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Synthesis and Characterization of Monomeric Bis(η^2-alkyne)silver(I) Compounds: Crystal Structure of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}AgNO_2$

Heinrich Lang,* Mathias Herres, and Laszlo Zsolnai

Anorganisch-Chemisches Institut der Universität, Im Neuenheimer Feld 270,
69120 Heidelberg, Germany

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*Summary: The application of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv C\text{-}SiMe_3)_2$ (1) as an organometallic chelate ligand to break down $[AgX]_n$ aggregates into monomeric AgX units is discussed. Compounds of type $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}Ag^IX$ (3) (**3a**, X = Cl; **3b**, X = CN; **3c**, X = SCN; **3d**, X = NO_2; **3e**, X = ClO_4) were synthesized in high yields by the reaction of 1 with $(1/n)[AgX]_n$ (2). Complexes 3 are the first stable compounds in which alkyne units are η^2-side-on coordinated to monomeric Ag^IX building blocks. The identity of all new compounds has been documented by analytical, as well as by spectroscopic (IR, ^1H NMR, MS), data. In addition, the solid-state structures of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2$ (1) and $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}AgNO_2$ (**3d**) were established by X-ray crystallography.*

Introduction

Ag^I compounds are, in general, polymeric species $[AgX]_n$.[1] To break down $[AgX]_n$ aggregates into monomeric AgX building blocks, σ-donor ligands such as PR_3, $R_2PCH_2CH_2PR_2$, SR_2, ...[1] or macrocyclic ligands containing chalcogenic donors have been used.[2]

In order to stabilize monomeric Ag^IX units, we used the organometallic fixed chelate ligand $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2$ (1).[3] Complex 1 has already been used for the synthesis of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}ML_n$ complexes, where ML_n is Ni(CO),[4] Co(CO),[5] CuCl, $FeCl_2$, $CoCl_2$, or $NiCl_2$.[6] In $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}ML_n$ each of the two alkynyl ligands of 1 is cooperatively side-on coordinated to the ML_n fragment.[4-6]

Here, we describe the synthesis and characterization of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}Ag^IX$ compounds, the first examples in which monomeric Ag^IX units are stabilized by side-on coordination of the two alkynyl ligands of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2$ (1). Furthermore, the solid-state structure of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2\}AgNO_2$ (**3d**) will be discussed.

Results and Discussion

$(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv CSiMe_3)_2$ (1)[3] reacts in refluxing acetone with equimolar amounts of the appropriate silver(I) salt $(1/n)[AgX]_n$ (X = Cl, CN, SCN, NO_2, ClO_4) (**2**) to yield the complexes **3** in almost quantitative yields (Scheme I). Compounds **3** are the only isolated products obtained upon filtration of the reaction mixtures through silica gel with dichloromethane. Evaporation of the solvent under high vacuum and recrystallization of the orange residues from THF/*n*-pentane at -30 °C give pure **3** (Experimental Section). All complexes **3** are soluble in most common organic solvents (THF, CH_2Cl_2, ...); crystals of **3** are remarkably stable to air for a period of several months.

Another procedure for the preparation of compounds of type **3** is the reaction of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C\equiv C\text{-}SiMe_3)_2\}FeCl_2$ (**4**)[6] with $(1/n)[AgX]_n$ (**2**) in refluxing THF (Scheme II). Additionally, **3b** and **3c** can be obtained in quantitative yield by treatment of **3a** with 1 equiv of AgCN (**2b**) or AgSCN (**2c**) in THF at 25 °C. The characterization of **3** is based on analytical and spectroscopic (IR, ^1H NMR, MS) data (Experimental Section).

In order to establish the solid-state structures of compounds **1** and **3**, an X-ray diffraction study was carried out on single crystals of **1** and **3d**. Their structures are shown in Figure 1.

Compound **1** crystallizes in the monoclinic space group $P2_1$ with two independent molecules. Complex **3d** crystallizes in the monoclinic space group $P2_1/c$ with two independent molecules of **3d** and two THF molecules per molecule of **3d** in the unit cell (Experimental Section). Figure 1 clearly shows that **3d** is monomeric and that each of the two (trimethylsilyl)ethynyl ligands is cooperatively side-on coordinated to the $AgNO_2$ moiety. The atoms Ti, Ag, C11-C14, Si1, and Si2 form a plane (maximum atomic deviation 0.002 Å), which is almost perpendicular to the Ag, O1, O2, N1 plane (interplanar angle 87.9°).

As a result of the side-on coordination of the (trimethylsilyl)ethynyl units in **3d** to $AgNO_2$, the angle C11-Ti-C13 (94.5°) is considerably reduced compared to the analogue angle in **1** (102.8°) (Figure 1).[6] This leads to a deformation of the Ti—C≡C—Si units in **3d** (Ti-C11-C12 = 171°; C11-C12-Si1 = 170°), which are almost linear in **1** (Ti-C11-C12 = 178.2°; C11-C12-Si1 = 178.3°) (Figure 1).[6] The D1-Ti-D2 angles (D1, D2 = centroids of the cyclopentadienyl ligands) (**1**, 133.7°; **3d**, 133.3°) are similar to angles in other metallocene compounds.[7] The observed bond lengthening of the CC triple bonds from 1.21 Å (C11-C12) and 1.20 Å (C13-C14) in **1** to 1.26 Å (C11-C12) and 1.27 Å (C13-C14) in **3d**, is additionally confirmed by IR spectroscopy: The $\nu(C\equiv C)$ vibration is shifted from 2012 cm^{-1} for **1**[3] to 1947 cm^{-1} for **3d**. The same behavior is found for all other compounds of type **3** (Experimental

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[•] Abstract published in *Advance ACS Abstracts,* October 15, 1993.

[1] van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 2, p 710 (Chapter 14) and literature cited therein.

[2] For example: (a) Stephan, D. W. J. *J. Chem. Soc., Chem. Commun.* **1991**, 129 and literature cited therein. (b) Nadashi, T. T.; Stephan, D. W. *Organometallics* **1992**, *11*, 116.

[3] Lang, H.; Seyferth, D. *Z. Naturforsch.* **1990**, *45B*, 212.

[4] Lang, H.; Imhof, W. *Chem. Ber.* **1992**, *124*, 1307.

[5] Lang, H.; Zsolnai, L. *J. Organomet. Chem.* **1991**, *406*, C5.

[6] For example: (a) Lang, H.; Herres, M.; Zsolnai, L.; Imhof, W. *J. Organomet. Chem.* **1991**, *405*, C7. (b) Herres, M. Ph.D. Thesis, University of Heidelberg, 1993.

[7] Huttenloch, M. E.; Diebold, J.; Reif, U.; Brintzinger, H. H.; Gilbert, A. M.; Katz, Th. J. *Organometallics* **1992**, *11*, 3600 and literature cited therein.

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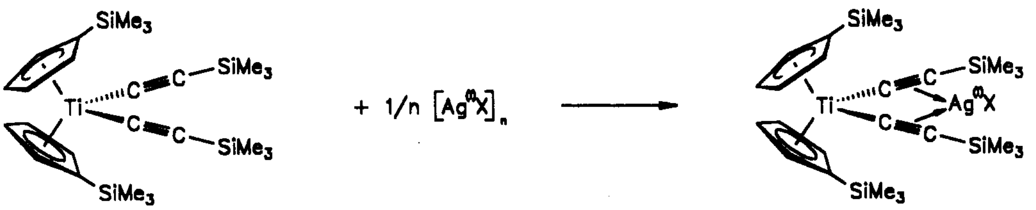
Scheme I



1

2

3a: X = Cl

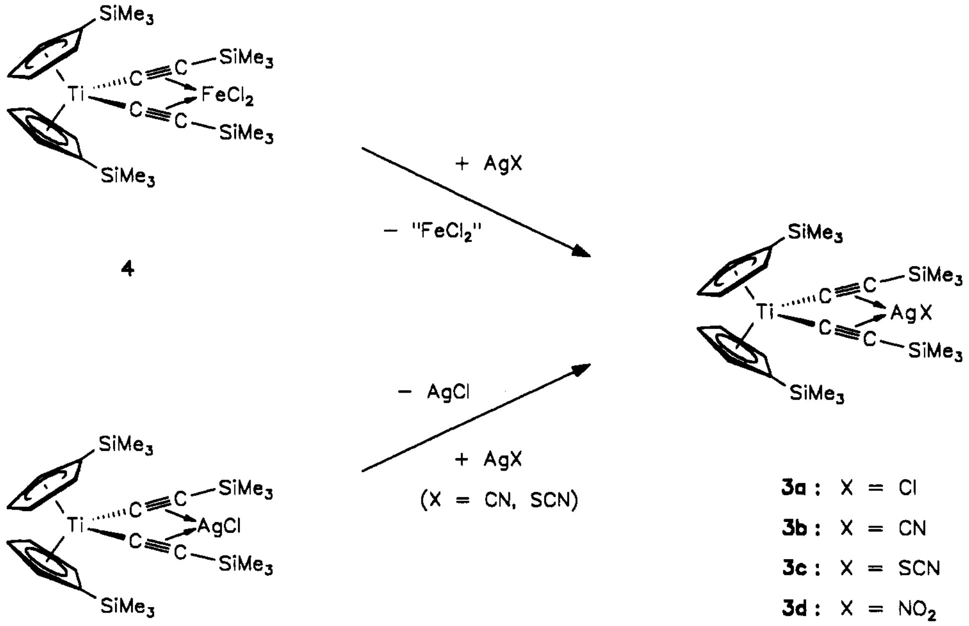
3b: X = CN

3c: X = SCN

3d: X = NO_2

3e: X = ClO_4

Scheme II



4

3a

3a : X = Cl

3b : X = CN

3c : X = SCN

3d : X = NO_2

3e : X = ClO_4

Section), as well as for $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}$-$CuCl$[6] and $(\eta^5\text{-}C_5H_5)Cu(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)$.[8]

A powerful method for using $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (1) as an organometallic chelate ligand for breaking down $[Ag^IX]_n$ aggregates into monomeric Ag^IX units has been described.

Experimental Section

General Comments. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) was purified by distillation from sodium/benzophenone ketyl; *n*-pentane and dichloromethane were purified by distillation from calcium hydride. Infrared spectra were obtained with a Perkin-Elmer 983G spectrometer. ^1H NMR spectra were recorded on a Bruker AC 200 spectrometer operating at 200.132 MHz in the Fourier transform mode. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal. FD and EI mass spectra were recorded on a Finnigan 8230 mass spectrometer operating in the positive-ion mode. Melting points were determined with use of analytically pure samples, which were sealed in nitrogen-purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Chemische Institute der Universität Heidelberg.

(A) General Procedure for the Synthesis of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag^IX$ (3) by Reaction of 1 with 2. To 0.5 g (0.97 mmol) of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2$ (1)[3] dissolved in 150 mL of acetone at 25 °C was added an equimolar amount of $(1/n)[AgX]_n$ (X = Cl, **2a**; X = CN, **2b**; X = SCN, **2c**; X = NO_2, **2d**; X = ClO_4, **2e**) in one portion. The reaction mixture was stirred at reflux for 3 h; it gradually turned deep yellow. After the mixture was cooled to 25 °C, the solvent was evaporated under high-vacuum, the resulting orange residue was extracted

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[8] (a) Macomber, D. W.; Rausch, M. D. *J. Am. Chem. Soc.* **1983**, *105*, 5325. (b) Alexsandrov, G. G.; Gol'ding, I. R.; Sterlin, S. R.; Sladkov, A. M.; Struchkov, Yu. T.; Garbuzova, I. A.; Alexanyan, V. T. *Izv. Akad. Nauk SSR, Ser. Khim.* **1980**, 2679.

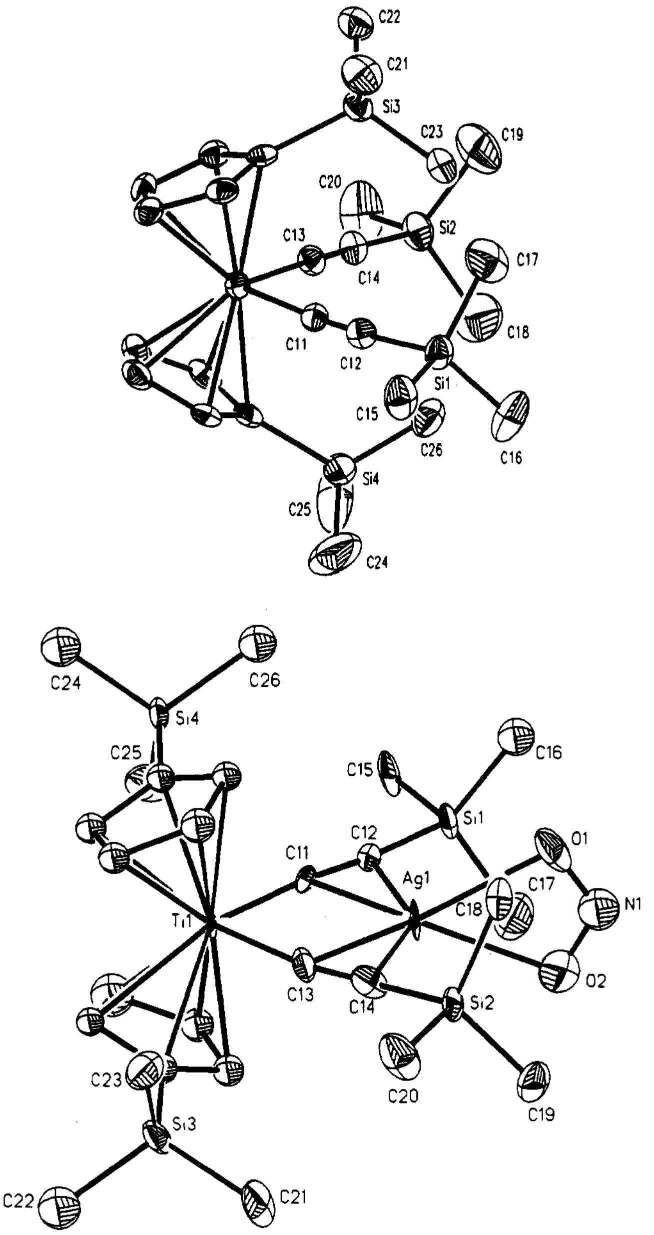

Figure 1. Molecular geometries and atom labeling schemes for 1 (top) and **3d** (bottom) (D1, D2: centroids of the cyclopentadienyl ligands). Important selected interatomic distances (Å) and angles (deg) are as follows. 1:[6] Ti–C11 2.124(5), Ti–C13 2.103(5), C11–C12 1.214(6), C13–C14 1.203(9), Ti–D1 2.06, Ti–D2 2.05, C12–Si1 1.838(5), C14–Si2 1.840(6); Ti–C11–C12 178.2(5), Ti–C13–C14 175.8(4), C11–C12–Si1 178.3(5), C13–C14–Si2 174.8(4), C11–Ti–C13 102.8(2), D1–Ti–D2 134.7. **3d**: Ti–Ag 3.16(1), Ti–C11 2.12(2), Ti–C13 2.10(2), C11–C12 1.26(2), C13–C14 1.27(3), C12–Si1 1.84(2), C14–Si2 1.84(2), Ag–C11/C12 2.29(2)/2.41(2), Ag–C13/C14 2.33(2)/2.43(2), Ag–O1 2.45(1), Ag–O2 2.39(1), O1–N1 1.23(3), O2–N1 1.23(3), Ti–D1 2.05, Ti–D2 2.08; Ti–C11–C12 171(2), Ti–C13–C14 170(2), C11–C12–Si1 170(2), C13–C14–Si2 171(2), Ag–O1–N1 95.5(9), Ag–O2–N1 98(1), O1–N1–O2 116(2), Ti–Ag–O1 151.7(9), Ti–Ag–O2 157.4(4), C11–Ti–C13 93.8(7), D1–Ti–D2 133.

with dichloromethane, and the extract was filtered through a pad of silica gel. Evaporation of dichloromethane under reduced pressure gave **3** as orange, air-stable, crystalline solids. Recrystallization from THF/*n*-pentane at −30 °C gave pure crystalline materials.

$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}AgCl$ (3a): yield 0.62 g (0.94 mmol, 97%); mp 203 °C dec. IR (CH_2Cl_2/CaF_2 cells): ν(C≡C) 1948 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.28 (s, 18 H, $SiMe_3$), 0.31 (s, 18 H, $SiMe_3$), 6.48 (m, 8 H, Cp). FD mass spectrum (CH_2Cl_2): molecular ion at *m/e* (relative intensity) 660 (17), M^+ − Cl 625 (26), M^+ − AgCl 516 (100). Anal. Calcd for $C_{26}H_{44}AgClSi_4Ti$: C, 47.30; H, 6.72; Cl, 5.37. Found: C, 47.01; H, 6.79; Cl, 5.42.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

Ti–C11	2.124(5)	Ti–D1[a]	2.06
Ti–C13	2.103(5)	Ti–D2[a]	2.05
C11–C12	1.214(6)	C12–Si1	1.838(5)
C13–C14	1.203(9)	C14–Si2	1.840(6)
Ti–C11–C12	178.2(5)	C13–C14–Si2	174.8(4)
Ti–C13–C14	175.8(4)	C11–Ti–C13	102.8(2)
C11–C12–Si1	178.3(5)	D1–Ti–D2[a]	134.7

[a] D1, D2: centroids of the cyclopentadienyl ligands.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) for 3d

Ti–Ag	3.16(1)	Ag–C13	2.33(2)
Ti–C11	2.12(2)	Ag–C14	2.43(2)
Ti–C13	2.10(2)	Ag–O1	2.45(1)
C11–C12	1.26(2)	Ag–O2	2.39(1)
C13–C14	1.27(3)	O1–N1	1.23(3)
C12–Si1	1.84(2)	O2–N1	1.23(3)
C14–Si2	1.84(2)	Ti–D1[a]	2.05
Ag–C11	2.29(2)	Ti–D2[a]	2.08
Ag1–C12	2.41(2)		
Ti–C11–C12	171(2)	O1–N1–O2	116(2)
Ti–C13–C14	1.70(2)	Ti–Ag–O1	151.7(9)
C11–C12–Si1	170(2)	Ti–Ag–O2	157.4(4)
C13–C14–Si2	171(2)	C11–Ti–C13	93.8(7)
Ag–O1–N1	95.5(9)	D1–Ti–D2[a]	133
Ag–O2–N1	98(1)		

[a] D1, D2: centroids of the cyclopentadienyl ligands.

$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}AgCN$ (3b): yield 0.57 g (0.87 mmol, 90%); mp 185 °C dec. IR (CH_2Cl_2/CaF_2 cells): ν(C≡N) 2126 cm^{-1} (s), ν(C≡C) 1944 cm^{-1} (m). ^1H NMR ($CDCl_3$): δ 0.25 (s, 18 H, $SiMe_3$), 0.37 (s, 18 H, $SiMe_3$), 6.19 (t, 4 H, J_{HH} = 2 Hz, Cp), 6.22 (t, 4 H, J_{HH} = 2 Hz, Cp). EI mass spectrum, *m/e*: M^+ − $SiMe_3$ 578 (2), M^+ − AgCN 516 (5), M^+ − $2SiMe_3$ 505 (4), M^+ − AgCN − $SiMe_3$ 444 (4), $(C_5H_4SiMe_3)_2TiC{\equiv}CSiMe_3^+$ 419 (80), $(C_5H_4SiMe_3)_2TiC_3^+$ 358 (19), $(C_5H_4SiMe_3)_2TiC_2^+$ 346 (12), $(C_5H_4SiMe_3)_2Ti^+$ 322 (39), $(C_5H_4SiMe_3)(C_5H_4)Ti^+$ 249 (7), $C_4(SiMe_3)_2^+$ 194 (18), $(C_5H_5)_2Ti^+$ 179 (100), $Ti(C_4SiMe_3)^+$ 169 (9), $SiMe_3^+$ 73 (41). Anal. Calcd for $C_{27}H_{44}AgNSi_4Ti$: C, 49.84; H, 6.82; N, 2.15. Found: C, 49.68; H, 6.84; N, 2.20.

$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}AgSCN$ (3c): yield 0.58 g (0.85 mmol, 88%); mp 108 °C dec. IR (CH_2Cl_2/CaF_2 cells): ν(C≡C) 1947 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.26 (s, 18 H, $SiMe_3$), 0.32 (s, 18 H, $SiMe_3$), 6.29 (t, 4 H, Cp, J_{HH} = 2 Hz), 6.31 (t, 4 H, Cp, J_{HH} = 2 Hz). FD mass spectrum (CH_2Cl_2), *m/e*: M^+ − SCN 625 (6), M^+ − AgSCN 516 (65), M^+ − SCN − $2SiMe_3$ 477 (100). Anal. Calcd for $C_{27}H_{44}AgNSSi_4Ti$: C, 47.49; H, 6.50; N, 2.05. Found: C, 46.96; H, 6.49; N, 2.12.

$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}AgNO_2$ (3d): yield 0.63 g (0.93 mmol, 97%); mp 108 °C dec. IR (CH_2Cl_2/CaF_2 cells): ν(C≡C) 1947 cm^{-1}. ^1H NMR (acetone-d_6): δ 0.14 (s, 18 H, $SiMe_3$), 0.28 (s, 18 H, $SiMe_3$), 6.49 (m, 8 H, Cp). FD mass spectrum (CH_2Cl_2): M^+ − NO_2 *m/e* 625. Anal. Calcd for $C_{26}H_{44}AgNO_2Si_4Ti$: C, 46.56; H, 6.61; N, 2.09. Found: C, 46.30; H, 6.79; N, 2.12.

$\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}AgClO_4$ (3e): yield 0.67 g (0.93 mmol, 96%); mp 148 °C dec. IR (CH_2Cl_2/CaF_2 cells): ν(C≡C) 1950 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.21 (s, 18 H, $SiMe_3$), 0.28 (s, 18 H, $SiMe_3$), 6.64 (t, 4 H, Cp, J_{HH} = 2 Hz), 6.74 (t, 4 H, Cp, J_{HH} = 2 Hz). Anal. Calcd for $C_{26}H_{44}AgClO_4Si_4Ti$: C, 43.12; H, 6.12. Found: C, 42.94; H, 6.12.

X-ray Structure Determinations of 1 and 3d. The structures of compounds 1 and 3d were determined from single-crystal

Table III. Crystallographic Parameters for 1 and 3d

	1	**3d**
formula	$C_{26}H_{44}Si_4Ti$	$C_{26}H_{44}AgNO_2Si_4Ti$
fw	516.87	670.76
cryst syst	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$
a (Å)	10.669(8)	17.00(2)
b (Å)	18.51(1)	24.37(3)
c (Å)	16.47(1)	20.71(2)
β (deg)	106.93(5)	90.05(9)
V (Å)	3111(4)	8515(2)
D_{calc} (g cm^{-3})	1.10	1.13
Z	4	8
cryst dimens (mm)	0.2 × 0.30 × 0.30	0.20 × 0.25 × 0.25
μ(Mo Kα) (cm^{-1})	11.7	11.7
radiation (λ (Å))	Mo Kα (0.710 69)	Mo Kα (0.710 69)
temp (K)	210	213
scan mode	ω scan	ω scan
scan range (deg)	2.0–45	2.0–45
scan speed (deg min^{-1})	$2.8 \leq \dot{\omega} \leq 29.3$	$2.8 \leq \dot{\omega} \leq 29.3$
bdgd/scan ratio	0.4	0.4
index range	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of unique data	4216	8110
no. of reflns no. collected [$F \geq 4\sigma(F)$]	3900	5648
R (%)	3.4	9.9
R_w (%)	3.2	9.2

X-ray diffraction data, which were collected using a Siemens R3m/V (Nicolet Syntex) diffractometer. Crystallographic data for **1** and **3d** are given in Table III.

The structures of **1** and **3d** were solved by direct methods (SHELXTL-PLUS: G. M. Sheldrick, University of Göttingen, 1986). An empirical absorption correction was applied. The carbon atoms of the cyclopentadienyl rings (C1–C10) were refined isotropically. All other heavy atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions, and their temperature factors were refined isotropically.

(B) Synthesis of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag^IX$ (3) by Reaction of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}FeCl_2$ (4) with $(1/n)[AgX]_n$. To 0.5 g (0.78 mmol) of $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}FeCl_2$ (**4**)[6] in 100 mL of THF was added a 2-fold excess of $(1/n)[AgX]_n$ (**2**) (X = Cl, **2a**; X = CN, **2b**; X = SCN, **2c**; X = NO_2, **2d**; X = ClO_4, **2e**) in one portion. The reaction mixture was stirred at 25 °C for 2 h. During this period, it slowly turned from deep purple to yellow. Appropriate workup similar to that used for the preparation described in section A gave **3a–e** in quantitative yields (for analytical and spectroscopic data see section A).

(C) Synthesis of $\{(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2\}Ag^IX$ (3b,c) by Reaction of 3a with 2b,c. To 0.5 g (0.76 mmol) of **3a** was added 1 equiv of AgCN (**2b**) (0.10 g) or AgSCN (**2c**) (0.13 g) in one portion at 25 °C. Workup similar to that described earlier yielded orange **3b** and **3c** in quantitative yields (for analytical and spectroscopic data see section A).

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Supplementary Material Available: Tables giving X-ray diffraction structure summaries, bond distances and angles, atomic coordinates and isotropic thermal parameters, and anisotropic thermal parameters, along with additional structural diagrams (14 pages).

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