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SYNTHESIS, CHARACTERIZATION AND CRYSTAL STRUCTURE OF HETERO-METAL CLUSTERS $RCCo_2M(CO)_8(CH_3Cp)$ AND $RCCoM_2(CO)_7(CH_3Cp)_2$†

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Abstract—Six hetero-metal clusters $RCCo_2M(CO)_8Cp'$ and $RCCoM_2(CO)_7Cp'_2$ (R = Ph, $C_2H_5O_2C$; M = Mo,W; Cp′ = CH_3Cp) were synthesized by refluxing a solution of the clusters $RCCo_3(CO)_9$ and $NaM(CO)_3Cp'$ in THF through metal exchange reactions, in which the metal unit $Co(CO)_3$ in the $RCCo_3(CO)_9$ cluster was exchanged by $M(CO)_2Cp'$. The clusters were characterized by elemental analysis, IR and ^1H NMR along with the crystal structure of $[C_2H_5O_2CCCoMo_2(CO)_7Cp'_2]$.

The hetero-metal tetrahedral clusters can be formed directly in one-step[1] or in multi-step addition and substitution reaction by systematic addition and incorporation of organometallic units[2,3] or by the metal exchange reaction using $Me_2AsM(CO)_3Cp$, $[M(CO)_3Cp]_2$, $HM(CO)_3Cp$, $ClM(CO)_3Cp$ and $NaM(CO)_3Cp$ as metal exchange reagent.[4–7] In these synthetic methods, the metal exchange reaction, which was reported by Vahrenkamp and his co-workers, is the most simple and direct method because it exhibits advantages in both the yield and preparative process. Some μ_3-alkylidyne Co_2M and CoM_2 clusters have been synthesized by reaction of $RCCo_3(CO)_9$ with metal exchange reagents mentioned above, but no clusters Co_2M and CoM_2 containing methyl cyclopentadienyl have been reported up to now. In order to explore the generality of this kind of metal exchange reaction, we have studied the reaction of clusters $RCCo_3(CO)_9$ (R = Ph, $C_2H_5O_2C$) with new metal reagents $NaM(CO)_3Cp'$ (M = Mo, W; Cp′ = CH_3Cp) by the metal exchange reaction. We report elemental analysis, IR and ^1H NMR of six new hetero-metal clusters and the X-ray crystallography structure of cluster $[C_2H_5O_2CCCoMo_2(CO)_7(CH_3Cp)_2]$.

RESULTS AND DISCUSSION

Synthesis

All clusters were prepared by refluxing a solution of $RCCo_3(CO)_9$ clusters with $NaM(CO)_3Cp$ [starting material ratio (mol): $RCCo_3(CO)_9$: $NaM(CO)_3Cp'$ = 1 : 1.5–2.0 for Co_2M and 1 : 4 for CoM_2] in THF, refluxing time about 3–8 h and 48–54 h for Co_2Mo and CoM_2, respectively. Synthesis routes are as follows:

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$$\mathrm{RCCo_3(CO)_9 + NaM(CO)_3Cp'} \longrightarrow \mathrm{RCCo_2M(CO)_8Cp'}$$

R = Ph(**1**), $\mathrm{C_2H_5O_2C}$(**1′**) R = Ph, M = Mo(**2a**);

R = $\mathrm{C_2H_5O_2C}$, M = Mo(**3a**), W(**3b**).

$$(\mathbf{1'}) + \mathrm{2NaM(CO)_3Cp'} \longrightarrow \mathrm{RCCoM_2(CO)_7Cp'_2}$$

R = Ph, M = Mo(**4a**); R = $\mathrm{C_2H_5O_2C}$,

M = Mo(**5a**), W(**5b**).

The clusters are air-stable black solids, but they are air-sensitive in solution. Yields of products are in the range of 30.0–56.9%. A trace red by-product $\mathrm{[M(CO)_3Cp']_2}$ which was confirmed by C/H analysis and ^{1}H NMR spectra as obtained. Reaction of (**1,1′**) with $\mathrm{NaMo(CO)_3Cp'}$ produced higher yields than that with $\mathrm{NaW(CO)_3Cp'}$. It is because $\mathrm{NaW(CO)_3Cp'}$ was more easily oxidized into the dimer $\mathrm{[W(CO)_3Cp']_2}$ than $\mathrm{NaMo(CO)_3Cp'}$ during the reaction. Data for elemental analysis for the clusters mentioned above are consistent with the expected formulae. The results showed that one or two $\mathrm{Co(CO)_3}$ units in the cluster (**1,1′**) could be exchanged by one or two equal electron $\mathrm{Mo(CO)_2Cp'}$ units and gave hetero-metal $\mathrm{Co_2M}$ and $\mathrm{CoM_2}$ clusters. A trace of the $\mathrm{Co_2M}$ cluster was obtained during procedure of preparing $\mathrm{Co_2M}$. The reactive process for clusters $\mathrm{CoM_2}$ is as follows: $\mathrm{Co_3 \rightarrow Co_2M \rightarrow CoM_2}$. The results agreeed with the literature[4b] showing the generality of this kind of reaction.

Spectra

For the IR spectra, all clusters exhibited a large number of absorption bands between 2077 and 1847 cm^{-1}, which were assigned to terminal carbonyl peaks. Vibration absorption of the carbonyl group —CO— in the bridging substituent $\mathrm{C_2H_5OCO}$— gives 1776 ($\mathrm{Co_3}$), 1664 ($\mathrm{Co_2M}$), 1647 ($\mathrm{CoM_2}$), respectively. This result suggested that the C═O absorption peak shifts to lower wavenumbers with increasing number of $\mathrm{Co(CO)_3}$ displaced by $\mathrm{M(CO)_2Cp'}$.

For ^{1}H NMR assignment, an apparent triplet and a quartet at 1.28–1.37 and 4.20–4.28 ppm were assigned to protons of $\mathrm{CH_3}$ and $\mathrm{CH_2}$ in group $\mathrm{CH_3CH_2OC}$. The chemical shift value of $\mathrm{CH_3}$ on the cyclopentadienyl ring was in the range 2.05–2.25 ppm. Apparent single peaks at 4.95–5.28 and 7.18 ppm were assigned to protons of cyclopentadienyl and the benzenyl ring, respectively.

Crystal structure analysis

Selected bond lengths (Å) and bond angles (°) are listed in Table 1. As seen from Fig. 1, the titled

Table 1. Selected bond lengths (Å) and bond angles (°) for the non-hydrogen atoms of cluster (**5a**)

Bond lengths					
Mo(1)—Mo(1)	2.960(2)	Mo(1)—Co	2.731(2)	Mo(2)—Co	2.7356(9)
C(1)—Mo(1)	2.090(4)	C(1)—Mo(2)	2.117(5)	C(1)—Co	1.935(4)
Mo(1)—C(CO)	1.984ave.	Mo(2)—C(CO)	1.953ave.	Co—C(CO)	1.791ave.
$(\mathrm{C—O})_{\mathrm{Mo(1)}}$	1.145ave.	$(\mathrm{C—O})_{\mathrm{Mo(2)}}$	1.157ave.	$(\mathrm{C—O})_{\mathrm{Co}}$	1.133ave.
$(\mathrm{C_{Cp}—C_{Cp}})_{\mathrm{Mo(1)}}$	1.400(9)–1.416(8)			$(\mathrm{C_{Cp}—C_{Cp}})_{\mathrm{Mo(2)}}$	1.401(8)–1.418(8)
$\mathrm{Mo(1)—C_{Cp}}$	2.291(5)–2.377(5)			$\mathrm{Mo(2)—C_{Cp}}$	2.319(5)–2.375(5)
C(1)—C(2)	1.485(6)	C(2)—O*(2)	1.210(5)	C(2)—O(1)	1.346(5)
O(1)—C(3)	1.461(6)	C(2)—C(4)	1.479(8)		
Bond angles					
Mo(1)—C(1)—Mo(2)	89.4(2)	Mo(1)—C(1)—Co	85.3(2)	Mo(2)—C(1)—Co	84.5(2)
Mo(1)—Co—Mo(2)	65.58(4)	Mo(1)—Mo(2)—Co	57.13(4)	Mo(2)—Mo(1)—Co	57.29(4)
C(2)—C(1)—Mo(1)	131.3(3)	C(2)—C(1)—Mo(2)	12.0(3)	C(2)—C(1)—Co	128.4(3)
O(01)—C(01)—Mo(1)	177.45(5)	O(02)—C(02)—Mo(1)	176.8(4)	O(03)—C(03)—Mo(2)	168.7(5)
O(04)—C(04)—Mo(2)	173.7(5)	O—C—Co	177.0(5)–178.4(6)		
C(16)—C(11)—Mo(1)	126.0(4)	C(16)—C(11)—C(15)	126.7(6)	C(16)—C(11)—C(12)	126.7(5)
C(26)—C(21)—Mo(2)	127.4(4)	C(26)—C(21)—C(22)	126.3(6)	C(26)—C(21)—C(25)	126.1(6)
$\mathrm{(C_{Cp}—C_{Cp}—C_{Cp})Mo(1)}$	106.3(5)–109.5(5)	$\mathrm{(C_{Cp}—C_{Cp}—C_{Cp})Mo(2)}$	105.6(5)–110.5(5)		
C(1)—C(2)—O(1)	113.0(4)	C(1)—C(2)—O(2)	126.0(4)	O(1)—C(2)—O(2)	121.1(4)
C(2)—O(1)—C(3)	115.8(4)	O(1)—C(3)—C(4)	106.9(4)		

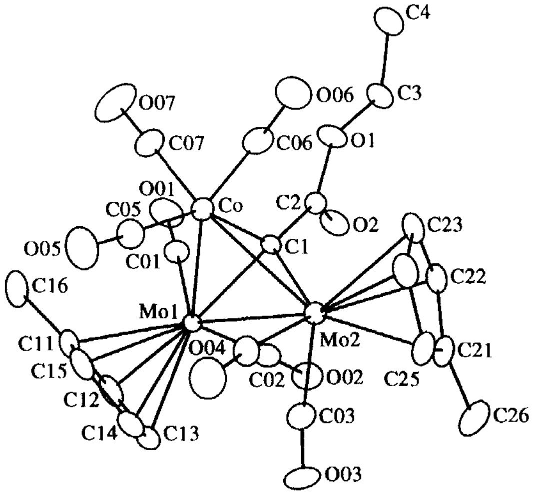

Fig. 1. The crystal structure of **4a**.

cluster was a tetrahedral skeleton formed by C, Co and two Mo atoms. The C atom caps the triangular $CoMo_2$ plane. Seven two-electron terminal carbonyl ligands are bonded to Co and Mo, and two five-electron cyclopentadienyl ligands, which are bonded to two Mo atoms, distribute above and below the $CoMo_2$ plane. This is due to the steric requirement of two cyclopentadienyls. Structural data of the cluster (**5a**) were compared with values for the cluster $CH_3CCoMo_2(CO)_7Cp_2$ in the literature.[4h] Bond lengths Co—Mo and Mo—Mo in the cluster (**5a**) are longer than values in $CH_3CCoMo_2(CO)_7Cp_2$, but bond lengths between the C atom and Co and Mo in (**5a**) are shorter than in $CH_3CCoMo_2(CO)_7Cp_2$. Other bond lengths in (**5a**) for Mo—C(CO), Co—C(CO), Mo—C(Cp) are basically equal to values in $CH_3CCoMo_2(CO)_7Cp_2$. C(2)—C(1)—Mo and C(2)—C(1)—Co bond angles 123(3)/131(3) and 128(3)° of (**5a**) are not equal to values 127(1)/133(1) and 125(1)° or $CH_3CCoMo_2(CO)_7Cp_2$. The dihedral plane angle of triangle plane $CoMo_2$ with the plane formed by C(1)—C(2)—O(1)—O(2) is 92.97°. The two planes are approximately perpendicular to each other.

EXPERIMENTAL

All operations were carried out under highly pure nitrogen using standard Schlenk and vacuum line techniques. The solvents were treated by the usual method for preparing anhydrous and deoxygenated solvents. Clusters $PhCCo_3(CO)_9$ and $C_2H_5O_2CCo_3(CO)_9$ were prepared according to the literature.[8,9] IR spectra were recorded on a Nicolet FT-IR 10DX infrared spectrophotometer; ^1H NMR spectra were recorded on a FT-80 NMR spectrometer; C/H analysis determination was performed by a 1106-type analyser, respectively.

Preparation of clusters Co_2M *and* CoM_2

To a solution of $NaM(CO)_3Cp'$ in THF was added $RCCo_3(CO)_9$. The mixture was refluxed for certain time (about 3–8 and 48–54 h for Co_2M and CoM_2). Solvent was evaporated under reduced pressure and the residue was extracted with benzene. The extracts were chromatographed on a 45×2.5 cm silica gel column using benzene/*n*-hexane as eluant. Products were recrystallized in 5:1 hexane/benzene at −20°C. **2a**: Yield: 56.1%. Found: C, 43.8; H, 2.2. Calc. for $C_{21}Co_2H_{12}O_8Mo$: C, 41.0; H, 2.0%. IR(KBr disk): ν(terminal CO) 2066s, 2029s, 2019s, 2008s, 1995vs, 1982s, 1968s, 1932s cm^{-1}. ^1H NMR($CDCl_3$): δ 2.08 (s, 3H, CH_3Cp); 5.11 (s, 4H, C_5H_4); 7.18 (s, 5H, C_6H_5).

3a: Yield: 56.9%. Found: C, 35.9; H, 1.9. Calc. for $C_{18}Co_2H_{12}MoO_{10}$: C, 35.9; H, 2.0%. IR(KBr disk): ν(C=O) 1664s, ν(terminal CO) 2077vs, 2036vs, 2020vs, 1999vs, 1991s, 1970s, 1951s, 1927w. ^1H NMR($CDCl_3$): δ 1.37 (t, 3H, CH_3); 4.28 (q, 2H, CH_2); 2.12 (s, 3H, CH_3Cp); 5.25 (s, 4H, C_5H_4).

3b: Yield: 30.9%. Found: C, 30.9; H, 1.7. Calc. for $C_{18}Co_2H_{12}O_{10}W$: C, 31.3; H, 1.7%. IR(KBr disk): ν(C=O) 1665s, ν(terminal CO) 2077s, 2035s, 2020s, 1665s, 1989vs, 1967vs, 1940s. ^1H NMR($CDCl_3$): δ 1.30 (t, 3H, CH_3); 4.21 (q, 2H, CH_2); 2.25 (s, 3H, CH_3); 4.21 (q, 2H, CH_2).

4a: Yield: 37.9%. Found: C, 44.9; H, 2.9. Calc. for $C_{25}CoH_{15}Mo_2O_7$: C, 45.0; H, 2.7%. IR(KBr disk): ν(terminal CO) 2032s, 2006s, 1989vs, 1970vs, 1952s, 1944s, 1911s, 1946m. ^1H NMR ($CDCl_3$): δ 2.05 (s, 6H, $2CH_3Cp$): 4.95 (s, 8H, C_5H_4); 7.18 (s, 5H, C_6H_5).

5a: Yield: 48.9%. Found: C, 39.5; H, 2.7. Calc. for $C_{23}CoH_{19}Mo_2O_9$: C, 40.0; H, 2.7%. IR(KBr disk): ν(C=O) 1647s, ν(terminal CO) 2031vs, 2006vs, 1967s, 1912vs, 1854vs. ^1H NMR($CDCl_3$): δ 1.37 (t, 3H, CH_3); 4.28 (q, 2H, CH_2); 2.12 (s, 3H, CH_3Cp); 5.12 (s, 4H, C_5H_4).

5b: Yield: 32.6%. Found: C, 31.1; H, 2.1. Calc. for $C_{23}CoH_{19}O_9W_2$: C, 31.9; H, 2.2%. IR(KBr disk): ν(C=O) 1647s, ν(terminal CO) 2039vs, 2002vs, 1647s, 1975vs, 1848vs. ^1H NMR($CDCl_3$): δ 1.28 (t, 3H, CH_3); 4.20(q, 2H, CH_2); 2.12 (s, 6H, $2CH_3Cp$); 5.20 (s, 8H, $2C_5H_4$).

Crystallography of (**5a**)

A black crystal (**5a**) was obtained from 5:1 hexane/benzene at −20°C. A crystal of approximate dimensions 0.85×0.55×0.225 mm^3 was mounted on a glass fibre. Preliminary examination and data collection were performed with Mo-K_α radiation ($\lambda = 0.71069$ Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite monochromator. A total of 4947 reflections measured was collected in 2θmax $= 25°$ by the scan technique, of which 3947 reflections with $I > 3\sigma(I)$ were considered to be observed. The corrections for Lp factors and empirical absorption were applied to the intensity data.

The crystal is monoclinic space group $P2_1/c$, with $a = 8.486(6)$, $b = 12.624(5)$, $c = 23.594(5)$ Å, $\beta = 97.11(5)°$, $M_r = 690.21$, $Z = 4$, $D_x = 1.83$ g cm^{-3}, $\mu = 16.62$ cm^{-1}, $F(000) = 1360$, $R = 0.064$, $R_W = 0.060$, $\rho = 0.08$ e Å^{-1}.

The structure was solved by the Patterson/Heavy Atom method. Fourier and difference Fourier methods revealed all non-hydrogen atoms in chemically acceptable positions. The final refinement by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms converge with unweighted and weighted R factors of 0.046 and 0.060. The highest peak on the final difference Fourier map is at a height of 0.803 e Å^{-3}.

All calculations were performed on a Micro Vax 3100 computer using the Texsan V.2.1 program system. A weighting scheme $\omega = 1/\sigma^2\ (|F_o|)$ was used in the later stages of refinement.

REFERENCES

1. S. A. Khatlab, L. Mark, G. Bor and B. Marko, *J. Organomet. Chem.* 1964, **1**, 373.
2. P. C. Steinhardt, W. L. Gladfelter, D. Harley, J. R. Fox and G. L. Geoffroy, *Inorg. Chem.* 1980, **19**, 332.
3. H. Beurich and H. Vahrenkamp, *Angew. Chem.* 1978, **90**, 915; *Angew. Chem., Int. Ed. Engl.* 1978, **17**, 863.
4. (a) H. Beurich and H. Vahrenkamp, *Chem. Ber.* 1982, **115**, 2385; (b) R. Blumhofer, K. Fischer and H. Vahrenkamp, *Chem. Ber.* 1986, **119**, 194.
5. H. Beurich, R. Blumhofer and H. Vahrenkamp, *Chem. Ber.* 1982, **115**, 2409.
6. H. T. Schach and H. Vahrenkamp, *J. Organomet. Chem.* 1990, **381**, 261.
7. S. Jensen, B. H. Robinson and J. Simpson, *J. Chem. Soc., Chem. Commun.* 1983, 1081.
8. D. Seyferth, *Adv. Organomet. Chem.* 1976, **14**, 997.
9. D. Seyferth, J. E. Hallgren and P. L. K. Hung, *J. Organomet. Chem.* 1973, **50**, 265.