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An easy entry to novel early–late oligonuclear transition metal complexes containing π-conjugated systems

Stephan Back [a], Wolfgang Frosch [a], Ignacio del Río [b], Gerard van Koten [b], Heinrich Lang [a,*]

[a] *Technische Universität Chemnitz, Institut für Chemie, Lehrstuhl Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany*

[b] *Debye Institute, Department of Metal-Mediated Synthesis, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

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Abstract

Heterotrinuclear Ti–Cu–Ru (**5**) and heterotetranuclear Ti–Cu–Pt–Fe (**7**) containing complexes are accessible by using $\{[Ti](C{\equiv}C^tBu)_2\}CuMe$ (**1**) ($[Ti]=(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$) as key molecule; in **5** and **7**, the corresponding early and late transition metal atoms are linked by π-conjugated organic moieties.

Keywords: Heterometallic complexes; Conjugated ligand complexes; π-Tweezer complexes; Early–late complexes; Transition metal complexes; Oligonuclear complexes

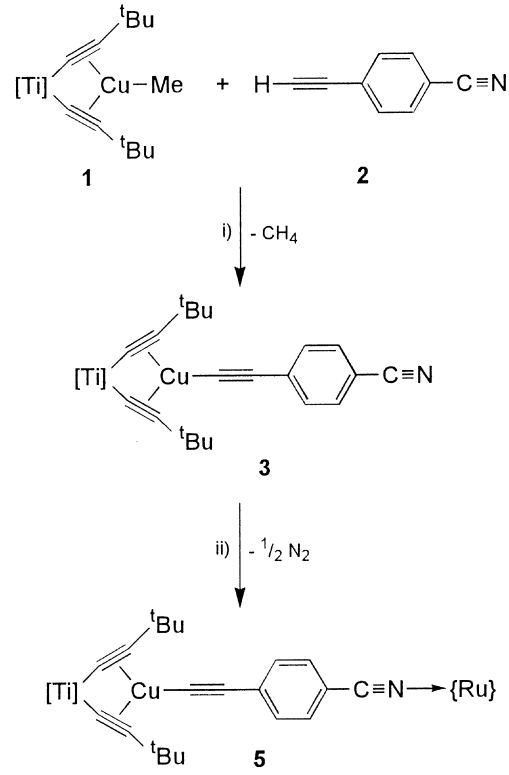
1. Introduction

Since the early work of Creutz and Taube (see Ref. [1]), there has been a growing interest in the synthesis, chemical and physical properties of transition metal (TM) complexes in which a π-conjugated organic ligand spans the corresponding TM atoms [2–6]. Besides homometallic complexes [7–10], a number of heterometallic species, which mainly feature late TM ions, are also known [11–16]. In contrast, little is known about early–late TM complexes [17–19]. We report in this communication, the preparation of TM complexes of the latter type containing up to four different TM centres.

2. Results and discussion

A key step in the synthesis of heteronuclear TM complexes in which the corresponding early and/or late TM centres are spanned by π-conjugated organic ligands, is the reaction of monomeric alkyne-stabilised CuMe, $\{[Ti](C{\equiv}C^tBu)_2\}$-CuMe (**1**) [20] ($[Ti]=(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$), with CH-acidic organic molecules. Thus, complex **1** reacted with an equimolar amount of $HC{\equiv}CC_6H_4CN$-4 (**2**) [21] at −70°C to yield the yellow Ti–Cu acetylide complex $\{[Ti](C{\equiv}C^tBu)_2\}CuC{\equiv}CC_6H_4CN$-4 (**3**) (Scheme 1).

The heterodinuclear complex **3** contains a CN group which can further coordinate. When **3** is treated with



Scheme 1. Preparation of complexes **3** and **5**. (i) 0°C, n-pentane; (ii) 1/2 $\{Ru\}N{\equiv}N\{Ru\}$, 0°C, THF.

* Corresponding author. Tel.: +49 371 531 1200; fax: +49 371 531 1833; e-mail: heinrich.lang@chemie.tu-chemnitz.de

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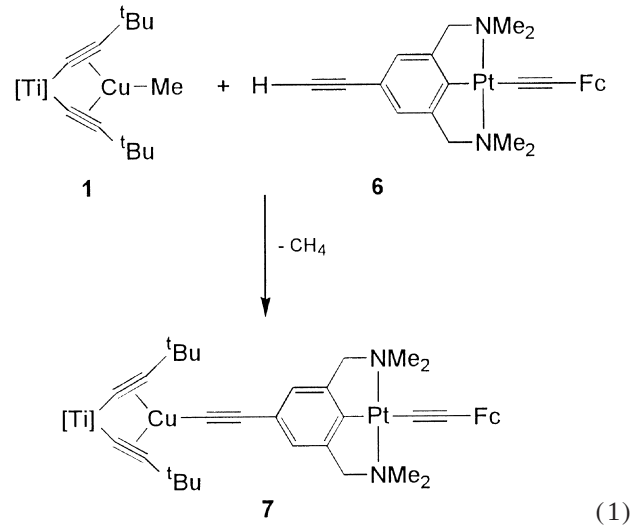
{Ru}N≡N{Ru} (**4**) ({Ru} = [η^3-mer-(2,6-{Me_2NCH_2}$_2$-C_5H_3N}$RuCl_2$]) [22] in molar ratio of 2:1 in THF at 0°C, N_2 is eliminated and heterotrinuclear **5** is formed (Scheme 1) [1].

An access to a heterotetranuclear complex is given by joining dinuclear **1** with the preformed late–late Pt–Fe organometallic acetylide HC≡C{Pt}C≡CFc (**6**) (HC≡C{Pt} = [Pt(C_6H_2{CH_2NMe_2}$_2$-2,6-{C≡CH}-4], Fc = (η^5-C_5H_4)-Fe(η^5-C_5H_5)) [23]. In THF at 0°C, the Ti–Cu–Pt–Fe complex {[Ti](C≡C^{t}Bu)$_2$}CuC≡C{Pt}C≡CFc (**7**) is obtained in almost quantitative yield accompanied by the loss of CH_4 (Eq. (1)) [2].



(1)

The heterometallic complexes **5** and **7** are less stable as compared to **1** [20], **3** or **6** [23].

The formation of **5** and **7** has been inferred through the IR spectroscopic data. The C≡N stretching vibration for **5** has been shifted to lower wavenumbers (2208 cm^{-1}) as compared to that of **3** (2220 cm^{-1}), indicating the N-coordination of the CN group to ruthenium. A similar observation has been made for {Ru}N≡CPh [24] showing a slight decrease in bond order in C≡N. Besides the $\nu_{(C\equiv N)}$ frequency, two typical C≡C stretching vibrations have been found at 1922 cm^{-1} (TiC≡C^{t}Bu) and 2080 cm^{-1} (CuC≡CC_6H_4). These two absorptions are in characteristic regions observed for tweezer-stabilised Cu(I)-acetylides [25,26]. Complex **7** exhibits $\nu_{(C\equiv C)}$ frequencies in this region for the corresponding organometallic acetylide units TiC≡C^{t}Bu (1942 cm^{-1}), PtC≡CFc (2071 cm^{-1}) and CuC≡CC_6H_2 (2080 cm^{-1}).

With the exception of the acetylide linkage, in the $^{13}C\{^1H\}$ NMR of **7**, the signals of the respective organic fragments are found at chemical shifts typical for the independent molecules **1** and **6**. However, adequate $^{13}C\{^1H\}$ NMR studies for **5** could not be carried out due to its instability in solution. This decomposition leads to a mixture of products of which {[Ti](C≡C^{t}Bu)$_2$}CuCl [25] could be separated and characterised unequivocally by spectroscopic means.

In contrast thereto, ^1H NMR studies of **5** reveal that the *ortho*-CH_2NMe_2 substituents of the $C_5H_3N(CH_2NMe_2)_2$-2,6 ligand remain datively bonded to the Ru(II) centre. The respective resonance signals are shifted to lower field by 0.5 ppm (CH_2) and 0.3 ppm (NMe_2) upon η^1-*N*-coordination of the C≡N moiety [24].

The result of this study shows that organic and organometallic π-systems, such as TiC≡C^{t}Bu, $C_6H_2(CH_2NMe_2)_2$-2,6-(C≡C)-4, C≡CC_6H_4CN-4 and C≡CC_5H_4, can act as linkage for different early and/or late TM complexes. This gives an entry into the synthesis of novel heterometallic complexes with the TM centres in different coordination modes.

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[1] Synthesis of **5**. 33 mg (0.05 mmol) of **3** [26] and 17 mg (0.02 mmol) of **4** [21] were dissolved in 10 ml THF (0°C). After stirring for 4 h at 0°C the mixture was evaporated to dryness and washed with n-pentane (5×5 ml) and then dried in vacuo to yield **5** (40 mg, 0.04 mmol, 80%); m.p. 112°C (decomp.). IR (KBr) (cm^{-1}): ν 2208 (CN), 2080, 1922 (C≡C). ^1H NMR (250.13 MHz, $CDCl_3$): δ 0.22 (s, 18 H, $SiMe_3$), 1.38 (s, 18 H, ^{t}Bu), 2.52 (s, 12 H, NMe_2), 4.01 (s, 4 H, CH_2), 5.95 (t, $^3J_{HH}$ = 1.3 Hz, C_5H_4), 6.01 (t, $^3J_{HH}$ = 1.3 Hz, C_5H_4), 7.1–7.8 (m, 3 H, C_5H_3N).

[2] Synthesis of **7**. To **1** (100 mg, 0.18 mmol) [20] in THF (50 ml, 25°C), **6** [23] (110 mg, 0.18 mmol) was added in one portion. After stirring for 1 h, the mixture was filtered through a pad of Celite. Then, all volatiles were removed in vacuo to yield **7** (200 mg, 0.17 mmol, 95%); m.p. 176°C (decomp.). IR (KBr) (cm^{-1}): 2080, 2071, 1942 (C≡C). ^1H NMR (250.13 MHz, $CDCl_3$): δ 0.27 (s, 18 H, $SiMe_3$), 1.38 (s, 18 H, ^{t}Bu), 3.20 (s, $^3J_{PtH}$ = 46.2 Hz, 12 H, NMe_2), 4.05 (t, $^3J_{HH}$ = 1.2 Hz, 2 H, C_5H_4), 4.08 (s, 4 H, CH_2), 4.16 (s, 5 H, C_5H_5), 4.37 (t, $^3J_{HH}$ = 1.2 Hz, 2 H, C_5H_4), 5.49 (t, $^3J_{HH}$ = 1.5 Hz, 2 H), 5.69 (t, $^3J_{HH}$ = 1.5 Hz, 2 H), 7.03 (s, 2 H, C_6H_2). $^{13}C\{^1H\}$ NMR (62.895 MHz, $CDCl_3$): δ 0.3 ($SiMe_3$), 31.1 (^{t}Bu), 32.0 (C/^{t}Bu), 55.3 (NMe_2), 67.1 (C_5H_4), 68.9 (C_5H_5), 70.5 (C_5H_4), 75.2 (*ipso*-C, C_5H_4), 79.6 (CH_2), 110.2 (C_5H_4), 113.5 (C_5H_4), 113.9 (CuC≡C), 115.2 (*ipso*-C, C_5H_4), 116.1 (CuC≡C), 123.4 (C≡CSi), 138.2 (C_6H_2), 144.2 (*ipso*-C, C_6H_2), 146.1 (TiC), 168.1 (*ipso*-C, C_6H_2); due to the instability of **7** in solution the carbon signals of PtC≡C could not be detected.

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