SHORT COMMUNICATION

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The First Heterohexametallic Transition-Metal Complex

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The synthesis and characterisation of a first heteromultimetallic transition metal complex with six different metal atoms (Fe, Ru, Re, Au, Cu and Ti), connected through carbon-rich bridging units, are reported. Complex {1-[(η^2-dppf)(η^5-C_5H_5)RuC≡C]-3-[(bipy*)$(CO)_3$ReC≡C]-5-[PPh_2AuC≡C-bipy({[Ti](μ-σ,π-C≡$CSiMe_3$)$_2$}Cu)]C_6H_3}PF_6 is accessible in a consecutive reaction sequence by applying building blocks from a ligand and coordination complex library.

Introduction

The linking of modular constructed transition-metal building blocks by carbon-rich bridging units to generate heteromultimetallic assemblies has increasingly gained interest during the last years.[1] A straightforward method to prepare such complexes is given by using the principle of the molecular “tinkertoy” approach.[2–4] This generally requires the prior preparation of multifunctional organic, coordination and/or organometallic molecules, which allow the stepwise synthesis of multitopic transition-metal-containing species. In particular, as different binding sites of the connecting units reactive groups, such as acetylides, phosphanes and N,N-donor systems (N,N = bi- or tridentate Lewis bases) can be used to control the synthesis of (hetero)multimetallic complexes. In context with this background, heteromultimetallic complexes with up to four different transition metals were synthesised, a hitherto scarcely explored class of compounds in transition-metal chemistry.[5] Very recently we reported the successful preparation of a heteromultimetallic species in which five different transition metals (Fe-Ru-Au-Cu-Ti) are spanned by carbon-rich organic units.[6] Extending this idea, we describe here for the first time the synthesis of an even heterohexanuclear transition-metal complex supported by applying the precoordinated multitopic organometallic building block 1-[(η^2-dppf)(η^5-C_5H_5)RuC≡C]-3-[(bipy*)$(CO)_3$ReC≡C]-5-(PPh_2)-C_6H_3.

Results and Discussion

The heterohexanuclear complex prepared was of the type {1-[(η^2-dppf)(η^5-C_5H_5)RuC≡C]-3-[(bipy*)$(CO)_3$ReC≡C]-5-[PPh_2AuC≡C-bipy({[Ti](μ-σ,π-C≡$CSiMe_3$)$_2$}Cu)]C_6H_3}-PF_6 (**5**) by using the versatile starting material 1-[(η^2-dppf)-(η^5-C_5H_5)RuC≡C]-3-[(bipy*)$(CO)_3$ReC≡C]-5-(PPh_2)C_6H_3 (**1**) {dppf = 1,1′-bis(diphenylphosphanyl)ferrocene; bipy = 2,2′-bipyridine-5-yl; bipy* = 4,4′-di-*tert*-butyl-2,2′-bipyridine; [Ti] = (η^5-$C_5H_4SiMe_3$)$_2$Ti} and the relevant organometallic fragments. The newly synthesised transition-metal complexes and the overall synthetic methodology employed are depicted in Scheme 1.

Molecule **1** was prepared as described earlier by starting from 1,3,5-tribromobenzene.[7] Treatment of **1** with (tht)-AuC≡C-bipy (**2**), in situ generated from (tht)AuCl and 5-ethynyl-2,2′-bipyridine (tht = tetrahydrothiophene)[7] gave by replacement of the S-donor ligand tetrahydrothiophene by tertiary phosphane **1** coordination complex 1-[(η^2-dppf)(η^5-C_5H_5)RuC≡C]-3-[(bipy*)$(CO)_3$ReC≡C]-5-(PPh_2-AuC≡C-bipy)C_6H_3 (**3**) (Scheme 1). After appropriate workup, compound **3** could be isolated as a yellow powder in moderate yield.

When we attempted to crystallise complex **3** by diffusion of *n*-hexane into a dichloromethane solution containing **3**, it was discovered that this complex is not stable because it decomposes to produce (bipy*)$(CO)_3$ReC≡C-bipy along with an insoluble yellow precipitate that does not dissolve in common organic solvents. This observation underlies an unexpected transmetallation reaction between the Re and Au alkynyls. The insoluble precipitate probably evinces a polymeric structure formed by the remaining phosphane gold(I) acetylide building block. Nevertheless, complex **3** with its four different transition-metal atoms is a key starting material for the synthesis of organometallic assemblies of higher nuclearity owing to the presence of a pendant 2,2′-bipyridine entity as a further N-ligating site.

{1-[(η^2-dppf)(η^5-C_5H_5)RuC≡C]-3-[(bipy*)$(CO)_3$Re-C≡C]-5-[PPh_2AuC≡C-bipy({[Ti](μ-σ,π-C≡$CSiMe_3$)$_2$}-Cu)]C_6H_3}PF_6 (**5**) is formed in a straightforward manner when **3** is treated with the organometallic π-tweezer

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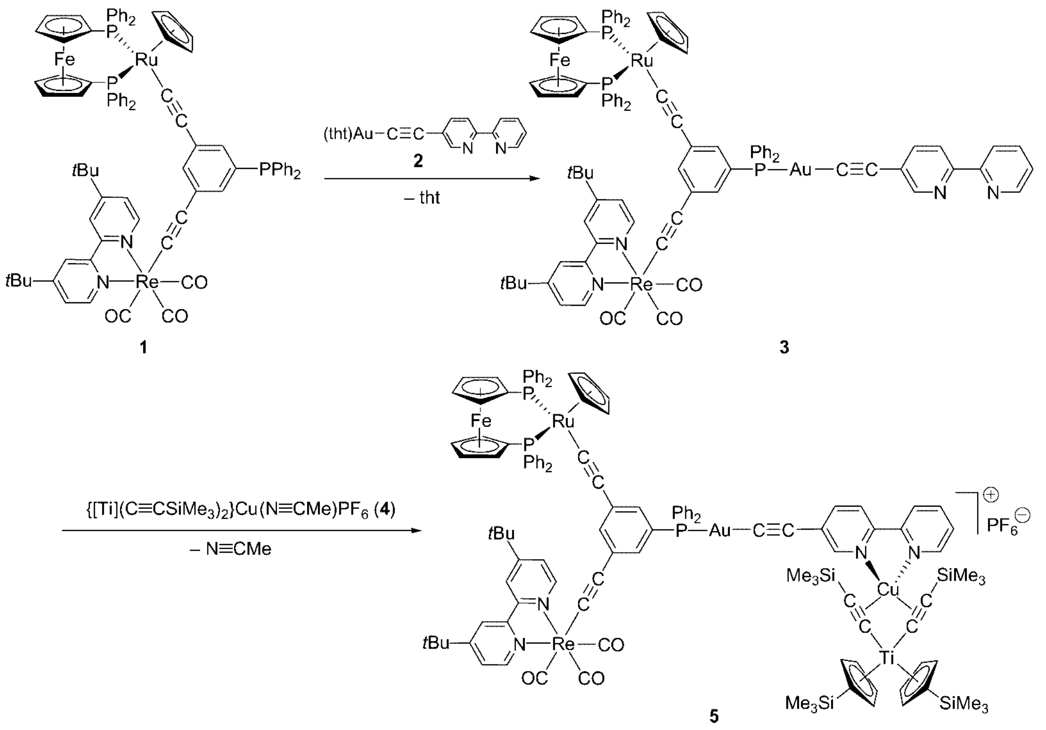

Scheme 1. Synthesis of heterotetrametallic **3** and heterohexanuclear **5** {[Ti] = (η^5-$C_5H_4SiMe_3)_2Ti$}.

[{[Ti](μ-σ,π-$C{\equiv}CSiMe_3)_2$}Cu($N{\equiv}CMe$)]PF_6 (**4**), whereby the acetonitrile ligand in **4** is substituted by the bipyridine entity of **3**. Within this reaction, the coordination number at copper(I) changes from three (planar) to four (pseudotetrahedral).

Orange **5** is only soluble in polar solvents such as tetrahydrofuran or chloroform as a result of its ionic character. This complex is stable in the solid state, that is, no intramolecular redox processes are observed. However, it should be mentioned that all efforts to produce X-ray quality crystals of **5** failed owing to the instability of this complex in solution over prolonged periods. In **5** the appropriate transition metals Ti, Re, Fe, Ru, Cu and Au are connected by carbon-rich organic bridging units.

The synthetic protocol developed to prepare heteromutlinuclear **3** and **5** is directed to the use of modular-shaped organometallic building blocks (vide supra). In this respect, IR and NMR (^1H, $^{31}P\{^1H\}$) spectroscopy allow the progress of the reactions to be monitored, and thus the structure and composition of the final assemblies can be verified. In addition, ESI-TOF mass spectrometric studies were carried out with **3** and **5**.

Most characteristic in the IR spectra of **3** and **5** is the appearance of $\nu_{C\equiv C}$ and ν_{CO} vibrations typical for the individual σ alkynyl organometallic transition-metal fragments, which are diagnostic and represent a useful monitoring tool. The introduction of the gold acetylide building block at the phosphane is evidenced by the respective $\nu_{C\equiv C}$ absorption at 2117 cm^{-1} (AuC≡C), which is typical for phosphane-stabilised gold(I) acetylides and also found in **5**.[8]

The $^{31}P\{^1H\}$ NMR spectra of **3** and **5** show the expected resonance signals. In all complexes, a signal at $\delta \approx 54$ ppm is observed for the dppf entity. Owing to the coordination of the phosphane to gold(I), a representative shift to lower field from –5.4 (**1**) to 41.2 (**3**) ppm is observed which is, however, not influenced by further metal coordination as given in **5**.[8]

The ^1H NMR spectroscopic properties of **3** and **5** nicely correlate with their formulations as heteromultinuclear assemblies based on the 1,3-diethynyl-5-diphenylphosphanylbenzene core, and the spectra show the respective resonance signal patterns for the organic units. Most distinctive for the formation of **5** is the chemical shift of the bipyridine protons H6/H6′ (**3**: H6′, 8.66; H6, 8.79 ppm; **5**: H6/H6′, (m) 8.49–8.58 ppm). Furthermore, as a result of the coordination of the bipyridine unit to the organometallic π-tweezer-stabilised copper(I) centre in **5**, a highfield shift of the $Me_3SiC{\equiv}C$ protons is observed relative to **4**,[9] which can be explained by the ring current of the bipyridine ligand.

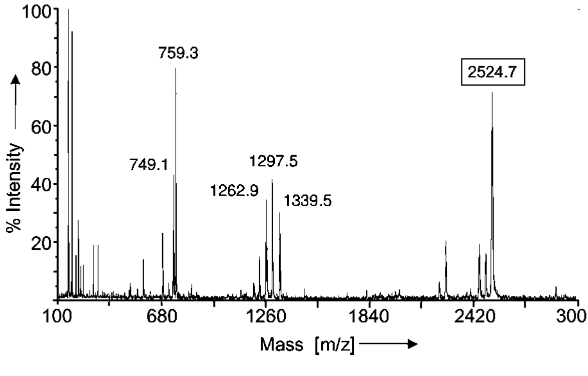

Figure 1. ESI-MS spectra of heterohexanuclear **5**.

The identity of heterotetranuclear **3** and heterohexametallic **5** was additionally evidenced from mass spectrometric investigations. The electrospray ionisation mass spectrum (ESI-MS) of **3** shows an ion peak at *m*/*z* = 1944.7, which corresponds to $[\mathbf{3} + H]^+$. The spectrum of **5** (Figure 1) exhibits a prominent ion peak at *m*/*z* = 2524.7, whose mass and isotope distribution pattern comply to $[\mathbf{5} - PF_6]^+$ and confirm the elemental composition and charge state.

Conclusions

This report pertaining to the first synthesis of an organometallic complex in which a total of six different early and late transition metals, such as titanium, rhenium, iron, ruthenium, copper and gold, are connected by carbon-rich π-conjugated bridging units demonstrates that such large heteronuclear assemblies can be synthesised in a straightforward manner by combining different organic and/or organometallic building blocks of lower nuclearity from a ligand and coordination complex library that was particularly built for this purpose. This procedure allows the composition and structure of such novel molecules to be controlled, but it also should be mentioned that unexpected reactions can occur that make this field of chemistry even more challenging than initially anticipated. Similar to racing cars, from which we learn experience for everyday vehicles, the chemistry described above will surely provide the impetus for future detailed investigations in this field of chemistry, including spectroelectrochemical studies and material properties.

Experimental Section

Starting Materials, Reaction Conditions and Instrumentation: All manipulations were carried out under anhydrous and anaerobic conditions by using standard Schlenk techniques. Tetrahydrofuran and *n*-hexane were purified by distillation from sodium/benzophenone. $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}Cu(N\equiv CMe)]PF_6$[9a] was prepared according to a published procedure. Infrared spectra were recorded with a Perkin–Elmer FTIR spectrometer Spectrum 1000. NMR spectra were recorded with a Bruker Avance 250 spectrometer; chemical shifts are given in δ units (parts per million) and are referenced to residual solvent resonances (^1H NMR: $CDCl_3$, $\delta = 7.26$) or an external 85% H_3PO_4 standard ($^{31}P\{^1H\}$).

5: To $[\{[Ti](\mu\text{-}\sigma,\pi\text{-}C\equiv CSiMe_3)_2\}Cu(N\equiv CMe)]PF_6$ (**4**) (25 mg, 0.033 mmol) dissolved in tetrahydrofuran (25 mL) was added in a single portion $1\text{-}[(\eta^2\text{-dppf})(\eta^5\text{-}C_5H_5)RuC\equiv C]\text{-}3\text{-}[(bipy^*)(CO)_3ReC\equiv C]\text{-}5\text{-}(PPh_2AuC\equiv C\text{-bipy})C_6H_3$ (**3**) (60 mg, 0.031 mmol). The resulting reaction mixture was stirred for 2 h at 25 °C, whereby the colour of the solution changed from orange to red. The solvent was reduced in volume, and the product was precipitated by the addition of *n*-hexane, washed twice with *n*-hexane and dried under vacuum to afford an orange-red solid. Yield: 70 mg (0.026 mmol, 85%). ^1H NMR (250 MHz, $CDCl_3$, 25 °C, TMS): $\delta = -0.50$ (s, 18 H, SiMe_3), 0.27 (br. s, 18 H, SiMe_3), 1.41 (s, 18 H, *t*Bu), 3.93 (dpt, $J_{HP} = 1$ Hz, $J_{HH} = 2.4$ Hz, 2 H, C_5H_4), 4.02 (br. s, 2 H, C_5H_4), 4.20 (s, 5 H, C_5H_5), 4.25 (br. s, 2 H, C_5H_4), 5.00 (br. s, 2 H, C_5H_4), 6.23–6.30 (m, 8 H, $C_5H_4/C_5H_4SiMe_3$), 6.83 (dpt, $J_{HP} = 12.8$ Hz, $J_{HH} = 1.5$ Hz, 1 H, C_6H_3), 7.00 (dpt, $J_{HP} = 15$ Hz, $J_{HH} = 1.5$ Hz, 1 H, C_6H_3), 7.06–7.53 [m, 26 H (C_6H_5) + 1 H (C_6H_3) + 2 H (*H5*/bipy*)], 7.62–7.75 [m, 4 H (C_6H_5) + 1 H (*H5′*/bipy)], 8.12 (dd, $^3J_{H4H3} = 8.4$ Hz, $^4J_{H4H6} = 2.0$ Hz, *H4*/bipy), 8.18–8.27 (m, 3 H, *H3*/bipy* + *H4′*/bipy), 8.42 (d, $^3J_{H3H4} = 8.4$ Hz, 1 H, *H3*/bipy), 8.49–8.58 (m, 3 H, *H3′*,*H6*,*H6′*/bipy), 8.97 (d, $^3J_{H6H5} = 6.0$ Hz, 2 H, *H6*/bipy*) ppm. $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = -145.1$ (septuplet, $J_{PF} = 713$ Hz, PF_6), 40.8 (AuPPh_2), 53.7 (dppf) ppm. IR (KBr): $\tilde{\nu} = 1893$, 1904, 2003 (s, CO), 2060 (m, $C\equiv CRu$), 2117 (w, $C\equiv CAu$) cm^{-1}. MS (ESI-TOF): *m*/*z* (%) = 2524.7 (70) $[M - PF_6]^+$. $C_{120}H_{121}AuCuF_6FeN_4O_3P_4ReRuSi_4Ti$ (2669.03): calcd. C 54.00, H 4.57, N 2.10; found C 54.76, H 4.80, N 2.04.

Supporting Information (see footnote on the first page of this article): Synthetic details and characterisation for compounds **1** and **3**.

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