of **6** suggest C_s molecular symmetry in solution; however, decreasing

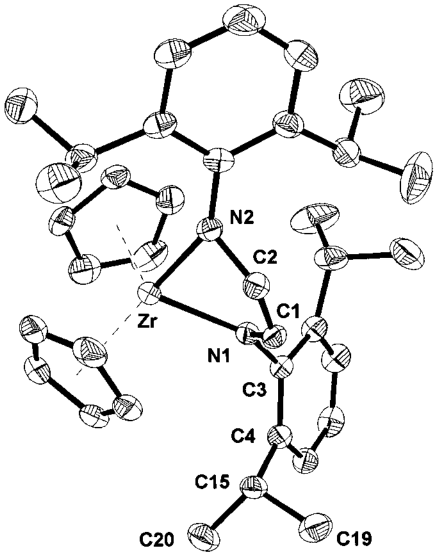


Figure 1. Molecular structure of complex **4a**, shown by an ORTEP plot. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Zr−N1, 2.134(2); Zr−N2, 2.107(2); N1−C1, 1.386(3); N1−C3, 1.439(3); N2−C2, 1.390(3); N2−C9, 1.425(4); C1−C2, 1.358(4); C4−C15, 1.512(4); C15−C19, 1.536(4); N1−Zr−N2, 83.63(8); C1−N1−Zr, 92.8(2); C2−N2−Zr, 92.7(2); C1−N1−C3, 120.5(2); C2−N2−C9, 117.9(2); C1−C2−N2, 122.6(3); C3−C4−C15, 123.5(3); C19−C15−C20, 109.8(3).

the temperature reveals a nonplanar molecular geometry and the ^{1}H NMR spectrum at 220 K displays two diastereotopic Cp units (5.06 (s, 5H), 5.21 ppm (s, 5H)) as well as two nonequivalent methylene protons (0.65 (broad, 1H), 2.16 (broad, 1H)). The broad signals of the nonequivalent methylene protons did not show the expected fine structure.

NMR spectra of the titanocene complex **10** are very much like those of the corresponding zirconocene complex **9**.[8] Besides the signals of the four chemically equivalent phenyl groups, only a single Cp resonance has been found at δ 5.77 (**9**), 5.57 (**10**) (^{1}H NMR, 10 H) and δ 108.8 (**9**), 109.4 (**10**) (^{13}C NMR) and the N=C signal was found at δ 170.3 (**9**), 165.8 (**10**) (^{13}C NMR).

NMR spectra of **11** show the resonances corresponding to the phenyl groups and two different Cp units in the ratio of 2:1. In addition, the ^{1}H and ^{13}C signals of the azine CH function appear at 10.70 ppm (s, 2H) and 170.5 ppm, respectively.

Structural Investigations. Complexes **4a**, **7**, **8**, **10**, **11**, and **12** were investigated by an X-ray crystal structure analysis. The ORTEP structure of complex **4a** is presented in Figure 1.

The type of structure is not new, but to the best of our knowledge, this is the first example of a zirconocene complex with hydrogen atoms in β positions to the metal. Titanium complexes with hydrogen atoms in β positions to the metal have been descibed, but with ligands being different from Cp.[7] All structural data are in good agreement with the structure of the previously described zirconocene enediamido (diazadiene) complex $Cp_2Zr(\eta^2\text{-}1{:}4\text{-}PhNCPh{=}CPhNPh)$.[7f] This five-membered metallacyclic ring system adopts an "envelope" conformation and exhibits a dynamic NMR spectrum indicating a rapid intramolecular migration of the bent metallocene unit Cp_2M from one "face" of the reduced diazadiene to the other (see also above). The Zr−N amido distances of this complex of 2.100(4), 2.107(4) Å and 2.125(5), 2.112(4) Å are only slightly different from those of complex **4a** of 2.107(2) and 2.134(2) Å. The C=C distance of 1.358(4) Å and the N−C distances of 1.386(3) and 1.390(3) Å are within the normal ranges for double and single bonds.

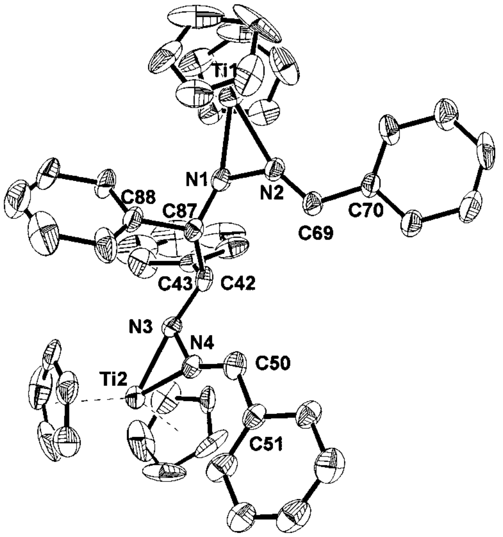


Figure 2. Molecular structure of complex **7** (two symmetry-independent molecules per asymmetric unit; one is selected) shown by an ORTEP plot. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Ti1−N1, 2.057(8); Ti1−N2, 2.096(10); Ti2−N3, 2.054(8); Ti2−N4, 2.129(9); N1−C87, 1.456(12); N2−C69, 1.298(12); N3−C42, 1.458(12); N4−C50, 1.309(12); N1−N2, 1.343(11); N3−N4, 1.344(10); C42−C87, 1.586(12); C42−C43, 1.522(13); C50−C51, 1.450(15); C69−C70, 1.455(15); C87−C88, 1.502(13). N1−Ti1−N2, 37.7(3); N3−Ti2−N4, 37.4(3); N1−N2−C69, 127.9(9); N3−N4−C50, 129.9(9); N2−C69−C70, 121.7(7); N4−C50−C51, 122.7(12); N2−N1−C87, 122.1(8); N4−N3−C42, 120.0(8); N1−C87−C88, 110.6(8); N3−C42−C43, 108.7(8); N1−C87−C42, 112.1(7); N3−C42−C87, 111.8(7).

Due to its paramagnetism, the structure of **7** was determined by X-ray crystallography (Figure 2).

The structure analysis was mentioned before[2e] in a short communication and reveals a binuclear titanium(III) complex resulting from a reductive C−C coupling[10] which converts two azine molecules into a dianionic bridging ligand. Each Ti(III) center is complexed by an amido nitrogen and additionally coordinated by the electron pair of the second imine nitrogen. The structure of the ligand chain is characterized by two C−N double bonds and two C−N single bonds, respectively, intact N−N single bonds, and the newly formed central C−C single bond.

The molecular structure of complex **8** is presented in Figure 3.

This type of structure is new. In the five-membered 1-zircona-2-azacyclopent-4-ene **8** species the nitrogen atoms of the N=CHPh substituents in the position α to the zirconium atom coordinate additionally. The five-membered-ring system is similar to that which was found in the reaction products resulting from oxidative coupling of imines C=N with acetylenes. On the other side the ring opening of benzazoles and benzthiazoles also gives similar five-membered-ring systems,[4b] which

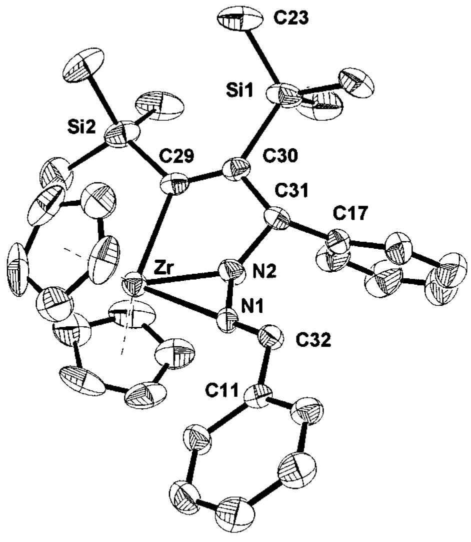


Figure 3. Molecular structure of complex **8**, shown by an ORTEP plot. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Zr−N1, 2.324(4); Zr−N2, 2.021(5); Zr−C29, 2.447(5); C11−C32, 1.452(7); C17−C31, 1.520(7); C29−C30, 1.366(7); C30−C31, 1.547(7); C23−Si1, 1.868(7); C29−Si2, 1.874(5); C30−Si1, 1.902(5); N1−N2, 1.331(6); N1−C32, 1.289(6); N2−C31, 1.435(6); N1−Zr−N2, 34.79(15); N2−Zr−C29, 67.5(2); Zr−C29−C30, 113.9(4); Zr−N2−C31, 136.0(3); Zr−N1−C32, 163.2(4); C29−C30−C31, 118.2(4); C29−C30−Si1, 130.4(4).

are additionally stabilized by the coordination of *o*-phenylenealcoholate and -thiolate substituents. The distances and angles in the five-membered 1-zircona-2-azacyclopent-4-ene ring in the *o*-phenylenealcoholate complex (Zr−C = 2.426(3), Zr−N = 2.301(3), N−C(3) = 1.287(4), C(3)−C(4) = 1.458(4), C(4)−C(5) = 1.373(5) Å; N−Zr−C(5) = 69.2(10), Zr−C(5)−C(4) = 115.7(2), C(3)−C(4)−C(5) = 114.3(3)°) and *o*-phenylenethiolate complex (Zr−C = 2.405(11), Zr−N = 2.330(8), N−C(3) = 1.293(13), C(3)−C(4) = 1.477(14), C(4)−C(5) = 1.380(15) Å; N−Zr−C(5) = 69.7(17), Zr−C(5)−C(4) = 114.8(7), C(3)−C(4)−C(5) = 113.9(4)°) are comparable to those of **8** (Zr−C(29) = 2.447(5), Zr−N(2) = 2.021(5), N(2)−C(31) = 1.435(6), C(30)−C(31) = 1.547(7), C(29)−C(30) = 1.366(7) Å; N(2)−Zr−C(29) = 67.5(2), Zr−C(29)−C(30) = 113.9(4), C(29)−C(30)−C(31) = 118.2(4)°). Whereas the part Zr−C(29)=C(30) is very similar, the other part Zr−N(2)−C(31) is different due to the coordination of the −N=CHPh group in the α-position, which gives a three-membered-ring system. The *o*-XC$_6$H$_4$− units (X = O, S) form by coordination a five-membered second ring. At 2.324(4) Å, the Zr−N(1) bond distance of the coordinating −N=CHPh is typical for coordinated imines.

The molecular structure of complex **10** is presented in Figure 4.

This type of structure is known from the zirconocene complex Cp$_2$Zr(−N=CPh$_2$).[8a] A detailed bonding description for N=CPh$_2$ complexes as organometallic heteroallene-type Schiff base derivatives was given by Erker et al.[8b] For complex **10** it is interesting to study the influence of titanium in comparison to the zirconium atoms. Both complexes show nearly identical structural parameters of the N=CPh$_2$ ligands. The Zr−N bond distances of 2.058(2) and 2.063(2) Å are slightly longer compared to the corresponding Ti−N distances of 1.944(3) and 1.956(2) Å. The N=C distances in the zirconocene complex of 1.259(4) and 1.266(4) Å are nearly identical with those found in the titanocene complex (1.265(3) and 1.263(3) Å). Also, the angles Zr−N=C of 173.7(2) and 164.1(2)° are larger than those found for the titanocene complex, 160.8(2) and 161.0(2)°. The different distances and angles might be explained by the larger zirconium atom.

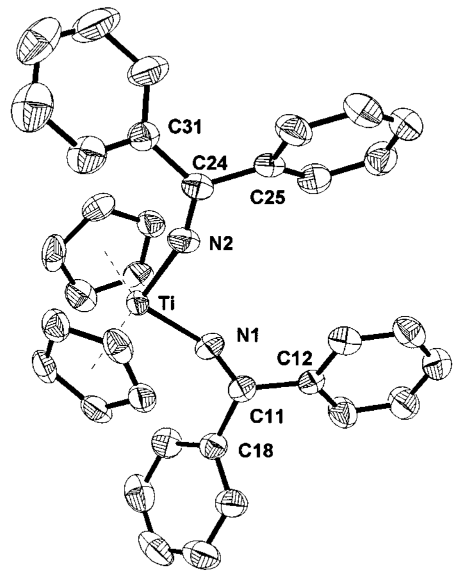


Figure 4. Molecular structure of complex **10**, shown by an ORTEP plot. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Ti−N1, 1.944(3); Ti−N2, 1.956(2); N1−C11, 1.265(3); N2−C24, 1.263(3); C11−C12, 1.505(4); C11−C18, 1.497(4); C24−C25, 1.495(4); C24−C31, 1.516(4); N1−Ti−N2, 99.27(11); Ti−N1−C11, 160.8(2); Ti−N2−C24, 161.0(2); N1−C11−C12, 120.7(3); N2−C24−C25, 121.4(3); C12−C11−C18, 118.3(3); C25−C24−C31, 115.9(2).

The structure of **11** was unambiguously determined by an X-ray diffraction analysis (Figure 5).

The structure was mentioned before in a short communication.[2e] The bond distances and angles support the nitrogen-bridged coordination with a central four-membered Ti−N−Co−N cycle. Additionally, there seems to be an interaction between the titanium and the cobalt center. The average Ti−Co distance of 2.568(6) Å in the bridged complex **11** is compatible to the Ti−Co distances of 2.565 Å in (^{t}BuO)$_3$Ti−Co(CO)$_4$[13] and 2.614 Å in [(CO)$_9$Co$_3$CO]Ti−Co(CO)$_4$.[14] Unequal steric demands of the different metallocene units cause a slight bending of the bridging alkylideneamido ligands toward the smaller CpCo moiety (average angles: Ti−N1−C16, 148(2)°; Ti−N2−C23, 148(2)°; Co−N1−C16, 128(2)°; Co−N2−C23, 128(2)°). Although there are bimetallic examples known containing bridging alkylideneamido ligands,[15] **11** represents the first heterobimetallic complex of its type and the facile formation could be an easy way to synthesize complexes of various metal combinations.

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(14) Schmidt, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239.

(15) For example: (a) Evans, W. J.; Meadows, J. H.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 1291. (b) Klose, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C.; Re, N. *J. Am. Chem. Soc.* **1994**, *116*, 9123.

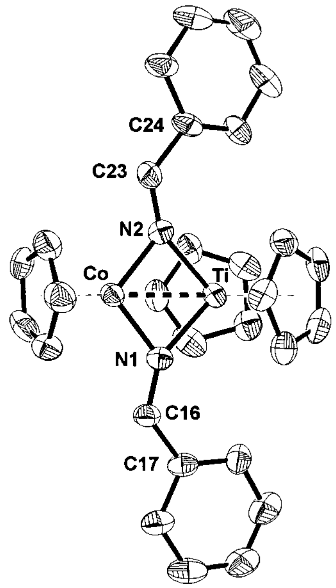

Figure 5. Molecular structure of complex **11**, shown by an ORTEP plot. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Co−Ti, 2.569(3); Ti−N1, 1.996(10); Ti−N2, 1.975(10); Co−N1, 1.856(10); Co−N2, 1.851(10); N1−C16, 1.31(2); N2−C23, 1.30(2); C16−C17, 1.47(2); C23−C24, 1.53(2); N1−Ti−N2, 91.7(4); N1−Co−N2, 100.5(4); Co−N1−Ti, 83.6(4); Co−N2−Ti, 84.3(4); Co−N1−C16, 127.7(9); Co−N2−C23, 127.0, N1−C16−C17, 128.6(12); N2−C23−C24, 127.4(13).

The structure of **12** was determined also by an X-ray diffraction analysis (Figure 6).

A structure for this type of homobimetallic cobalt(II) complex was at first established by Floriani et al. for the complex (CpCo)(μ-N=CPh$_2$)(CpCo).[9] The structure of complex **12** shows an interesting influence of the substituents R and R′ on the structures of the homobimetallic cobalt complexes as well as the influence of the metals in comparison to the structure of the heterobimetallic and isoelectronic complex **11**. Some relevant data for these complexes (CpCo)(μ-N=CRR′)(Cp$_n$M) are listed in Table 2.

Conclusion

We have demonstrated substitution reactions of titanocene and zirconocene bis(trimethylsilyl)acetylene complexes with 1,4-diazadienes giving enediamido complexes. In the corresponding reaction with azines the reactions depend on the different metals and substituents which were used. With titanium the substitution of the alkyne is favored, whereas with zirconium a coupling of one C=N double bond with the alkyne was found. With other azines, after substitution of the acetylene a subsequent C−H activation or a C−C coupling is observed. “Early−late” heterobimetallics can be obtained by reactions of azines with two metal centers. In these reactions an N−N single bond is cleaved and bis(alkylideneamido) complexes are formed.

The different reactions of metallocene alkyne complexes with azines show a broad scope. Again the influence of metals and of the substituents of the substrates on the obtained products, formed by unexpected and manifold reaction pathways, is obvious. Further studies aimed at the scope of the bimetallic reactions are in progress.

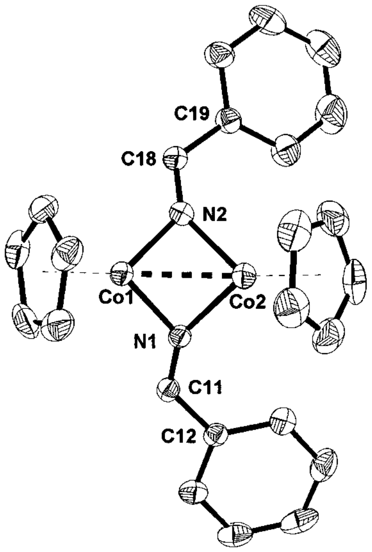

Figure 6. Molecular structure of complex **12** (C_s-symmetric product), shown by an ORTEP plot. The thermal ellipsoids correspond to 30% probability. Selected bond lengths (Å) and angles (deg): Co1−N1, 1.846(3); Co1−N2, 1.846(3); Co2−N1, 1.870(3); Co2−N2, 1.869(3); Co1−Co2, 2.3472(8); N1−C11, 1.271(5); N2−C18, 1.272(5); C18−C19, 1.476(5); C11−C12, 1.477(6); N1−Co1−N2, 81.87(14); N1−Co2−N2, 80.62(13); Co1−N1−Co2, 78.36(12); Co1−N2−Co2, 78.34(14); N1−C11−C12, 126.9(4); N2−C18−C19, 128.7(4).

Table 2. Structural Parameters of the Complexes (CpCo)(μ-N=CRR′)(Cp$_n$M)

	M = Co, n = 1, R = R′ = Ph	M = Co, n = 1, R = Ph, R′ = H (**12**)	M = Ti, n = 2, R = Ph, R′ = H (**11**)
		Distances (Å)	
Co-M	2.335(1)	2.3472(8)	2.569(3)
Co−N	1.881(8)	1.846(3)	1.851(10)
Co−N′	1.896(7)	1.869(3)	1.856(10)
M−N		1.846(3)	1.975(10)
M−N′		1.870(3)	1.996(10)
N=C	1.268(10)	1.272(5), 1.271(5)	1.31(2), 1.30(2)
		Angles (deg)	
N−Co−N′	79.7(3)	81.87(14)	100.5(4)
Co−N−Co′	76.4(3)	78.36(12)	
N−M−N′		80.62(13)	91.7(4)
Co−N−M		78.34(14)	83.6(4), 84.3(4)

Acknowledgment. This work was supported by the Max-Planck-Gesellschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles and figures giving additional views for **4b**, **7**, **8**, **11**, and **12** (37 pages). Ordering information is given on any current masthead page.

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