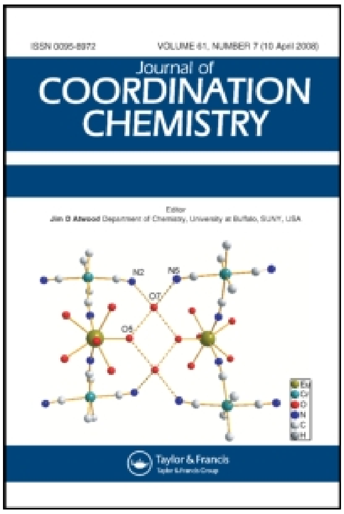

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and characterization of linked alkyne-bridging Co_2C_2 tetrahedral clusters and expansion reactions of $(Co_2(CO)_6(\mu\text{-}HCCCH_2OOC))_2R$ with $Fe_3(CO)_{12}$

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To cite this Article Zhu, Bao-Hua , Bai, Yan-Hong , Hong, Hong and Gao, Shuang-Yu(2009) 'Synthesis and characterization of linked alkyne-bridging Co_2C_2 tetrahedral clusters and expansion reactions of $(Co_2(CO)_6(\mu\text{-}HCCCH_2OOC))_2R$ with $Fe_3(CO)_{12}$', Journal of Coordination Chemistry, 62: 7, 1086 — 1090, First published on: 29 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958970802401089

URL: http://dx.doi.org/10.1080/00958970802401089

Journal of Coordination Chemistry
Vol. 62, No. 7, 10 April 2009, 1086–1090

Synthesis and characterization of linked alkyne-bridging Co_2C_2 tetrahedral clusters and expansion reactions of $(Co_2(CO)_6(\mu\text{-}HCCCH_2OOC))_2R$ with $Fe_3(CO)_{12}$

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(*Received 11 November 2007; in final form 25 June 2008*)

Two new linked alkyne-bridging tetrahedral carbonyl clusters containing Co_2C_2 $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_3COOCH_2CCH\text{-}\mu)Co_2(CO)_6$, **1**, and $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_8COOCH_2CCH\text{-}\mu)Co_2(CO)_6$, **2**, have been prepared by reactions of two dipropargyl esters $(HC{\equiv}CCH_2OOC)_2R$ ($R = (CH_2)_3$, $(CH_2)_8$) with $Co_2(CO)_8$. Expansion reactions of **1** and $Co_2(CO)_6(\mu\text{-}HCCCH_2OOCCOOCH_2CCH\text{-}\mu)Co_2(CO)_6$, **3**, with $Fe_3(CO)_{12}$ give two new mixed-metal linked clusters $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_3COOCH_2CCH\text{-}\mu,\eta^4)Co_2Fe_2(CO)_{12}$, **4**, and $Co_2(CO)_6(\mu\text{-}HCCCH_2OOCCOOCH_2CCH\text{-}\mu,\eta^4)Co_2Fe_2(CO)_{12}$, **5**. The new clusters were characterized by elemental analysis, IR, ^{1}H-NMR and ESI-MS analysis.

Keywords: Alkyne-bridging; Linked cobalt-iron cluster; Expansion reaction

1. Introduction

Interest in transition metal complexes bridged by unsaturated hydrocarbons result from the relevance to metal-catalyst surfaces and materials science [1–7]. Linked clusters have also attracted attention due to potential applications as polymeric materials and their unusual structures and reactions [8–19]. Our previous work has shown that linked alkyne-bridging $Co_2(CO)_6C_2$ clusters react with $Rh_2(CO)_4Cl_2$ to form linked distorted *closo*-$Rh_2Co_2C_2$ octahedral clusters [19]. It has also been reported that $Fe_3(CO)_{12}$ can provide a mononuclear or binuclear carbonyl iron fragment during reaction with alkyne compounds [20].

To investigate the reactivity of linked metal-alkyne carbonyl clusters with $Fe_3(CO)_{12}$ and obtain the heterometal alkyne-bridging carbonyl clusters, we prepared two new linked cobalt carbonyl clusters, $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_3COOCH_2CCH\text{-}\mu)Co_2(CO)_6$ **1** and $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_8COOCH_2CCH\text{-}\mu)Co_2(CO)_6$ **2**, and one known linked cobalt cluster $Co_2(CO)_6(\mu\text{-}HCCCH_2OOCCOOCH_2CCH\text{-}\mu)Co_2(CO)_6$ **3** by reactions of $Co_2(CO)_8$ with three dipropargyl esters. Then, we carried

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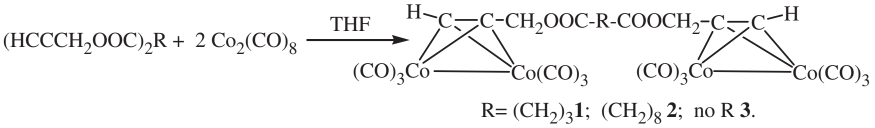
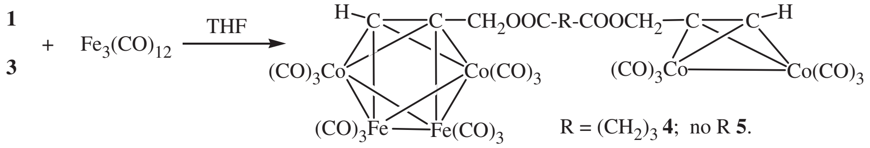
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802401089



Scheme 1. The synthesis of linked clusters **1**–**3**.



Scheme 2. The reaction of **1** and **3** with $Fe_3(CO)_{12}$ to give linked clusters **4** and **5**.

out the reactions of **1** and **3** with $Fe_3(CO)_{12}$, obtaining two new heterometal alkyne-bridging carbonyl clusters, $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_3COOCH_2CCH\text{-}\mu,\eta^4)Co_2Fe_2(CO)_{10}$ **4** and $Co_2(CO)_6(\mu\text{-}HCCCH_2OOCCOOCH_2CCH\text{-}\mu,\eta^4)Co_2Fe_2(CO)_{12}$ **5** (schemes 1 and 2). All new linked clusters were characterized by elemental analysis and spectroscopic methods.

2. Experimental

2.1. *General details*

All reactions were carried out under an argon atmosphere by standard Schlenk techniques. All solvents were dried and distilled from sodium benzophenone or CaH_2 before use. Chromatographic separations were performed on silica gel columns (160–200 mesh) of varying length. Thin-layer chromatography (TLC) was performed on commercial Merck plates coated with a 0.20 mm layer of silica gel.

$(HC{\equiv}CCH_2OOC)_2R$ ($R = (CH_2)_3$ [21], $(CH_2)_8$ [22]) and $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC)_2Co_2(CO)_6$ **3** [13] were prepared by literature methods. $Co_2(CO)_8$ and $Fe_3(CO)_{12}$ were used as received from a commercial source.

Infrared spectra were recorded on a Nicolet NEXUS 670 FT-IR spectrophotometer. ^1H NMR spectra were measured on a Bruker Avance DPX-400 MHz spectrometer in chloroform-d_1. Chemical shifts are quoted in parts per million (ppm) and referenced to tetramethylsilane (TMS). ESI-MS positive ion spectra were obtained on an Agilent 1100 LC-MSD-Trap-XCT instrument. Elemental analyses (C, H) were performed on a Perkin–Elmer 2400.

2.2. *Reaction of $(HC{\equiv}CCH_2OOC)_2(CH_2)_3$ with $Co_2(CO)_8$ to give* 1

To a solution of $Co_2(CO)_8$ (924.8 mg, 2.7 mmol) in 30 mL of THF was added dropwise a solution of $(HC{\equiv}CCH_2OOC)_2(CH_2)_3$ (562.4 mg, 2.7 mmol) in 15 mL of THF at room temperature. The reaction mixture was stirred at 60°C for 8 h and monitored by TLC.

THF was removed under reduced pressure. The residue was separated by column chromatography on silica gel. Elution with petroleum ether afforded the orange-red $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_3COOCH_2CCH\text{-}\mu)Co_2(CO)_6$ (282.4 mg, 26.8%, based on $Co_2(CO)_8$), m.p. 126°C; Anal. Found: C, 36.01; H, 1.52%. Calcd for $C_{23}H_{12}O_{16}Co_4$: C, 35.41; H, 1.55%. IR (KBr disc): ν(CO) 2098m, 2055vs, 2022vs cm^{-1}; ν(C=O) 1741s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.07 (s, 2H, 2≡CH), 4.82 (s, 4H, $2OCH_2$), 2.50 (s, 4H, $2CH_2$), 2.04 (s, 2H, CH_2) ppm. ESI − MS m/z: 802.7, $M + Na^+$; complex fragmentation.

2.3. *Reaction of* $(HC{\equiv}CCH_2OOC)_2(CH_2)_8$ *with* $Co_2(CO)_8$ *to give* **2**

To a solution of $Co_2(CO)_8$ (924.8 mg, 2.7 mmol) in 30 mL of THF was added dropwise a solution of $(HC{\equiv}CCH_2OOC)_2(CH_2)_8$ (750.6 mg, 2.7 mmol) in 15 mL of THF at room temperature. The reaction mixture was stirred at 60°C for 7 h and monitored by TLC. After the solvent was removed under reduced pressure, the residue was extracted by a small amount of CH_2Cl_2 and purified by column chromatography (silica gel eluent: petroleum ether) to afford the orange-red $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_8COOCH_2CCH\text{-}\mu)Co_2(CO)_6$ (340.4 mg, 29.6%, based on $Co_2(CO)_8$), m.p. 132°C; Anal. Found: C, 40.10; H, 3.01%. Calcd for $C_{28}H_{22}O_{16}Co_4$: C, 39.56; H, 2.61%. IR (KBr disc): ν(CO) 2097m, 2059vs, 2029vs cm^{-1}; ν(C=O) 1742m cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.06 (s, 2H, 2≡CH), 4.68 (s, 4H, $2OCH_2$), 2.37 (s, 4H, $2CH_2$), 1.64 (s, 4H, $2CH_2$), 1.31 (s, 8H, $4CH_2$) ppm. ESI-MS m/z: 872.8, $M + Na^+$; complex fragmentation.

2.4. *Reaction of* **1** *with* $Fe_3(CO)_{12}$ *to give* **4**

To a solution of **1** (114.4 mg, 0.15 mmol) in 20 mL of THF at 60°C was added $Fe_3(CO)_{12}$ (75.1 mg, 0.15 mmol) under argon. The reaction mixture was stirred for 12 h and the color gradually changed from orange-red to brown. A TLC analysis of the reaction mixture showed the disappearance of **1**. After solvent was removed under reduced pressure, the residue was separated by column chromatography on silica gel. Elution with CH_2Cl_2/petroleum ether (1:1) gave $Co_2(CO)_6(\mu\text{-}HCCCH_2OOC(CH_2)_3COOCH_2CCH\text{-}\mu,\eta^4)Co_2Fe_2(CO)_{12}$ (24.7 mg, 13.2%, based on **1**), m.p. 144°C; Anal. Found: C, 33.01; H, 1.32%. Calcd for $C_{29}H_{12}O_{22}Co_4Fe_2$: C, 32.87; H, 1.14%. IR (KBr disc): ν(CO) 2097s, 2058vs, 2026vs cm^{-1}; ν(C=O) 1741s cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (s, H, ≡CH), 6.08 (s, H, ≡CH), 5.52 (s, 2H, OCH_2), 5.11 (s, 2H, OCH_2), 2.38 (s, 4H, $2CH_2$), 1.87 (s, 2H, CH_2) ppm. ESI-MS m/z: 1082.2, $M + Na^+$; complex fragmentation.

2.5. *Reaction of* **3** *with* $Fe_3(CO)_{12}$ *to give* **5**

The preparation procedure for **5** was similar to that described above.

$Co_2(CO)_6(\mu\text{-}HCCCH_2OOCCOOCH_2CCH\text{-}\mu,\eta^4)Co_2Fe_2(CO)_{12}$ **5** (31.2 mg, 20.5%, based on **3**). Anal. Found: C, 34.14; H, 1.64%. Calcd for $C_{26}H_6Co_4Fe_2O_{22} \cdot 4/5C_6H_{14}$: C, 34.02; H, 1.60%. IR (KBr disc): ν(CO) 2096s, 2039vs, 1992(sh) cm^{-1}; ν(C=O) 1658cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (s, 1H, ≡CH), 5.96 (s, 1H, ≡CH), 5.08

(s, 2H, OCH_2), 4.24 (s, 2H, $2OCH_2$) ppm. ESI-MS m/z: 1063.9, $M+2Na^+$; complex fragmentation.

3. Results and discussion

3.1. *Characterization of* 1, 2, 4 *and* 5

IR spectra show intense terminal carbonyl absorption bands in the range 2098–2022 cm^{-1}, and a characteristic absorption band of the ester carbonyl at about 1741 cm^{-1} for **1**, **2**, **4** and 1658 cm^{-1} for **5**. Comparison with the literature data reveals that **1** and **2** show three main terminal carbonyl absorption bands in positions similar to reported cobalt-alkyne linked clusters (table 1). Clusters **4** and **5** have similar IR spectra to that of reported mixed-metal alkyne clusters (table 2); **4**'s carbonyl absorption positions are more similar to the mono-expanded linked octahedral rhodium-cobalt cluster $Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{-}C_6H_4\text{-}1,4\text{-}OCH_2C_2H\text{-}\mu)Co_2(CO)_6$ than to *tri*-nuclear iron-cobalt cluster $(\mu_3\text{-}FcCCH)FeCo_2(CO)_9$.

The ^1H NMR spectra of the new linked clusters are consistent with diyne ligand-capped cluster structures and show the presence of hydrogen atoms in their corresponding organic groups. For **1** and **2**, singlets at about δ 6.07–6.06 can be assigned to protons of the terminal alkyne (C_2H) groups coordinated to Co–Co cores. The signals at δ 4.82–4.68 are caused by $-OCH_2-$ groups and the peaks at δ 2.50–2.37, δ 2.04–1.64 and δ 1.31 reveal protons of different CH_2 groups of the dipropargyl ester ligands.

The ^1H NMR spectra of **4** and **5** are not the same as that of their precursors. For instance, the two protons of two C_2H groups appear as singlets at δ 8.08 and 6.08, δ 7.83 and 5.96 for **4** and **5**, respectively. Comparing ^1H-NMR spectra with those of reported alkyne-bridging cobalt clusters [8–10, 13], cobalt-iron clusters [23] and

Table 1. The IR $\nu(C\equiv O)$ data of **1**, **2** and other $Co_2(CO)_6(\mu\text{-}HCCR)$ clusters.

Cluster	IR $\nu(C\equiv O)/cm^{-1}$	Ref.
1	2098, 2055, 2022	This work
2	2097, 2059, 2029	This work
$(HOCC_2H\text{-}\mu)Co_2(CO)_6$	2097, 2062, 2050, 2026	4
$[CH_2(CO_2CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6]_2$	2099, 2058, 2029, 2008	13
$[C_6H_4(CO_2CH_2C_2H\text{-}\mu)_2][Co_2(CO)_6]_2$	2100, 2060, 2029, 1979	13

Table 2. The IR $\nu(C\equiv O)$ data of **4**, **5** and other $M_xCo_2(CO)_6(\mu\text{-}HCCR)$ clusters.

Cluster	IR $\nu(C\equiv O)/cm^{-1}$	Ref.
4	2097, 2058, 2026	This work
5	2096, 2039, 1992 (sh)	This work
$(\mu_3\text{-}FcCCH)FeCo_2(CO)_9$	2095, 2056, 2027, 2008, 1971	[23]
$Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{-}C_6H_4\text{-}1,4\text{-}OCH_2C_2H\text{-}\mu)Co_2(CO)_6$	2098, 2056, 2026, 1876 (μ-C≡O)	[19]

cobalt-rhodium cluster, $Rh_2Co_2(CO)_{10}(\mu_4,\eta^2\text{-}HC_2CH_2O\text{-}C_6H_4\text{-}1,4\text{-}OCH_2C_2H\text{-}\mu)Co_2(CO)_6$ [19], the singlets at δ 8.08 and 7.83 can be assigned to protons of the terminal alkynes (C_2H) coordinated to Fe_2Co_2 and at δ 6.08 and 5.96 to protons of the C_2H group coordinated to Co–Co. Signals at δ 5.52 and 5.11 for **4** and at δ 5.08 and 4.24 for **5** also identify two different OCH_2 groups. Resonances at δ 2.38 and 1.87 show the presence of different CH_2 groups in **4**.

On the basis of the IR and NMR spectra and elemental analysis and MS, we propose these new linked clusters' structures as that shown in schemes 1 and 2. During the thermo-expansion reactions of linked cobalt-alkyne carbonyl clusters $(Co_2(CO)_6(\mu\text{-}HCCCH_2OOC))_2R$ with $Fe_3(CO)_{12}$ at 60°C, the *tri*-nuclear iron carbonyl cluster provides the $Fe_2(CO)_6$ fragment to insert into the Co–Co bond forming an alkyne-bridging butterfly Fe–Co mixed-metal cluster.

Acknowledgements

We are grateful to the National Science Foundation of China (20561002) and the Education Department of Inner Mongulia Autonomous Region (NJ04079) and the "513" project of Inner Mongulia University for financial support of this work.

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