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Research paper

Revisiting reactions of alkynes with $Ru_3(CO)_{12}$: Effects of alkyne substituents and solvents on the structures of ruthenium cluster products

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ABSTRACT

The reactions of $Ru_3(CO)_{12}$ with alkynes $R_1C{\equiv}CR_2$ (R_1 = pyridyl, R_2 = Ph (**1**); R_1 = pyridyl, R_2 = ferrocenyl (**2**); R_1 = R_2 = Ph (**3**)) in toluene afforded a linear triruthenium cluster (**1a**/**1b**), a triangular triruthenium cluster (**2a**) and two biruthenium clusters (**3a** and **3b**). All clusters were characterized by FT-IR, NMR, ESI-MS spectrometry and single-crystal X-ray diffraction. The structures of **1a**/**1b** (two polymorphs) contain each a Ru3 linear skeleton, which arises from the coupling and coordination of two ligands **1** with the ruthenium centers and formation of two six-membered rings with a common edge. The structure of **2a** contains a metallacyclopentadienyl framework formed by two coupled ligands **2** bonding with a triangular-arranged ruthenium skeleton via a μ_4-η^1:η^2:η^1:η^1 bonding mode, and a four-membered ring formed by the third ligand **2** bonding with ruthenium atom in a μ_3-η^1:η^1 bonding mode and linking of its pyridyl N atom with another ruthenium atom. The reaction of **3** and $Ru_3(CO)_{12}$ in toluene gave unexpected ruthenole **3a** and a reported cluster **3b**. A detailed investigation on the reaction processes suggested that the nitrogen atoms of the pyridyl groups in the alkyne ligand **1**–**2** directs the formation of the triruthenium clusters **1a**/**1b** and **2a**. The electronic and steric effects of a ferrocenyl group are distinctly different from those of a phenyl group and lead to the diverse structures of the products **1a**/**1b** and **2a** in the reactions of $Ru_3(CO)_{12}$ with alkynes **1**–**2**, respectively. Moreover, the solvent properties exert great effects on the product distribution.

1. Introduction

Reactions of transition metal clusters containing functionalized alkynes have been widely studied for many years [1–7]. It has become one of the most rapidly flourishing areas within the inorganic and organometallic fields because of their potential applications in catalysis and as candidates in microelectronics and nanolithography [8–11]. In recent years, $Ru_3(CO)_{12}$ as an important precursor of transition metal clusters attracted great interest of researchers by its unique activity in homogeneous catalytic reactions [12–15]. Some carbonyl ruthenium clusters formed via reaction of $Ru_3(CO)_{12}$ and alkynes were extensively investigated [16–26]. And it was found that the versatile coordination patterns are usually relevant strongly to many catalytic processes involving polynuclear species and unsaturated organic molecules [27,28]. These results provide more possibilities for $Ru_3(CO)_{12}$ to become a potential catalyst for the conversion of alkyne compounds [13,29,30].

The reactivity of $Ru_3(CO)_{12}$ has been well explored with different alkyne derivatives. Earlier P. J. Low et al studied the reaction of $Ru_3(CO)_{12}$ with 1,6-bis(trimethylsilyl)*hexa*-1,3,5-triyne and separated a series of Ru2-Ru4 clusters [16]. M. I. Alcalde and co-workers also synthesized ruthenium clusters containing sulfur-bridged diynyl ligands via reaction of $Ru_3(CO)_{12}$ with $S(C{\equiv}CSiMe_3)_2$ in toluene [17]. Then M. Akita and co-workers revealed a new type of iron, ruthenium and mixed-metal dicarbide clusters with higher nuclearity through the reaction of ethynyliron complexes FP-C≡C-H and Fp*-C≡C-Fp* [Fp = (η^5-C_5H_5)-Fe$(CO)_2$; Fp* = (η^5-C_5Me_5)Fe$(CO)_2$,] with $Ru_3(CO)_{12}$ in refluxing benzene [18]. In 2004, B. Alonso and co-workers reported the trinuclear complexes [$Ru_3(CO)_9$(μ_3-η^2:η^4:η^3-$Me_3SiCC(C_2Fc)$SC(Fc)CSC≡CSi-Me_3)], [$Ru_3(CO)_9$(μ,η^2-SC≡CFc)(μ_3,η^2-C≡CSiMe$_3$)] and the dinuclear complex [$Ru_2(CO)_6$-(μ-SC≡CSiMe$_3$)(μ-C≡CFc)] by reaction of $Ru_3(CO)_{12}$ with FcC≡CSC≡CSiMe$_3$ (Fc = ferrocenyl) [22]. In addition, P. Mathur et al, systematically investigated the reactivity of FcC_2C_2Ph with $Ru_3(CO)_{12}$ and a series of [Ru$(CO)_3$(η^4-ruthenole)] derivatives were separated [11,24]. Recently, V. González-López and co-workers isolated several Ru1-Ru4 framework clusters during the reactions of $Ru_3(CO)_{12}$ with disubstituted acetylene $Me_3SiC{\equiv}CSiMe_3$ and two terminal alkynes $HC{\equiv}CSiMe_3$ and $HC{\equiv}CSiPh_3$ [26]. Therefore, the reactions of $Ru_3(CO)_{12}$ with different acetylenes can afford a variety of unexpected products [16–26]. In our recent studies, we have found that the electronic and steric effects of substituents in 1,3-ynones play an

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very important role in the intermediates and final products distribution and in their molecular structural diversity during the reactions of $Ru_3(CO)_{12}$ with the 1,3-ynones [31–33]. R. Rosseto and co-workers thoroughly studied the reactions of $[PPN][Ru_3(\mu\text{-}Cl)(CO)_{10}]$ with a number of symmetrical and asymmetrical alkynes in which the substituents are ferrocenyl groups or phenyl rings containing electron donor or electron withdrawing groups at their *para* positions and they claimed that the substituents in the alkynes did not change the reaction results [21]. Therefore, we believe that a small modification of the substituent properties of an alkyne do not change the reaction results of alkynes and $Ru_3(CO)_{12}$. Herein, we choose alkynes containing substituents with distinct difference like pyridyl (with strong coordination ability) and ferrocenyl (special electronic and steric effects) groups and study influences of these groups on the product distribution and the molecular structures of the products during the reactions of alkynes with $Ru_3(CO)_{12}$. Meanwhile, the reaction of 1,2-diphenylethyne and $Ru_3(CO)_{12}$ is employed as a comparable experiment.

In this paper, we examined in detail the reaction process of $Ru_3(CO)_{12}$ with three alkyne derivatives R1C≡CR2 (R1 = pyridyl, R2 = Ph (**1**); R1 = pyridyl, R2 = ferrocenyl (**2**); R1 = R2 = Ph (**3**)). The coupling and coordination of the alkynes with $Ru_3(CO)_{12}$ formed a new linear triruthenium cluster**1a/1b** (there are two polymorphs of the same triruthenium cluster), a new triangular triruthenium cluster **2a** and two unexpected biruthenium products **3a-3b**. Through a detailed examination of the reaction process, we found that the coordination of the nitrogen atoms of the pyridyl groups in **1** and **2** with the ruthenium centers directs the structures of **1a/1b** and **2a**. Meanwhile, the ferrocenyl group in **2** exhibits strong electronic and steric effects on the reaction process and **2a** structures. Although the reaction of 1,2-diphenylethyne **3** with $Ru_3(CO)_{12}$ has been examined in a few solvents except toluene by G. Cetini and co-workers [34], the similar reaction performed in toluene afforded two unexpected biruthenium clusters **3a** and **3b**.

2. Experimental

2.1. Materials and equipment

All manipulations were carried out using standard Schlenk, and solvents were purified, dried and distilled under nitrogen atmosphere prior to use. ^1H and $^{13}C\{^1H\}$ NMR spectra were performed on a Bruker Avance 400 MHz spectrometers. IR spectra were recorded on a Bruker Tensor 27 Fourier-transform spectrometer (KBr pellet). ESI-mass spectra were recorded on a Thermo Deca Max (LCMS) mass spectrometer with an ion-trap mass detector, and the high-resolution mass spectra were recorded in ESI mode on a Waters UPLC-Q-TOF mass spectrometer. Elemental analyses were performed by Vario EL III Elemental Analyzer. The structural measurements of single crystals were carried out with a Bruker D8 QUEST with a Photo 100 CMOS detector.

2.2. Synthesis

1-(2-pyridyl)-2-phenylethyne (**1**), 1-(2-pyridyl)-2-ferrocenylethyne (**2**) and 1,2-diphenylethyne (**3**) were used to react with $Ru_3(CO)_{12}$, respectively. In order to get an optimum reaction condition for the reactions of **1**–**3** with $Ru_3(CO)_{12}$, influences of molar ratio of $Ru_3(CO)_{12}$ to **1**–**3** (1:1–1:5), reaction time (20 min – 3 h) and reaction temperature (60 °C – 110 °C) were investigated. We found that the optimum molar ratio and reaction temperature are 1:3 and 90 °C for all reactions, respectively, and the optimum reaction time is 1 h, 1.5 h and 0.5 h for the reactions of **1**, **2** and **3** with $Ru_3(CO)_{12}$, respectively. Since their experimental procedures were similar, the reaction of **1** and $Ru_3(CO)_{12}$ is detailed as an example. Both **1** (0.1613 g, **0.9** mmol) and $Ru_3(CO)_{12}$ (0.1918 g, **0.3** mmol) were added in 15 mL toluene and heated at 90 °C for 1 h, until the reaction solution gradually changed from orange to red-brown. The red-brown solution was cooled and the unreacted orange-red $Ru_3(CO)_{12}$ was precipitated and recovered (0.0530 g, **0.08** mmol). The residue was chromatographed by 305 mm length and 40 mm internal diameter chromatographic column on silica gel with dichloromethane and petroleum ether, the main products was eluted in the sequence of **1a/1b** with the eluent dichloromethane/petroleum ether (v:v) 1:4, and then recrystallized the products by dichloromethane/hexane (v:v = 1:5). The yield of the product was calculated based on the added $Ru_3(CO)_{12}$ in the beginning of a reaction.

2.2.1. $[Ru_2(CO)_5\{(\mu_3\text{-}\eta^2{:}\eta^4{:}\eta^2\text{-}(C_5H_4N)C(CPh)C(CPh)(C_5H_4N)\}Ru(CO)_3]$ (**1a/1b**)

Brown powder. Yield: 40%. FT-IR (KBr, cm^{-1}): 2925 w, 2852 w, 2067 vs, 2036 vs, 1997 vs, 1774 m. ^1H NMR (400 MHz, $CDCl_3$) δ 8.63–8.68 (d, 2H, C_5H_4N), 7.42–8.06 (m, 6H, C_6H_5, C_5H_4N) , 6.44–7.19 (m, 10*H*, C_6H_5, C_5H_4N). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 207.66 (CO), 203.14 (CO), 196.53 (CO), 193.15 (CO), 173.44 (C≡C), 166.13 (C≡C), 154.29 (C_5H_4N), 149.91 (C_5H_4N), 136.64 (C_5H_4N), 135.90 (C_6H_5), 135.26 (C_6H_5), 128.67 (C_6H_5), 126.58 (C_6H_5), 121.60 (C_5H_4N), 120.37 (C_5H_4N). MS (*m/z*, ESI^+), 858.830 (M^+ – CO), 830.835 (M^+ – 2CO). Anal. calcd. for $C_{34}H_{18}N_2O_8Ru_3$: 886.822. Anal. found: C, 45.97; H, 2.13; N, 3.02%. $C_{34}H_{18}N_2O_8Ru_3$ requires: C, 46.11; H, 2.05; N, 3.16.

2.2.2. $[Ru_3(CO)_5(\mu\text{-}CO)\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^1\text{-}(C_5H_4N)CC(Fc)C(Fc)C(C_5H_4N)\}\{\mu_3\text{-}\eta^1{:}\eta^1\text{-}(Fc)CC(C_5H_4N)\}]$ (**2a**)

Red powder. Yield: 32%. FT-IR (KBr, cm^{-1}): 3087 w, 2918 m, 2848 m, 2063 s, 2035 vs, 1988 vs, 1922 s. ^1H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 4.0 Hz, 2H, C_5H_4N), 8.59 (d, *J* = 4.0 Hz, 1H, C_5H_4N), 7.53–7.57 (s, 2H, C_5H_4N), 7.28–7.37 (m, 4H, C_5H_4N), 6.94–6.97 (s, 2H, C_5H_4N), 6.28 (d, *J* = 8.0 Hz, 1H, C_5H_4N), 3.48–4.69 (m, 27H, $C_{10}H_9$). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.40 (CO), 197.22 (CO), 196.94 (CO), 196.92 (CO), 195.82 (CO), 175.05 (C≡C), 158.14 (C≡C), 154.28 (C_5H_4N), 148.29 (C_5H_4N), 136.13 (C_5H_4N), 134.73 (C_5H_4N), 131.41 (C_5H_4N), 126.67 (C_5H_4N), 123.85 (C_5H_4N), 123.53 (C_5H_4N), 122.25 (C_5H_4N), 120.74 (C_5H_4N), 100.96 (C≡C), 84.32 (C≡C), 78.21 ($C_{10}H_9$), 73.91 ($C_{10}H_9$), 70.73 ($C_{10}H_9$), 70.33 ($C_{10}H_9$), 70.09 ($C_{10}H_9$), 69.29 ($C_{10}H_9$), 68.49 ($C_{10}H_9$), 66.27 ($C_{10}H_9$), 66.17 ($C_{10}H_9$), 65.68 ($C_{10}H_9$). MS (*m/z*, ESI^+), 1303.805 (M^+ – CO), 1247.806 (M^+ – 3CO). Anal. calcd. for $C_{57}H_{39}N_3O_6Fe_3Ru_3$: 1331.803. Anal. found: C, 51.16; H, 3.06; N, 3.03. $C_{57}H_{39}N_3O_6Fe_3Ru_3$ requires: C, 51.37; H, 2.95; N, 3.15.

2.2.3. $[Ru(CO)_3\{\mu_4\text{-}\eta^1{:}\eta^2{:}\eta^1{:}\eta^1\text{-}(Ph)CC(Ph)C(Ph)C(Ph)Ru(CO)_3(\mu\text{-}CO)\}]$ (**3a**)

Yellowy powder. Yield: 20%. FT-IR (KBr, cm^{-1}): 3079 w, 3020 w, 2960 m, 2925 m, 2854 m, 2085 vs, 2030 vs, 1999 vs, 1975 vs, 1940 vs. ^1H NMR (400 MHz, $CDCl_3$) δ 6.93–6.97 (s, 4H, C_6H_5), 6.84–6.88 (m, 12H, C_6H_5), 6.72–6.76 (s, 4H, C_6H_5). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.41 (CO), 194.71 (CO), 191.36 (CO), 163.96 (C≡C), 147.33 (C≡C), 138.27 (C_6H_5), 133.95 (C_6H_5), 131.19 (C_6H_5), 127.48 (C_6H_5), 126.36 (C_6H_5), 126.18 (C_6H_5), 126.06 (C_6H_5), 124.56 (C_6H_5). MS (*m/z*, ESI^+) 724.933 (M^+). Anal. calcd. for $C_{34}H_{20}O_6Ru_2$: 724.936. Anal. found: C, 56.01; H, 2.83. $C_{34}H_{20}O_6Ru_2$ requires: C, 56.20; H, 2.77.

2.2.4. $[Ru(CO)_3\{\mu_3\text{-}\eta^1{:}\eta^2{:}\mu_3\text{-}\eta^2{:}\eta^1\text{-}(Ph)CC(Ph)C(O)C(Ph)C(Ph)Ru(CO)_3\}]$ (**3b**)

Yellowy powder. Yield: 30%. FT-IR (KBr, cm^{-1}): 2925 vs, 2855 s, 2090 m, 2063 s, 2020 s, 1673 m. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21–7.30 (m, 8H, C_6H_5), 7.06–7.18 (m, 12H, C_6H_5). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 194.18 (CO), 187.32 (CO), 162.45 (C≡C), 149.15 (C≡C), 138.55 (C_6H_5), 130.98 (C_6H_5), 127.95 (C_6H_5), 127.86 (C_6H_5), 127.47 (C_6H_5), 127.34 (C_6H_5), 126.73 (C_6H_5), 126.57 (C_6H_5). MS (*m/z*, ESI^+) 752.930 (M^+), 724.936 (M^+ – CO), 696.945 (M^+ – 2CO). Anal. calcd. for $C_{35}H_{20}O_7Ru_2$: 752.931. Anal. found: C, 55.51; H, 2.79. $C_{35}H_{20}O_7Ru_2$ requires: C, 55.70; H, 2.67.