J. Chem. Research (S), 1998, 344–345†

Synthesis and Characterization of μ-Alkyne Molybdenum– and Tungsten–Cobalt Clusters containing Functionally Substituted Cyclopentadienyl Ligands†

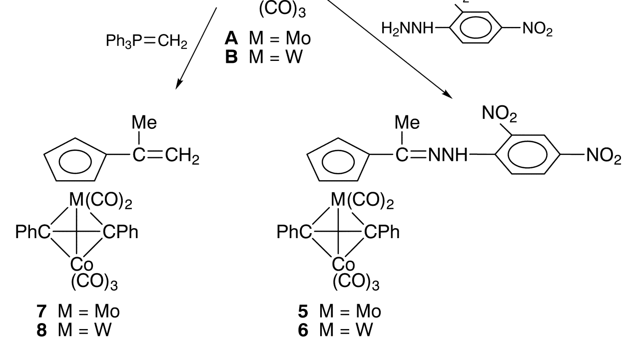
Li-Cheng Song,* Qing-Mei Hu, Jin-Song Yang and Jin-Yu Shen

Department of Chemistry, Nankai University, Tianjin 300071, China

Eight new μ-alkyne molybdenum– and tungsten–cobalt clusters containing functionally substituted cyclopentadienyl ligands have been synthesized *via* organic carbonyl transformation reactions of clusters $[(\eta^5\text{-MeCOC}_5\text{H}_4)(\text{OC})_2\text{M}(\mu\text{-C}_2\text{Ph}_2)\text{Co(CO)}_3]$ (M = Mo or W).

Transition-metal clusters, particularly those containing functionally substituted cyclopentadienyl ligands are of great interest due to their potential applications in catalytic processes[1–4] and for synthesizing a variety of novel cluster derivatives which would be difficult or even not possible by other methods.[5,6] Herein we report some transformation reactions of the carbonyl group on the cyclopentadienyl ring of clusters $[(\eta^5\text{-MeCOC}_5\text{H}_4)(\text{OC})_2(\mu\text{-C}_2\text{Ph}_2)\text{Co(CO)}_3]$ (M = Mo or W), from which eight new μ-alkyne molybdenum– and tungsten–cobalt cluster derivatives were obtained.

We found that clusters $[(\eta^5\text{-MeCOC}_5\text{H}_4)(\text{OC})_2\text{M}(\mu\text{-C}_2\text{Ph}_2)\text{Co(CO)}_3]$ (**A**, M = Mo; **B**, M = W) could be reduced by NaBH_4 in methanol to give secondary alcohol clusters **1** and **2**, whereas they reacted with MeMgI followed by acidic hydrolysis to give tertiary alcohol clusters **3** and **4**, respectively. More interestingly, reactions of **A** and **B** with 2,4-dinitrophenylhydrazine afforded their phenylhydrazone derivatives **5** and **6**, whereas when treated with Wittig reagent $\text{Ph}_3\text{P{=}CH}_2$ they gave corresponding olefinic cluster derivatives **7** and **8**, respectively. All the reactions mentioned are summarized in Scheme 1.



Scheme 1

Compounds **1**–**8** are all new functional cyclopentadienyl MCoC_2 clusters (M = Mo or W), which have been well characterized by elemental analysis, IR, ^{1}H NMR and MS data. For example, the IR spectra of **1**–**4** show the hydroxyl group absorption bands at 3400–3436 cm^{-1}; **5**–**8** exhibit the absorption bands characteristic of the functional groups of C=N at 1614 cm^{-1} and C=C at 1625–1630 cm^{-1}, respectively. The ^{1}H NMR spectra of **1**–**8** reveal all the corresponding protons, such as those of the hydroxyl groups of **1**–**4** between δ 1.46 and 1.60, the protons of the 2,4-dinitrophenyl groups of **5**, **6** at δ 7.83–9.20, and those attached to the double bond of **7**, **8** at δ 4.84–5.13.

Experimental

IR and ^{1}H NMR spectra were recorded on a Nicolet FT-IR 5DX spectrophotometer and a JEOL FX 90Q spectrometer. Analyses (C, H), MS and melting point were determined using a Perkin-Elmer 240C model analyzer, a HP 5988A spectrometer and a Yanako MP-500 instrument, respectively. All reactions were carried out under nitrogen. Commercial NaBH_4, $\text{Ph}_3\text{PCH}_3\text{Br}$ and 2,4-dinitrophenylhydrazine were used as received; MeMgI[7] and $[(\eta^5\text{-MeCOC}_5\text{H}_4)(\text{OC})_2\text{M}(\mu\text{-C}_2\text{Ph}_2)\text{Co(CO)}_3]$ (M = Mo or W)[8] were prepared according to literature methods.

Preparations.—Compounds of **1** *and* **2**. A 50 ml two-necked flask was charged with $[(\eta^5\text{-MeCOC}_5\text{H}_4)(\text{OC})_2\text{M}(\mu\text{-C}_2\text{Ph}_2)\text{Co(CO)}_3]$ **A** (58 mg, 0.1 mmol) or $[(\eta^5\text{-MeCOC}_5\text{H}_4)(\text{OC})_2\text{W}(\mu\text{-C}_2\text{Ph}_2)\text{Co(CO)}_3]$ **B** (69 mg, 0.1 mmol), NaBH_4 (7.6 mg, 0.2 mmol) and MeOH (3 ml). The mixture was stirred for 1.5 h at r.t. and then subjected to TLC using CH_2Cl_2 as eluent to give **1** or **2**. **1**: red oil, yield 76%; $\tilde{\nu}_{\text{max}}$/cm^{-1} 2057, 2000, 1975, 1926 (C≡O), 3400 (OH); δ_H (CDCl_3) 1.40 (d, 3 H, *J* 7.2, CH_3), 1.46–1.60 (br, 1 H, OH), 4.48 (q, 1 H, *J* 7.2 Hz, CH), 5.18–5.54 (m, 4 H, C_5H_4), 7.10–7.58 (m, 10 H, $2\text{C}_6\text{H}_5$); *m*/*z* 402 ($\text{M}^+ - 2\text{Ph} - \text{CO}$, 1), 181 ($\text{C}_2\text{CoMo}^+$, 3%) (Found: C, 53.74; H, 3.26. $\text{C}_{26}\text{H}_{19}\text{CoMoO}_6$ requires C, 53.63; H, 3.29%). **2**: red oil, yield 51%; $\tilde{\nu}_{\text{max}}$/cm^{-1} 2049, 2000, 1975, 1926 (C≡O), 3435 (OH). δ_H (CDCl_3) 1.40 (d, 3 H, *J* 7.2, CH_3), 1.48–1.60 (br, 1 H, OH), 4.50 (q, 1 H, *J* 7.2 Hz, CH), 5.20–5.58 (m, 4 H, C_5H_4), 7.00–7.40 (m, 10 H, $2\text{C}_6\text{H}_5$); *m*/*z* 614 ($\text{M}^+ - 2\text{CO}$, 8), 267 (C_2CoW^+, 5%) (Found: C, 47.08; H, 2.63. $\text{C}_{26}\text{H}_{19}\text{CoO}_6\text{W}$ requires C, 46.59; H, 2.86%).

Compounds **3** *and* **4**. A 50 ml two-necked flask was charged sequentially with diethyl ether (10 ml), **A** (197 mg, 0.34 mmol) or **B** (227 mg, 0.34 mmol) and MeMgI–diethyl ether solution (0.59 M, 2.0 ml) with stirring at r.t. After stirring for 3 h, distilled water (50 ml) and dilute HCl (0.167 M, 10 ml) were added. The ether phase was separated and the aqueous phase extracted with diethyl ether (2 × 10 ml). All the ether layers were combined. After removal of the ether, the residue was subjected to TLC separation using CH_2Cl_2–light petroleum (bp 60–90 °C) (2:1) as eluent to give **3** or **4**. **3**: red oil, yield 12%; $\tilde{\nu}_{\text{max}}$/cm^{-1} 2049, 2000, 1975, 1934 (C≡O), 3436 (OH); δ_H (CDCl_3) 1.52 (s, 6 H, 2CH_3), 1.40–1.50 (br, 1 H, OH), 5.14 (t, 2 H, *J* 2.4, H^3, H^4), 5.48 (t, 2 H, *J* 2.4 Hz, H^2, H^5), 7.12–7.48 (m, 10 H, $2\text{C}_6\text{H}_5$); *m*/*z* 542 ($\text{M}^+ - 2\text{CO}$, 0.3), 181 (C_2CoMo^+, 0.4%) (Found: C, 54.80; H, 3.62. $\text{C}_{27}\text{H}_{21}\text{CoMoO}_6$ requires C, 54.38; H, 3.55%). **4**: red oil, yield 15%; $\tilde{\nu}_{\text{max}}$/cm^{-1} 2049, 2000, 1975, 1926 (C≡O), 3403 (OH); δ_H (CDCl_3) 1.54 (s, 6 H, 2CH_3), 1.46–1.56 (br, 1 H, OH), 5.32 (t, 2 H, *J* 2.4, H^3, H^4), 5.52 (t, 2 H, *J* 2.4 Hz, H^2, H^5), 7.28 (s, 10 H, $2\text{C}_6\text{H}_5$); *m*/*z* 628

---

*To receive any correspondence.

†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

($M^+ - 2CO$, 0.5), 267 (C_2CoW^+, 3%) (Found: C, 49.09; H, 3.02. $C_{27}H_{21}CoO_6W$ requires C, 47.40; H, 3.09%).

Compounds **5** *and* **6**. A 50 ml two-necked flask was charged with **A** (150 mg, 0.26 mmol) or **B** (400 mg, 0.26 mmol) and anhydrous ethanol (5 ml), to which was slowly added a 2,4-dinitrophenylhydrazine solution (1.5 ml, 0.52 mmol) (prepared by dissolving 1.0 g of 2,4-dinitrophenylhydrazine in 5 ml of 98% H_2SO_4, 10 ml of H_2O and 35 ml of 95% C_2H_5OH) with stirring. After stirring at r.t. for 1.5 h to give a precipitate, which was purified by TLC using CH_2Cl_2–light petroleum–diethyl ether (1:5:1) as eluent to afford **5** or **6**. **5**: brown-red solid, mp 95 °C (decomp.), yield 41%; $\tilde{\nu}_{max}/cm^{-1}$ 2049, 1983, 1942 ($C{\equiv}O$), 1614 ($C{=}N$); δ_H ($CDCl_3$) 1.72 (s, 3 H, CH_3), 5.52 (s, 2 H, H^3, H^4 of C_5H_4 ring), 5.76 (s, 2 H, H^2, H^5 of C_5H_4 ring), 7.20 (s, 10 H, $2C_6H_5$). 7.83 (d, 1 H, J 9.8, H^6 of benzene ring), 8.30 (d, 1 H, J 9.8 Hz, H^5 of benzene ring), 9.20 (s, 1 H, H^3 of benzene ring), 10.88 (s, 1 H, NH) (Found: C, 51.00; H, 3.29; N, 7.58. $C_{32}H_{21}CoMoN_4O_9$ requires C, 50.54; H, 2.78; N, 7.37%). **6**: brown-red solid, mp 128 °C (decomp.), yield 72%; $\tilde{\nu}_{max}/cm^{-1}$ 2049, 2000, 1975, 1934 ($C{\equiv}O$), 1614 ($C{=}N$); δ_H ($CDCl_3$) 1.70 (s, 3 H, CH_3), 5.62 (t, 2 H, J 2.5, H^3, H^4 of C_5H_4 ring), 5.82 (t, 2 H, J 2.5, H^2 H^5 of C_5H_4 ring), 7.21 (s, 10 H, $2C_6H_5$) 7.85 (d, 1 H, J 9.7, H^6 of benzene ring), 8.36 (d, 1 H, J 9.7 Hz, H^5 of benzene ring), 9.18 (s, 1 H, H^3 of benzene ring), 10.91 (s, 1 H, NH) (Found: C, 45.13; H, 2.60; N, 6.85. $C_{32}H_{21}CoN_4O_9W$ requires. C, 45.31; H, 2.50; N, 6.61%).

Compounds **7** *and* **8**. A 50 ml two-necked flask was charged with Ph_3PCH_3Br (528 mg, 1.48 mmol) and THF (20 ml), to which was slowly added a Bu^nLi–hexane solution (1.06 M, 1.4 ml) at 0 °C and then stirred for 4 h at r.t. to give a mixture containing Wittig reagent $Ph_3P{=}CH_2$. To this was added 10 ml of a THF solution of **A** (429 mg, 0.74 mmol) or **B** (494 mg, 0.74 mmol) and then the mixture was stirred for 3 h at r.t. It was subjected to TLC using CH_2Cl_2–light petroleum (1:3) as eluent to give **7** or **8**. **7**: red solid, mp 56–57 °C, yield 43%; $\tilde{\nu}_{max}/cm^{-1}$ 2041, 2007, 1975, 1934 ($C{\equiv}O$), 1625 ($C{=}C$); δ_H ($CDCl_3$) 1.76 (s, 3 H, CH_3), 4.84 (s, 1 H, $C{=}CH$), 5.13 (s, 1 H, $C{=}CH$), 5.20 (s, 2 H, H^3, H^4), 5.48 (s, 2 H, H^2, H^5), 7.23 (s, 10 H, $2C_6H_5$); m/z 524 ($M^+ - 2CO$, 7%) (Found: C, 56.88; H, 3.60. $C_{27}H_{19}CoMoO_5$ requires C, 56.94; H, 3.54%). **8**: red solid, mp 78–80 °C, yield 23%; $\tilde{\nu}_{max}/cm^{-1}$ 2041, 2000, 1975, 1942 ($C{\equiv}O$), 1631 ($C{=}C$); δ_H ($CDCl_3$) 1.72 (s, 3 H, CH_3), 4.86 (s, 1 H, $C{=}CH$), 5.10 (s, 1 H, $C{=}CH$), 5.30 (s, 2 H, H^3, H^4), 5.52 (s, 2 H, H^2, H^5), 7.18 (s, 10 H, $2C_6H_5$); m/z 610 ($M^+ - 2CO$, 9%) (Found: C, 48.95; H, 3.10. $C_{27}H_{19}CoO_5W$ requires C, 48.68; H, 2.87%).

We thank the National Natural Science Foundation of China, the Laboratory of Organometallic Chemistry and the Special Foundation of State Education Committee of China for financial support.

Received, 13th January 1998; Accepted, 2nd March 1998
Paper E/8/00350E

References

1 E. L. Muetterties and M. J. Krause, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 135.
2 M. D. Curtis, J. E. Penner-Hahn, J. Schwank, O. Baralt, D. J. McCabe, L. Thompson and G. Waldo, *Polyhedron*, 1988, **7**, 2411.
3 M. R. DuBois, *Chem. Rev.*, 1989, **89**, 1.
4 P. Braunstein and J. Rose, in *Comprehensive Organometallic Chemistry II*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 10, p. 351.
5 L-C. Song, J-Y. Shen, Q-M. Hu and X-Y. Huang, *Organometallics*, 1995, **14**, 98.
6 L-C. Song, J-Y. Shen, Q-M. Hu and X-Y. Huang, *Inorg. Chim. Acta*, 1996, **249**, 175.
7 H. Gilman, E. A. Zoellner and J. B. Dickey, *J. Am. Chem. Soc.*, 1929, **51**, 1576.
8 L-C. Song, J-Y. Shen, Q-M. Hu, B-S. Han, R-J. Wang and H-G. Wang, *Inorg. Chim. Acta*, 1994, **219**, 93.