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Organometallic π-tweezers incorporating pyrazine- and pyridine-based bridging units

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Abstract

Pyrazine- and pyridine-based π-conjugated σ-donor molecules, such as 4,4′-bipyridine, 1,2-di(4-pyridyl)ethylene, 3,5-dipyridyl-1,2,4-triazole, *N*,*N*′-bis(4-pyridylmethylidene)benzene-1,4-diamine, 2,5-di(pyridylmethylidene)cyclopentanone, 2,6-di(4-pyridylmethylidene)cyclohexanone (LL, **2a**–**2g**) can successfully be used to span heterobimetallic π-tweezer units of the type $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M]^+$ ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$; M = Cu, Ag). The thus accessible di-cationic species $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M{-}LL{-}M\{(Me_3SiC{\equiv}C\text{-}\mu\text{-}\sigma,\pi)_2[Ti]\}]^{2+}$ (**4**), which are formed via the formation of $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}M{-}LL]^+$ (**3**) complexes, can be isolated in yields between 66% and 99%.

However, when $C_5H_4N{-}CH{=}CH{-}C_6H_4{-}CH{=}CH{-}NC_5H_4$ (**5a**) and $C_5H_4N{-}CH{=}N{-}C_6H_4{-}CH{=}CH{-}NC_5H_4$ (**5b**), respectively, are reacted with $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}AgBF_4$ (**1c**) in a 1:1 molar ratio, then the silver(I) ion is released from the organometallic π-tweezer **1c** and coordination polymers $[AgBF_4\cdot\mathbf{5a}]_n$ (**6a**) and $[AgBF_4\cdot\mathbf{5b}]_n$ (**6b**) along with $[Ti](C{\equiv}CSiMe_3)_2$ (**7**) are formed in quantitative yield.

Keywords: Organometallic π-tweezers; Pyrazine; Pyridine; Oligopyridines; Titanium; Silver; Copper

1. Introduction

Recently, it could be shown that heterobimetallic organometallic π-tweezers of type $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CR)_2\}MX$ ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)_2Ti$, …; M = Cu, Ag; X = BF_4, ClO_4, PF_6; R = singly bound organic or organometallic ligand) [1] can successfully be used in the synthesis of (hetero)multimetallic assemblies in which the transition metals are bridged by π-conjugated organic or inorganic units [1,2]. Their electrochemical behaviour, with respect to intramolecular electron transfer, was reported as well [1,3]. Depending on the structural motif of the bridge and the nature of R electron-coupling between the transition metals is observed. For example, when $[Ti](C{\equiv}CFc)_2$ ($Fc = (\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$) is electrochemically or chemically oxidised, then cleavage of the titanium–carbon acetylide σ-bonds occurs and the all-carbon butadiyne $FcC{\equiv}C{-}C{\equiv}CFc$ is formed [4,5]. The latter molecule shows two reversible waves indicating two independent Fc moieties to be present. Similar observations have been made with $[Ti](C{\equiv}C{-}C{\equiv}CFc)_2$ and isostructural ruthenium species [6]. However, when the alkyne entities in $[Ti](C{\equiv}CFc)_2$ are chelate-bound to a low-valent transition metal building block, such as CuX, AgX (X = singly bound inorganic or organic group), Ni(CO), $Pd(PPh_3)_3$, etc., the latter species are significantly more stable towards oxidation processes [3]. In $[Pt](C{\equiv}CFc)_2$

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and $\{[\mathrm{Pt}](\mathrm{C}{\equiv}\mathrm{CFc})_2\}\mathrm{MX}$ complexes $\{[\mathrm{Pt}] = (\mathrm{bipy})\mathrm{Pt}, (\mathrm{Ph_3P})_2\mathrm{Pt}, \ldots;$ bipy = 2,2′-bipyridin], where stronger metal–carbon σ-bonds are typical, electron transfer between the two Fc units along $\mathrm{Pt(C{\equiv}C)_2}$ is characteristic [7].

In view of our earlier studies in this area we set-out to prepare multimetallic species in which organometallic π-tweezer units are bridged by pyrazine- or pyridine-based organic π-conjugated units.

Here we report on the synthesis of cationic $[\{[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{M{-}LL}]^+$ and $[\{[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{M{-}LL{-}M}\{(\mathrm{Me_3SiC{\equiv}C})_2[\mathrm{Ti}]\}]^{2+}$ species in which $[\{[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{M}]^+$ entities are spanned by LL bridges.

2. Results and discussion

Treatment of $\{[\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-}\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{AgClO_4}$ (**1b**) ($[\mathrm{Ti}] = (\eta^5\text{-}\mathrm{C_5H_4SiMe_3})_2\mathrm{Ti}$) with one equivalent of LL (LL = *p*yrazine, pz, **2a**; 4,4′-bipyridine, bipy, **2b**; 1,2-di(4-pyridyl)ethylene, dpe, **2c**) produces $[\{[\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-}\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{Ag\text{-}LL}]\mathrm{ClO_4}$ (LL = pz, **3a**; = bipy, **3b**; = dpe, **3c**) in tetrahydrofuran at 25 °C (Scheme 1) [8]. Subsequent reaction of **3a**–**3c** with **1b** in a 1:1 molar ratio under similar reaction conditions gives the tetra-nuclear heterobimetallic species $[\{[\mathrm{Ti}](\mu\text{-}\sigma,\pi\text{-}\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{Ag\text{-}LL\text{-}Ag}\{(\mathrm{Me_3SiC{\equiv}C}\text{-}\mu\text{-}\sigma,\pi)_2[\mathrm{Ti}]\}](\mathrm{ClO_4})_2$ (LL = pz, **4a**; = bipy, **4b**; = dpe, **4c**) in excellent yield (Scheme 1). The latter transition metal complexes in which two organometallic π-tweezer entities are bridged by LL units are also accessible, when **1b** is reacted with **2a**–**2c** in the ratio of 2:1 (Scheme 1). The yield is somewhat higher, when compared to the stepwise reaction of **1** with **2** and **3** with **1** (vide supra).

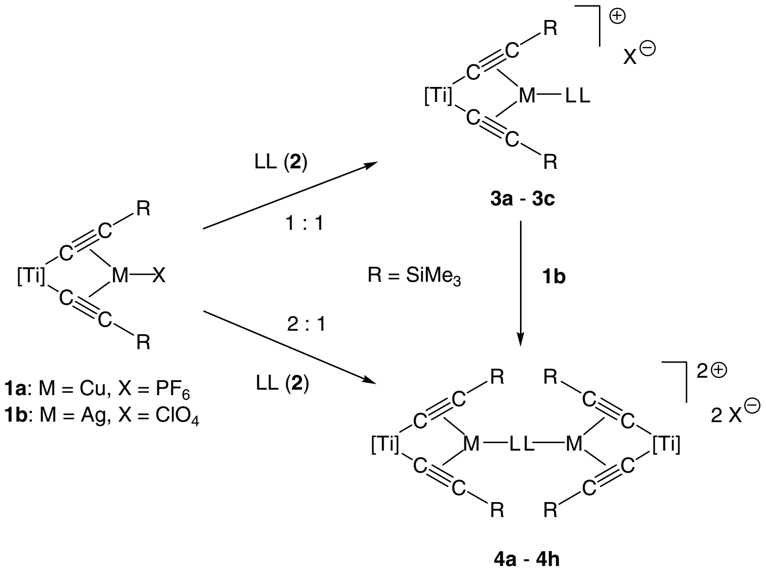
The straightforward synthesis of **4a**–**4c** by reacting **1b** with **2a**–**2c** can successfully be transferred to LL molecules, such as 3,5-dipyridyl-1,2,4-triazole (dpta, **2d**), (*E*,*E*)-*N*,*N*′-bis (4-pyridylmethylidene)benzene-1,4-diamine (bpmbd, **2e**), (*E*,*E*)-2,5-di(pyridylmethylidene)cyclopentanone (dpmcp, **2f**) or 2,6-*d*i(4-*p*yridyl*m*ethylidene) *c*yclo*h*exanone (dpmch, **2g**). The thus obtained $\mathrm{Ti_2Ag_2}$ (**4e**–**4h**) and $\mathrm{Ti_2Cu_2}$ (**4d**) complexes are formed in yields between 66% and 99% (Table 1).

After appropriate work-up, complexes **3** and **4** can be isolated as orange to dark brown solids, which are soluble in polar organic solvents, such as tetrahydrofuran, diethyl ether and dichloromethane. While **3**, **4e** and **4h** gradually decompose in the solid-state during heating,

Table 1
Synthesis of **3** and **4**

Compounds	LL	M	X	Yield[a] (%)
3a	pz	Ag	$\mathrm{ClO_4}$	90 [9]
3b	bipy	Ag	$\mathrm{ClO_4}$	84
3c	dpe	Ag	$\mathrm{ClO_4}$	89
4a	pz	Ag	$\mathrm{ClO_4}$	98
4b	bipy	Ag	$\mathrm{ClO_4}$	99
4c	dpe	Ag	$\mathrm{ClO_4}$	80
4d	dpe	Cu	$\mathrm{PF_6}$	75
4e	dpta	Ag	$\mathrm{ClO_4}$	70
4f	bpmbd	Ag	$\mathrm{ClO_4}$	78
4g	bpmcp	Ag	$\mathrm{ClO_4}$	66
4h	bpmch	Ag	$\mathrm{ClO_4}$	75

[a] Based on **1**.

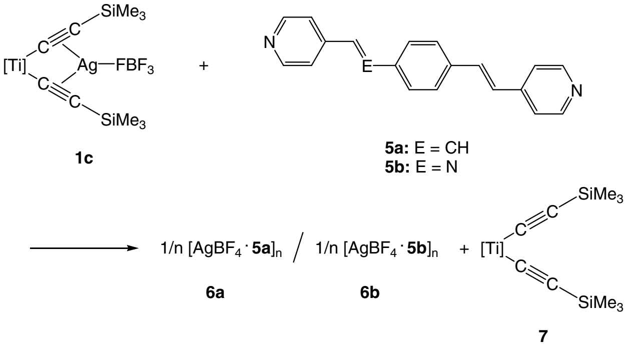


Scheme 1. Synthesis of **3** and **4** by the reaction of **1** with **2** (ratios 1:1 and 2:1) and **3** with **1b**.

all other species show the tendency to explode and hence, care must be taken during heating.

Furthermore, it is advisable to run all reactions (Scheme 1) in the dark, since otherwise slow decomposition of **3** and **4** may take place. On liberation of [Ti](C≡CSiMe$_3$)$_2$ and LL the formation of elemental silver is observed.

To extend the reaction protocol depicted in Scheme 1 to (*E*,*E*)-*N*,*N*′-bis(pyridylethylene) benzene (bpeb, **5a**) and (*E*,*E*)-4-(2-(4-pyridyl)ethylene)-pyridine-4-yl-methylidenephenylamine (pepmpa, **5b**) we treated **5a** and **5b** with {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgBF$_4$ (**1c**) under similar reaction conditions (vide supra). To our surprise the heterobimetallic titanium-tweezer molecule released the alkyne-bound silver(I) ion to give coordination polymers [AgBF$_4$·**5a**]$_n$ (**6a**) and [AgBF$_4$·**5b**]$_n$ (**6b**) along with the free π-tweezer [Ti](C≡CSiMe$_3$)$_2$ (**7**) (Eq. (1)).



(1)

During the course of the reaction, coordination polymers **6a** and **6b** precipitate from the reaction mixture. The preparation and characterisation of **6a** and **6b** was recently reported [9]. Slow diffusion of solutions of **5a** or **5b** in dichloromethane and silver(I) tetrafluoroborate in acetonitrile in the ratio of 2:1 produces **6a** or **6b**, respectively [10].

As shown in Eq. (1) complex **1c** can be used as template for the synthesis of coordination polymers, since **1c** smoothly releases the group-11 metal ion silver upon treatment with **5a** or **5b**, respectively. The same result is obtained, when a heterobimetallic titanium-silver perchlorate tweezer molecule is used. The formation of **6a** and **6b** takes presumable place *via* the intermediate formed Lewis-base adduct {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag(BF$_4$) (LL). Similar species could recently be isolated for other two-electron Lewis-base donor ligands, for example, phosphines, nitriles and amines [11].

Complexes **3** and **4** were fully characterised by elemental analysis, IR, ^{1}H and ^{13}C{^{1}H} NMRspectroscopy, while coordination polymers **6a** and **6b** were characterised by means of IR spectroscopic studies and elemental analysis, and compared with authentic samples of **6a** and **6b**. [9] X-ray powder diffraction analysis of the latter coordination polymers indicate that they are crystalline materials with similar main reflection sets [9].

The IR spectra of **3** and **4** exhibit characteristic $\nu_{C\equiv C}$ vibrations at ca. 1950 cm^{-1} for the appropriate silver(I) π-tweezer system, while **4d**, where a copper(I) ion is present, shows its C≡C stretching vibration at 1917 cm^{-1}, indicating that the Ag–LL entities are weaker coordinated by the TiC≡CSi units then the respective Cu–LL moieties. This behaviour is typical in organometallic π-tweezer chemistry [1]. From IR spectroscopic studies it also can be concluded that the perchlorate anion in **3** and **4** are of *non*-coordinating character, with exception of **3a** and **4a**. Only one sharp absorption is found at ca. 1100 cm^{-1}, which is characteristic for ClO$_4{}^-$ counter-ions [11]. The same observation is made for PF$_6{}^-$ (ν_{PF} = 835 cm^{-1}) present in **4d**.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **3** and **4** are well-defined and comprise of sharp resonance signals, with exception of **3**, where only broad signals are observed. This is most probably attributed to the silver(I) monohapto-bound ligand LL. Variable temperature NMR measurements did not significantly effect the shape of the resonance signals. In **4**, where the LL units symmetrically span two [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M]$^+$ building blocks, sharp resonance signals are observed for the aromatic, vinylic and aliphatic hydrogen atoms of the corresponding ligands LL and the Me$_3$Si and C$_5$H$_4$ groups. The Me$_3$Si entities of the cyclopentadienyl and alkynyl ligands of the organometallic π-tweezer part resonate at ca. 0.15 and 0.3 ppm. For the cyclopentadienyl ring protons two pseudo-triplets (AA′ BB′ pattern) are found at ca. 6.5 and 6.8 ppm with coupling constants J_{HH} between 2.0 and 2.4 Hz.

The ^{13}C{^{1}H} NMR spectra of all new synthesised complexes **3** and **4** show the expected resonance signals for the organic groups present (Me$_3$Si, C$_5$H$_4$, C≡C and LL).

3. Conclusion

A straightforward synthesis of a variety of tetra-nuclear heterobimetallic complexes of type [{[Ti](μ-σ, π-C≡CSiMe$_3$)$_2$}M—LL—M{(μ-σ, π-C≡CSiMe$_3$)$_2$[Ti]}]$^{2+}$ via the formation of [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}M—LL]$^+$ species (M = Cu, Ag; LL = pyrazine- and pyridine-based organic π-systems) is reported. In the latter complexes the two organometallic π-tweezer parts [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Ag]$^+$ are spanned by organic π-conjugated bridging units via the formation of dative nitrogen-silver bonds. Furthermore, it was found that depending on the nature of the bridging ligands LL (length, donor-capacity, etc.) coordination polymers of composition [AgBF$_4$·LL]$_n$ (LL = C$_5$H$_4$N—CH=CH—C$_6$H$_4$—CH=CH—C$_5$H$_4$N, C$_5$H$_4$N—CH=N—C$_6$H$_4$—CH=CH—C$_5$H$_4$N) are formed. This shows that the appropriate titanium-silver starting materials {[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgX (X = BF$_4$,

ClO_4) (**1**) can act as templates for the subsequent release of the silver(I) ion by the linear exo-bidentate bis-pyridine molecules LL (**5a**,**5b**). This reaction behaviour gives a straightforward entry into supramolecular chemistry by means of molecular recognition. Coordination polymers based on organic π-conjugated pyridine ligands (LL) and transition metal salts are accessible.

4. Experimental

4.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen; H_2O: molecular sieve 4 Å, Roth) using standard Schlenk techniques. Tetrahydrofuran and diethyl ether were purified and tried by distillation from sodium/benzophenone ketyl; petroleum ether was purified by distillation from calcium hydride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer Spectrum 1000. ^1H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 62.860 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal (^1H NMR, d^6 acetone, $\delta = 2.05$; $^{13}C\{^1H\}$ NMR, d^6 acetone, $\delta = 29.84$ (CH_3), 206.26 (CO)). Melting points were determined using analytically pure samples, sealed off in nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Institute of Organic Chemistry, Universität Heidelberg and partly by the Institute of Organic Chemistry, Chemnitz, University of Technology.

4.2. General remarks

Compounds $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Cu(N{\equiv}C\text{-}Me)]PF_6$ (**1a**), $\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}AgClO_4$ (**1b**) and $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}AgBF_4$ (**1c**) were prepared according to published procedures [1,12]. Compounds **2d**–**2g**, **5a** and **5b** were synthesised at the Chemistry Department of Moscow State University by M. Kovalkina, V. Nuriev and A. Chernikov [9]. All other chemicals were purchased by commercial suppliers and were used without further purification.

5. Synthesis of 3b

$\{[Ti](\mu\text{-}\sigma,\pi\text{-}C{\equiv}CSiMe_3)_2\}Ag(ClO_4)$ (**1b**) (338 mg, 0.47 mmol) is dissolved in 30 mL of tetrahydrofuran at 25 °C. To this solution one equivalent of **2c** (85 mg, 8.5 mmol) is added in one portion. After stirring the reaction mixture for 4 h, all volatiles are removed in oil-pump vacuum. The obtained dark brown residue is washed twice with 10 mL portions of petroleum ether to give analytical pure **3b** as a brownish-green solid. Yield: 375 mg (0.414 mmol, 89% based on **1b**).

M.p. 210 °C (decomp.). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1605 (s), $\nu_{C\equiv C}$ 1953 (m), $\nu_{O\text{–}Cl}$ 1080 (vs). ^1H NMR [1] (d_6 acetone): δ 0.10 (s, 18H, $SiMe_3$), 0.36 (s, 18H, $SiMe_3$), 6.67 (pt, $J_{HH} = 2.4$ Hz, 4H, C_5H_4), 6.78 (pt, $J_{HH} = 2.4$ Hz, 4H, C_5H_4), 7.76 (s, 2H, dpe), 7.9 (m, 4H, dpe), 8.84 (dd, $J_{HH} = 4.8$ Hz, $J_{HH} = 1.5$ Hz, 4H, dpe). $^{13}C\{^1H\}$ NMR [1] (d_6 acetone): δ 1.0 ($SiMe_3$), 1.2 ($SiMe_3$), 118.2 (CH/C_5H_4), 120.5 (CH/C_5H_4), 123.1 (dpe), 127.7 ($^iC/C_5H_4$), 132.1 (dpe), 138.9 ($C{\equiv}CSi$), 146.2 (dpe), 152.4 (dpe), 154.5 ($C{\equiv}CTi$). *Anal.* Calc. for $C_{38}H_{54}AgClN_2O_4Si_4Ti$ (906.33) C, 50.35; H, 6.00; N, 3.09. Found: C, 50.00; H, 5.15; N, 3.36%. [1]

6. Synthesis of 4a

400 mg (0.55 mmol) of **1b** and 22 mg (0.28 mmol) of pz (**2a**) are dissolved in 80 mL of tetrahydrofuran. This reaction mixture is stirred at 25 °C for 4 h. Afterwards all volatile materials are removed in oil-pump vacuum and the residue is washed twice with 20 mL of petroleum ether. A orange coloured solid is obtained. Yield: 415 mg (0.27 mmol, 98% based on **2a**).

M.p. 203 °C (decomp., explosive). IR [KBr, cm^{-1}]: $\nu_{C\equiv C}$ 1957 (w), $\nu_{O\text{–}Cl}$ 1112 (s). ^1H NMR (d_6 acetone): δ 0.15 (s, 36H, $SiMe_3$), 0.30 (s, 36 H, $SiMe_3$), 6.64 (pt, $J_{HH} = 2.3$ Hz, 8H, C_5H_4), 6.78 (pt, $J_{HH} = 2.3$ Hz, 8H, C_5H_4), 9.06 (s, 4H, pz). $^{13}C\{^1H\}$ NMR (d_6 acetone): δ 0.2 ($SiMe_3$), 0.5 ($SiMe_3$), 119.0 (CH/C_5H_4), 120.9 (CH/C_5H_4), 128.4 ($^iC/C_5H_4$), 139.8 ($C{\equiv}CSi$), 147.7 (CH, pz), 152.9 ($C{\equiv}CTi$). *Anal.* Calc. for $C_{56}H_{92}Ag_2Cl_2N_2O_8Si_8Ti_2$ (1528.44) C, 44.01; H, 6.07; N, 1.83. Found: C, 43.95; H, 5.98; N, 1.74%.

7. Synthesis of 4b

In a similar manner to the preparation of **4a**, 400 mg (0.55 mmol) of **1b** and 43 mg (0.28 mmol) of 4,4′-bipy are reacted in 80 mL of tetrahydrofuran. After appropriate work-up, complex **4b** can be isolated as a orange coloured solid. Yield: 450 mg (0.28 mmol, 99% based on 4,4′-bipyridine).

M.p. 194 °C (decomp.). IR [KBr, cm^{-1}]: $\nu_{C\equiv C}$ 1951 (w), $\nu_{O\text{–}Cl}$ 1110 (s). ^1H NMR (d_6 acetone): δ 0.08 (s, 36H, $SiMe_3$), 0.32 (s, 36H, $SiMe_3$), 6.64 (pt, $J_{HH} = 2.3$ Hz, 8H, C_5H_4), 6.76 (pt, $J_{HH} = 2.3$ Hz, 8H, C_5H_4),

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[1] Broad signals are observed.

8.26 (d, J_{HH} = 2.3 Hz, 4H, bipy), 9.06 (d, J_{HH} = 2.3 Hz, 4H, bipy). $^{13}C\{^1H\}$ NMR (d_6 acetone): δ 0.2 ($SiMe_3$), 0.4 ($SiMe_3$), 118.5 (CH/C_5H_4), 120.7 (CH/C_5H_4), 123.9 (CH/bipy), 127.8 ($^iC/C_5H_4$), 139.0 (d, $J_{109Ag-13C}$ = 5.2 Hz, C≡*C*Si), 147.0 (^{i}C/bipy), 153.6 (CH/bipy), 154.2 (d, $J_{109Ag-13C}$ = 14.3 Hz, C≡*C*Ti). *Anal.* Calc. for $C_{62}H_{96}Ag_2Cl_2N_2O_8Si_8Ti_2$ (1604.54) C, 46.41; H, 6.03; N, 1.75. Found: C, 45.66; H, 6.00; N, 1.82%.

8. Synthesis of 4c

{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgClO$_4$ (**1b**) (166 mg, 0.23 mmol) is dissolved in 30 mL of tetrahydrofuran and 22 mg (0.12 mmol) of dpe (**2c**) is added in one portion at 25 °C. Stirring is continued for 4 h. Afterwards the reaction mixture is filtrated through a pad of Celite and all volatiles are removed in oil-pump vacuum. The remaining solid is three times washed with 5 mL portions of petroleum ether. The obtained brown solid is dried in oil-pump vacuum for 24 h. Yield: 150 mg (0.092 mmol, 80% based on **1b**).

M.p. 230 °C (decomp., explosive). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1605 (s), $\nu_{C\equiv C}$ 1952 (m), ν_{O-Cl} 1084 (vs). ^1H NMR (d_6 acetone): δ 0.13 (s, 36H, $SiMe_3$), 0.36 (s, 36H, $SiMe_3$), 6.68 (pt, J_{HH} = 2.2 Hz, 8H, C_5H_4), 6.79 (pt, J_{HH} = 2.2 Hz, 8H, C_5H_4), 7.9 (bs, 2H, dpe), 8.95 (dd, J_{HH} = 4.9 Hz, J_{HH} = 1.5 Hz, 4 H, dpe), 9.10 (dd, J_{HH} = 4.9 Hz, J_{HH} = 1.5 Hz, 4H, dpe). $^{13}C\{^1H\}$ NMR (d_6 acetone): δ 1.0 ($SiMe_3$), 1.3 ($SiMe_3$), 118.4 (CH/C_5H_4), 120.5 (CH/C_5H_4), 124.1 (dpe), 127.8 ($^iC/C_5H_4$), 132.8 (dpe), 139.0 (C≡*C*Si), 147.4 (dpe), 152.9 (dpe), 153.8 (C≡*C*Ti). *Anal.* Calc. for $C_{64}H_{98}Ag_2Cl_2N_2O_8Si_8Ti_2$ (1630.53) C, 47.14; H, 6.06; N, 1.70. Found: C, 46.93; H, 6.19; N, 1.30%.

9. Synthesis of 4d

Complex **4d** can be synthesised as described earlier for the preparation of **4c**. In this respect [{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}Cu(CH$_3$C≡N)]PF$_6$ (**1a**) (166 mg, 0.21 mmol) is reacted with dpe (**2c**) (17.5 mg, 0.09 mmol). After appropriate work-up, **4d** can be isolated as a pale brown solid in 115 mg yield (0.07 mmol, 75% based on **1a**).

M.p. 190 °C (decomp., explosive). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1668 (s), 1609 (s), 1508 (s); $\nu_{C\equiv C}$ 1917 (s); ν_{P-F} 835 (vs). ^1H NMR (d_6 acetone): δ 0.15 (s, 36H, $SiMe_3$), 0.35 (s, 36H, $SiMe_3$), 6.58 (pt, J_{HH} = 2.1 Hz, 8H, C_5H_4), 6.58 (pt, J_{HH} = 2.1 Hz, 8H, C_5H_4), 8.0 (bs, 2H, dpe), 8.2 (bs, 4H, dpe), 9.0 (bs, 4H, dpe). $^{13}C\{^1H\}$ NMR (d_6 acetone): δ 0.1 ($SiMe_3$), 1.0 ($SiMe_3$), 116.7 (CH/C_5H_4), 118.8 (CH/C_5H_4), 124.7 (dpe), 127.2 ($^iC/C_5H_4$), 132.8 (dpe), 136.1 (C≡*C*Si), 147.6 (dpe), 152.6 (dpe), 167.3 (C≡*C*Ti). *Anal.* Calc. for $C_{64}H_{98}Cu_2F_{12}N_2P_2Si_8Ti_2$ (1550.05) C, 47.05; H, 6.05; N, 1.72. Found: C, 46.98; H, 6.43; N, 2.17%.

10. Synthesis of 4e

Complex **4e** can be prepared as described earlier for the synthesis of **4c**. **1b**: 109 mg (0.15 mmol), **2d**: 17 mg (0.08 mmol). Appropriate work-up affords 80 mg (0.05 mmol, 70% based on **1b**) of **4e** as a brown-green solid.

M.p. 156 °C (decomp.). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1610 (s), 1550 (s); $\nu_{C\equiv C}$ 1952 (s); ν_{O-Cl} 1100 (vs). ^1H NMR (d_6 acetone): δ 0.00 (s, 36H, $SiMe_3$), 0.26 (s, 36H, $SiMe_3$), 4.47 (s, 1H, dpta), 6.43 (pt, J_{HH} = 2.4 Hz, 8H, C_5H_4), 6.55 (pt, J_{HH} = 2.4 Hz, 8H, C_5H_4), 8.33 (d, J_{HH} = 5.6 Hz, 4H, dpta), 8.93 (d, J_{HH} = 5.6 Hz, 4H, dpta). *Anal.* Calc. for $C_{66}H_{99}Ag_2Cl_2N_5O_8Si_8Ti_2$ (1697.72) C, 46.69; H, 5.88; N, 4.12. Found: C, 47.06; H, 6.14; N, 5.60%. *Notice: Due to rapid decomposition of* **4e** *in solution, no* $^{13}C\{^1$ıtH$\}$ *NMR spectrum could be obtained.*

11. Synthesis of 4f

As outlined earlier for the synthesis of **4c**, complex **4f** can be prepared by the reaction of **1b** (104 mg, 0.14 mmol) with bpmbd (**2e**) (21 mg, 0.07 mmol). After appropriate work-up complex **4f** is obtained as a brown solid in 97 mg (0.056 mmol, 78% based on **1b**) yield.

M.p. 204 °C (decomp., explosive). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1610 (s), 1641 (s), 1550 (s); $\nu_{C\equiv C}$ 1952 (s); ν_{O-Cl} 1100 (s). ^1H NMR (d_6 acetone): δ 0.14 (s, 36H, $SiMe_3$), 0.28 (s, 36H, $SiMe_3$), 6.39 (pt, J_{HH} = 2.4 Hz, 8H, C_5H_4), 6.50 (pt, J_{HH} = 2.4 Hz, 8H, C_5H_4), 7.42 (s, 4H, bpmbd), 8.02 (d, J_{HH} = 5.0 Hz, 4H, bpmbd), 8.62 (s, 2 H, bpmbd), 8.91 (d, J_{HH} = 5.0 Hz, 4H, bpmbd). $^{13}C\{^1H\}$ NMR (d_6 acetone): δ 0.4 ($SiMe_3$), 0.7 ($SiMe_3$), 117.5 (CH/C_5H_4), 120.6 (CH/C_5H_4), 123.1 (bpmbd), 124.5 (bpmbd), 126.5 ($^iC/C_5H_4$), 141.3 (C≡*C*Si), 144.1 (bpmbd), 151.8 (bpmbd), 152.9 (bpmbd), 156.8 (bpmbd).[2] *Anal.* Calc. for $C_{70}H_{102}Ag_2Cl_2N_4O_8Si_8Ti_2$ (1734.75) C, 48.47; H, 5.93; N, 3.23. Found: C, 48.94; H, 5.61; N, 3.34%.

12. Synthesis of 4g

Complex **4g** can be prepared in an analogues manner as described earlier (synthesis of **4c**). The reaction of **1b** (94 mg, 0.13 mmol) with bpmcp (**2f**) (17.4 mg, 0.07 mmol) gives, after appropriate work-up, the title

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[2] The resonance signal for C≡*C* Ti could not be detected under the measurement conditions used.

complex in 74 mg yield (0.043 mmol, 66% based on **1b**) as a brown solid.

M.p. 204 °C (decomp., explosive). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1632 (bs), $\nu_{C\equiv C}$ 1948 (s), ν_{O-Cl} 1100 (s). ^{1}H NMR (d$_6$ acetone): δ 0.14 (s, 36H, SiMe$_3$), 0.25 (s, 36H, SiMe$_3$), 3.27 (s, 4H, dpmcp), 6.39 (pt, J_{HH} = 2.4 Hz, 8H, C$_5$H$_4$), 6.51 (pt, J_{HH} = 2.4 Hz, 8H, C$_5$H$_4$), 7.47 (s, 2H, dpmcp), 7.74 (d, J_{HH} = 6.3 Hz, 4H, dpmcp), 8.83 (d, J_{HH} = 6.3 Hz, 4H, dpmcp). ^{13}C{^{1}H} NMR (d$_6$ acetone): δ 0.3 (SiMe$_3$), 0.6 (SiMe$_3$), 26.9 (dpmcp), 117.5 (CH/C$_5$H$_4$), 120.6 (CH/C$_5$H$_4$), 126.3 (dpmcp), 126.6 (^{i}C/C$_5$H$_4$), 130.2 (dpmcp), 141.3 (C≡*C*Si), 143.8 (dpmcp), 145.7 (dpmcp), 152.6 (C≡*C*Ti), 195.5 (dpmcp). *Anal.* Calc. for $C_{69}H_{102}Ag_2Cl_2N_2O_9Si_8Ti_2$ (1710.67) C, 48.45; H, 6.00; N, 1.64. Found: C, 47.69; H, 6.30; N, 1.02%.

13. Synthesis of 4h

Complex **1b** (151 mg, 0.2 mmol) is reacted in an analogues manner to **4c** with dpmch (**2g**) (29.5 mg, 0.11 mmol) to produce **4h** as a brown solid. Yield: 126 mg (0.073 mmol, 75% based on **1b**).

M.p. 185 °C (decomp.). IR [NaCl, cm^{-1}]: $\nu_{C=N}$ 1642 (s), 1610 (s), 1550 (s); $\nu_{C\equiv C}$ 1953 (s); ν_{O-Cl} 1100 (vs). ^{1}H NMR (d$_6$ acetone): δ 0.09 (s, 36H, SiMe$_3$), 0.31 (s, 36H, SiMe$_3$), 1.82 (bs, 2H, dpmch), 6.63 (pt, J_{HH} = 2.2 Hz, 8H, C$_5$H$_4$), 6.84 (pt, J_{HH} = 2.2 Hz, 8H, C$_5$H$_4$), 7.77 (s, 2H, dpmch), 8.0 (m, 4H, dpmch), 9.05 (d, J_{HH} = 5.0 Hz, 4H, dpmch). ^{13}C{^{1}H} NMR (d$_6$ acetone): δ 1.0 (SiMe$_3$), 1.2 (SiMe$_3$), 22.4 (dpmch), 27.1 (dpmch), 118.3 (CH/C$_5$H$_4$), 120.6 (CH/C$_5$H$_4$), 126.7 (dpmch), 127.6 (^{i}C/C$_5$H$_4$), 132.6 (dpmch), 140.0 (dpmch), 142.2 (C≡*C*Si), 147.2 (dpmch), 152.5 (dpmch), 153.8 (C≡*C*Ti), 188.5 (dpmch). *Anal.* Calc. for $C_{70}H_{104}Ag_2Cl_2N_2O_9Si_8Ti_2$ (1724.75) C, 48.75; H, 6.08; N, 1.62. Found: C, 47.80; H, 6.39; N, 1.10%.

14. Synthesis of 6a and 6b

{[Ti](μ-σ,π-C≡CSiMe$_3$)$_2$}AgBF$_4$ (**1c**) (200 mg, 0.28 mmol) is reacted with equimolar amounts of **5a** (79.5 mg) or **5b** (80 mg) in 50 mL of tetrahydrofuran at 25 °C, whereby **6a** and **6b** precipitates. After 12 h of stirring at this temperature the supernatant solution is decanted from the solid. The solid is twice washed with petroleum ether (20 mL). From the liquid phase all volatiles are removed in oil-pump vacuum to give [Ti](C≡CSiMe$_3$)$_2$ (**7**) as a yellow solid. Yield: **6a**: 130 mg (0.27 mmol, 98% based on **1b**); **6b**: 128 mg (0.27 mmol, 95% based on **1b**); **7**: 145 mg (quantitative).

Compounds **6a**, **6b** and **7** have been characterised by elemental analysis, IR (**6a**, **6b**, **7**), ^{1}H and ^{13}C{^{1}H} NMR spectroscopy (**7**) [1,9,13].

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