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THE STUDY OF ISOLOBAL DISPLACEMENT REACTIONS. SYNTHESIS AND CHARACTERIZATION OF HETERONUCLEAR TRANSITION-METAL CLUSTERS $[(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_2\text{M}][(\eta^5\text{-R}'\text{C}_5\text{H}_4)(\text{CO})_2\text{M}']\text{Fe(CO)}_3(\mu_3\text{-S})$, $[(\eta^5\text{-R}'\text{C}_5\text{H}_4)(\text{CO})_2\text{M}']_2\text{Fe(CO)}_3(\mu_3\text{-S})$ (M,M′ = Mo or W) AND $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}][(\eta^5\text{-MeC(O)C}_5\text{H}_4)(\text{CO})_2\text{W}]\text{Fe(CO)}_3(\mu_3\text{-S})$

LI-CHENG SONG,* JIN-YU SHEN, QING-MEI HU and XIANG-DONG QIN

Department of Chemistry, Nankai University, Tianjin, 300071, China

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Abstract—The isolobal displacement reactions between cluster compounds $[(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_2\text{M}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$ and group 6 metal anions $\eta^5\text{-R}'\text{C}_5\text{H}_4(\text{CO})_3\text{M}'^-$ afforded eight heteronuclear transition-metal clusters $[(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_2\text{M}][(\eta^5\text{-R}'\text{C}_5\text{H}_4)(\text{CO})_2\text{M}']\text{Fe(CO)}_3(\mu_3\text{-S})$ (**1a**: R = CO_2Et, M = W, R′ = H, M′ = Mo; **1b**: CO_2Me, W, C(O)Me, Mo; **1c**: CO_2Me, W, CO_2Me, Mo; **1d**: CO_2Et, Mo, Me, W) and $[(\eta^5\text{-R}'\text{C}_5\text{H}_4)(\text{CO})_2\text{M}']_2\text{Fe(CO)}_3(\mu_3\text{-S})$ (**2a**: R′ = H, M′ = Mo; **2b**: C(O)Me, Mo; **2c**: CO_2Me, Mo; **2d**: Me, W). Similarly, the isolobal reaction between $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$ and $\eta^5\text{-MeC(O)C}_5\text{H}_4(\text{CO})_3\text{W}^-$ gave three heteronuclear transition metal clusters $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}][(\eta^5\text{-MeC(O)C}_5\text{H}_4)(\text{CO})_2\text{W}]\text{Fe(CO)}_3(\mu_3\text{-S})$ (**1e**), $[(\eta^5\text{-MeC(O)C}_5\text{H}_4)(\text{CO})_2\text{W}]_2\text{Fe(CO)}_3(\mu_3\text{-S})$ (**2e**) and $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}]_2\text{Fe(CO)}_3(\mu_3\text{-S})$ (**3**). All the compounds **1a–e**, **2a–e** and **3** were fully characterized by elemental and spectroscopic analyses. In addition, the possible reaction pathways for the formation of these products are preliminarily proposed.

In recent years the isolobal displacement reactions, due to their theoretical interest and wide uses in rational synthesis of transition-metal cluster complexes, have attracted considerable attention.[1–19] So far, many examples are known in which a d^9 ML_3 fragment Co(CO)_3 can be displaced by an isolobal d^5 ML_5 fragment $\text{Cp}^*(\text{CO})_2\text{M}$ (Cp^* = Cp or substituted Cp; M = Cr, Mo, W).[1–16] However, it remains obscure whether or not two different d^5 ML_5 fragments of the type $\text{Cp}^*(\text{CO})_2\text{M}$ could displace each other in the system involving Co(CO)_3-containing cluster complexes. In order to answer this question and to develop the rational synthetic method for transition-metal cluster complexes, we have carried out an investigation of the isolobal reactions between $[(\eta^5\text{-RC}_5\text{H}_4)(\text{CO})_2\text{M}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$ (R = CO_2Me, CO_2Et; M = Mo, W) and $\eta^5\text{-R}'\text{C}_5\text{H}_4(\text{CO})_3\text{M}'^-$(R = H, Me, C(O)Me, CO_2Me; M = Mo, W) and between $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$ and $\eta^5\text{-MeC(O)C}_5\text{H}_4(\text{CO})_3\text{W}^-$. Herein we report the results concerning this study.

EXPERIMENTAL

All reactions were carried out under dry nitrogen. Diglyme and THF were distilled from sodium benzophenone ketyl and purged with nitrogen prior to use. Mo(CO)_6 and W(CO)_6 were purchased from Strem Chemicals Inc., $\text{MeC(O)C}_5\text{H}_4\text{Na}$, $\text{MeO}_2\text{CC}_5\text{H}_4\text{Na}$,[20] $[\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3]_2$, $[\eta^5\text{-MeC}_5\text{H}_4\text{W(CO)}_3]_2$,[21] $[(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{Mo}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$, $[(\eta^5\text{-MeO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$, $[(\eta^5\text{-EtO}_2\text{CC}_5\text{H}_4)(\text{CO})_2\text{W}]\text{Fe(CO)}_3\text{Co(CO)}_3(\mu_3\text{-S})$[16] were prepared according to litera-

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*Author to whom correspondence should be addressed.

ture methods. The progress of the reactions was monitored by TLC and products were separated on silica gel plates (20 × 17 × 0.3 cm, 10–14 μ). IR spectra were recorded on a Nicolet FT-IR 5DX infrared spectrophotometer and ^1H NMR spectra on a JEOL FX 90Q NMR spectrometer. Combustion analysis, MS and melting points were obtained by using a Perkin–Elmer Model 240C analyser, an HP5988A spectrometer and a Yanako MP-500 instrument, respectively.

Reaction of η^5-$C_5H_5(CO)_3Mo^-$ *with* $[(\eta^5$-$EtO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3$-$S)$

A 100 cm^3 two-necked flask fitted with a magnetic bar, a rubber septum and a reflux condenser topped with a nitrogen inlet tube was charged with 142 mg (0.29 mmol) of $[\eta^5$-$C_5H_5Mo(CO)_3]_2$, excess sodium sand and 20 cm^3 of THF. The mixture was stirred until the colour of the solution changed from red to light yellow. The resulting THF solution of η^5-$C_5H_5(CO)_3MoNa$ was transferred to another 100 cm^3 two-necked flask and 200 mg (0.29 mmol) of $[(\eta^5$-$EtO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3$-$S)$ was added. After the mixture was stirred at reflux for 4 h, the solvent was removed at reduced pressure and the residue extracted by CH_2Cl_2. The extracts were concentrated and separated on silica gel plates using 2 : 1 CH_2Cl_2/petroleum ether as eluent to develop five bands (i) red (trace), (ii) red (trace), (iii) brown yellow (trace), (iv) brown yellow, (v) brown yellow. From the fourth and fifth bands, 25 mg (14%) of **2a** and 30 mg (14%) of **1a** were obtained as black solids respectively. **1a**, m.p. 126–128°C. Found: C, 30.8; H, 2.0. Calc. for $C_{20}H_{14}FeMoO_9SW$: C, 31.4; H, 1.8%. IR (KBr, disc) : $v(C\equiv O)$, 2041s, 1975s, 1893m, 1844m cm^{-1}; $v(C{=}O)$, 1713m cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm) : 1.34 (t, $J = 7.2$Hz, 3H, $CO_2CH_2CH_3$), 4.32 (q, $J = 7.2$Hz, 2H, $CO_2CH_2CH_3$), 5.36, 5.42–5.58 (s, m, 7H, C_5H_5, H^3, H^4), 5.74–5.96 (m, 2H, H^2, H^5). MS (EI), *m/z* (Mo^{98}, W^{184}, rel. int.) : 768 (P^+, 3.1%), 712 (P^+-2CO, 3.0), 684 (P^+-3CO, 4.9), 656 (P^+-4CO, 11.0), 628 (P^+-5CO, 44.1), 600 (P^+-6CO, 50.1), 572 (P^+-7CO, 12.0), 630 $[SFeMoW(C_5H_4)(CO)_7^+$, 29.6], 602 $[SFeMoW(C_5H_4)(CO)_6^+$, 32.8], 574 $[SFeMoW(C_5H_4)(CO)_5^+$, 7.8], 546 $[SFeMoW(C_5H_4)(CO)_4^+$, 5.3], 518 $[SFeMoW(C_5H_4)(CO)_3^+$, 10.8], 490 $[SFeMoW(C_5H_4)(CO)_2^+$, 2.3], 462 $[SFeMoW(C_5H_4)(CO)^+$, 12.9], 434 $[SFeMoW(C_5H_4)^+$, 15.0], 566 $[SFeMoW(CO)_7^+$, 6.8], 538 $[SFeMoW(CO)_6^+$, 22.7], 510 $[SFeMoW(CO)_5^+$, 40.1], 482 $(SFeMoW(CO)_4^+$, 5.2], 454 $[SFeMoW(CO)_3^+$, 9.3], 426 $[SFeMoW(CO)_2^+$, 7.3], 398 $[SFeMoW(CO)^+$, 4.3], 370 $[SFeMoW^+$, 2.5]. **2a**, m.p. 205–206°C. IR and ^1H NMR data are identical with those in literature.[22]

Reaction of η^5-$MeC(O)C_5H_4(CO)_3Mo^-$ *with* $[(\eta^5$-$MeO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3$-$S)$

To the flask described above 153 mg (0.58 mmol) of $Mo(CO)_6$, 75 mg (0.58 mmol) of $MeC(O)C_5H_4Na$ and 20 cm^3 of THF were added. The solution was refluxed for 15 h. After the reaction of the resulting η^5-$MeC(O)C_5H_4(CO)_3MoNa$ with 198 mg (0.29 mmol) of $[(\eta^5$-$MeO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3$-$S)$ and a similar method to that described above, 53 mg (23%) of **1b** and 10 mg (5%) of **2b** were obtained as brown–red solids and black solids respectively. **1b**, m.p. 122–124°C. Found: C, 31.7; H, 1.8. Calc. for $C_{21}H_{14}FeMoO_{10}SW$: C, 31.8; H, 1.8%. IR (KBr, disc) : $v(C\equiv O)$, 2041s, 1983s, 1901s, 1877m, 1835m, cm^{-1}; $v(C{=}O)$, 1729m, 1680m, cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm) : 2.40 [s, 3H, $C(O)CH_3$], 3.90 (s, 3H, CO_2CH_3), 5.10, 5.38, 5.46–5.64 [q, q, m, 4H, 2(H^3, H^4)], 5.70–6.06 [m, 4H, 2(H^2, H^5)]. MS (EI), *m/z* (Mo^{98}, W^{184}, rel. int.) : 656 (P^+-5CO, 7%), 628 (P^+-6CO, 11), 600 (P^+-7CO, 5), 554 $[SFeMoW(C_5H_4)_2(CO)_2^+$, 7], 630 $[SFeMoW(C_5H_4)(CO)_7^+$, 6], 490 $[SFeMoW(C_5H_4)(CO)_2^+$, 5], 462 $[SFeMoW(C_5H_4)(CO)^+$, 7], 566 $[SFeMoW(CO)_7^+$, 6], 538 $[SFeMoW(CO)_6^+$, 11], 510 $[SFeMoW(CO)_5^+$, 9], 482 $[SFeMoW(CO)_4^+$, 5], 426 $[SFeMoW(CO)_2^+$, 5]. **2b**, m.p. 129–130°C. Found: C, 35.9; H, 1.8. Calc. for $C_{21}H_{14}FeMo_2O_9S$: C, 36.6; H, 2.0%. IR (KBr, disc): $v(C\equiv O)$, 2032s, 1975s, 1950s, 1918m, 1860s cm^{-1}; $v(C{=}O)$, 1680s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm) : 2.40 [s, 6H, 2$C(O)CH_3$], 5.24, 5.48 [q, q, 4H, 2(H^3, H^4)], 5.84 [t, 4H, 2(H^2, H^5)]. MS (EI), *m/z*(Mo^{98}, rel. int.) : 526 (P^+-6CO), 10.9%), 498 (P^+-7CO, 3.8), 608 $[SFeMo_2(C_5H_4)_2(CO)_7^+$, 2.6], 552 $[SFeMo_2(C_5H_4)_2(CO)_5^+$, 4.1], 524 $[SFeMo_2(C_5H_4)_2(CO)_4^+$, 6.8], 496 $[SFeMo_2(C_5H_4)_2(CO)_3^+$, 8.3], 468 $[SFeMo_2(C_5H_4)_2(CO)_2^+$, 4.7], 404 $[SFeMo_2(C_5H_4)(CO)_2^+$, 3.2].

Reaction of η^5-$MeO_2CC_5H_4(CO)_3Mo^-$ *with* $[(\eta^5$-$MeO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3$-$S)$

To the flask described above were added 153 mg (0.58 mmol) of $Mo(CO)_6$, 85 mg (0.58 mmol) of $MeO_2CC_5H_4Na$ and 20 cm^3 of THF. The solution was refluxed for 15 h. After the reaction of the resulting η^5-$MeO_2CC_5H_4(CO)_3MoNa$ with 196 mg (0.29 mmol) of $[(\eta^5$-$MeO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3$-$S)$ and similar method to that described above, 33 mg (14%) of **1c** and 12 mg (6%) of **2c** were obtained as black solids respectively. **1c**, m.p. 131–132°C. Found: C. 31.1; H, 1.8. Calc. for

$C_{21}H_{14}FeMoO_{11}SW$: C, 31.1; H, 1.7%. IR (KBr, disc): ν(C≡O), 2032s, 1983s, 1950s, 1909m, 1860s cm^{-1}; ν(C═O), 1713s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 3.78 (s, 3H, CO_2CH_3), 3.82 (s, 3H, CO_2CH_3), 4.94–5.10, 5.14–5.30, 5.30–5.50 [m, m, m, 4H, 2(H^3, H^4)], 5.54–5.94 [m, 4H, 2(H^2, H^5)]. MS (EI), *m/z* (Mo^{98}, W^{184}, rel. int.): 728 (P^+-3CO, 22%), 700 (P^+-4CO, 7), 672 (P^+-5CO, 36), 644 (P^+-6CO, 99), 616 (P^+-7CO, 14), 666 [$SFeMoW(C_5H_4)_2(CO)_6^+$, 14], 638 [$SFeMoW(C_5H_4)_2(CO)_5^+$, 48], 582 [$SFeMoW(C_5H_4)_2(CO)_3^+$, 18], 554 [$SFeMoW(C_5H_4)_2(CO)_2^+$, 33], 526 [$SFeMoW(C_5H_4)_2(CO)^+$, 78], 498 [$SFeMoW(C_5H_4)_2^+$, 25], 546 [$SFeMoW(C_5H_4)(CO)_4^+$, 6], 518 [$SFeMoW(C_5H_4)(CO)_3^+$, 16], 490 [$SFeMoW(C_5H_4)(CO)_2^+$, 21], 462 [$SFeMoW(C_5H_4)(CO)^+$, 15], 434 [$SFeMoW(C_5H_4)^+$, 7], 538 [$SFeMoW(CO)_6^+$, 10], 510 [$SFeMoW(CO)_5^+$, 16], 482 [$SFeMoW(CO)_4^+$, 12], 454 [$SFeMoW(CO)_3^+$, 11], 426 [$SFeMoW(CO)_2^+$, 10], 398 [$SFeMoW(CO)^+$, 7]. **2c**, m.p. 119–120°C. Found: C, 34.8; H, 2.0. Calc. for $C_{21}H_{14}FeMo_2O_{11}S$: C, 35.0; H, 2.0%. IR (KBr, disc): ν(C≡O), 2041s, 1983s, 1959s, 1909m, 1868s cm^{-1}; ν(C═O), 1721s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 3.88 (s, 6H, $2CO_2CH_3$), 5.24, 5.48 [q, q, 4H, 2(H^3, H^4)], 5.94 [q, 4H, 2(H^2, H^5)], MS (EI), *m/z* (Mo^{98}, rel. int.): 586 (P^+-5CO, 4.6%), 558 (P^+-6CO, 8.6), 608 [$SFeMo_2(C_5H_4)_2(CO)_7^+$, 1.7], 580 [$SFeMo_2(C_5H_4)_2(CO)_6^+$, 11.9], 552 [$SFeMo_2(C_5H_4)_2(CO)_5^+$, 15.7], 524 [$SFeMo_2(C_5H_4)_2(CO)_4^+$, 2.8], 496 [$SFeMo_2(C_5H_4)_2(CO)_3^+$, 6.5], 468 [$SFeMo_2(C_5H_4)_2(CO)_2^+$, 5.7], 440 [$SFeMo_2(C_5H_4)_2(CO)^+$, 8.3], 412 [$SFeMo_2(C_5H_4)_2^+$, 6.6], 404 [$SFeMo_2(C_5H_4)(CO)_2^+$, 2.8], 376 [$SFeMo_2(C_5H_4)(CO)^+$, 4.8], 348 [$SFeMo_2(C_5H_4)^+$, 3.1], 340 [$SFeMo_2(CO)_2^+$, 4.1].

Reaction of η^5-$MeC_5H_4(CO)_3W^-$ *with* [(η^5-$EtO_2CC_5H_4$)$(CO)_2Mo$]$Fe(CO)_3Co(CO)_3$(μ_3-S)

To the flask described above were added 201 mg (0.29 mmol) of [η^5-$MeC_5H_4(CO)_3W$]$_2$, excess sodium sand and 20 cm^3 of THF. The mixture was stirred until the colour of the solution changed from red to light yellow. The resulting solution of η^5-$MeC_5H_4(CO)_3WNa$ in THF was transferred into another 100 cm^3 two-necked flask and 176 mg (0.29 mmol) of [(η^5-$EtO_2CC_5H_4$)$(CO)_2Mo$]$Fe(CO)_3Co(CO)_3$(μ_3-S) was added. The mixture was refluxed for additional 4 h. After the similar workup described above, 38 mg (17%) of **1d** and 91 mg (39%) of **2d** were obtained as black solids and brown red viscous oil respectively. **1d**, m.p. 125–127°C. Found: C, 32.4; H, 1.8. Calc. for $C_{21}H_{16}FeMoO_9SW$: C, 32.3; H, 2.1%. IR (KBr, disc): ν(C≡O), 2032s, 1991s, 1959s, 1893s, 1869s, 1836s cm^{-1}; ν(C═O), 1704s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 1.36 [t, *J* = 7.2Hz, 3H, $CO_2CH_2CH_3$], 2.30 (s, 3H, CH_3), 4.32 (q, *J* = 7.2Hz, 2H, $CO_2CH_2CH_3$), 4.88–5.56 [m, 6H, H^3 and H^4 of the $C_5H_4CO_2C_2H_5$ ring and 4H of the $C_5H_4CH_3$ ring], 5.84–6.12 [m, 2H, H^2 and H^5 of the $C_5H_4CO_2C_2H_5$ ring]. MS (EI), *m/z* (Mo^{98}, W^{184}, rel. int.): 642 (P^+-5CO, 37%), 614 (P^+-6CO, 25), 586 (P^+-7CO, 22), 638 [$SFeMoW(C_5H_4)_2(CO)_5^+$, 36], 610 [$SFeMoW(C_5H_4)_2(CO)_4^+$, 24], 582 [$SFeMoW(C_5H_4)_2(CO)_3^+$, 26], 554 [$SFeMoW(C_5H_4)_2(CO)_2^+$, 8], 526 [$SFeMoW(C_5H_4)_2(CO)^+$, 33], 498 [$SFeMoW(C_5H_4)_2^+$, 12], 518 [$SFeMoW(C_5H_4)(CO)_3^+$, 10], 462 [$SFeMoW(C_5H_4)(CO)^+$, 16], 538 [$SFeMoW(CO)_6^+$, 9], 510 [$SFeMoW(CO)_5^+$, 28], 482 [$SFeMoW(CO)_4^+$, 12], 454 [$SFeMoW(CO)_3^+$, 16], 426 [$SFeMoW(CO)_2^+$, 36], 398 [$SFeMoW(CO)^+$, 9]. **2d**, Found: C, 28.4; H, 1.8. Calc. for $C_{19}H_{14}FeO_7SW_2$: C, 28.2; H, 1.7%. IR (KBr, disc): ν(C≡O), 2065s, 2016s, 1983s, 1893s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 2.34 (s, 6H, $2CH_3$), 5.10–5.66 (m, 8H, $2C_5H_4$). MS (EI), *m/z*(W^{184}, rel. int.): 632 [$SFeW_2(C_5H_4)(CO)_4^+$, 0.6%], 604 [$SFeW_2(C_5H_4)(CO)_3^+$, 1.7], 576 [$SFeW_2(C_5H_4)(CO)_2^+$, 0.6], 548 [$SFeW_2(C_5H_4)(CO)^+$, 2.0], 520 [$SFeW_2(C_5H_4)^+$, 2.7].

Reaction of η^5-$MeO_2CC_5H_4(CO)_3Mo^-$ *with* **1c**

To the flask described above were added 106 mg (0.4 mmol) of $Mo(CO)_6$, 58 mg (0.4 mmol) of $MeO_2CC_5H_4Na$ and 15 cm^3 of THF. The solution was stirred at reflux for 15 h. After the reaction of the resulting η^5-$MeO_2CC_5H_4(CO)_3MoNa$ with 159 mg (0.20 mmol) of **1c**, followed by similar workup described above, 135 mg (85%) of **1c** was recovered.

Reaction of η^5-$MeC(O)C_5H_4(CO)_3W^-$ *with* [(η^5-$MeO_2CC_5H_4$)$(CO)_2W$]$Fe(CO)_3Co(CO)_3$(μ_3-S)

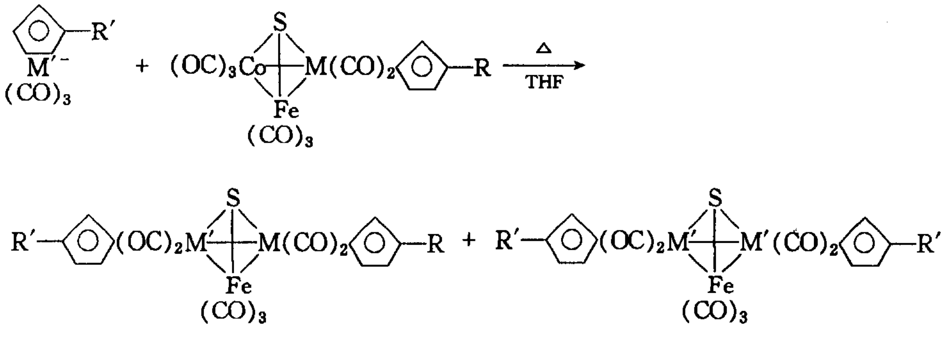
To the flask described above were added 415 mg (1.18 mmol) of $W(CO)_6$, 153 mg (1.18 mmol) of $MeC(O)C_5H_4Na$ and 20 cm^3 of diglyme. The mixture was refluxed for 6 h. After the solvent was removed at reduced pressure, 400 mg (0.59 mmol) of [(η^5-$MeO_2CC_5H_4$)$(CO)_2W$]$Fe(CO)_3Co(CO)_3$(μ_3-S) and 20 cm^3 of THF were added. The mixture was refluxed for an additional 4 h. After a similar method to that described above, 131 mg (25%) of **1e**, 69 mg (14%) of **2e** and 55 mg (10%) of **3** were obtained as brown, brown and black solids, respectively. **1e**, m.p. 72–74°C. Found: C, 29.0; H, 1.5. Calc. for $C_{21}H_{14}FeO_{10}SW_2$: C, 28.6; H, 1.6%. IR (KBr, disc): ν(C≡O), 2041s, 1975s, 1893m, 1836m cm^{-1}; ν(C═O), 1721m, 1680m cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 2.34 [s, 3H, $C(O)CH_3$], 3.84 [s, 3H, CO_2CH_3], 5.12–5.40, 5.40–5.60 [m, m, 4H, 2(H^3, H^4)], 5.72–5.96 [m, 4H, 2(H^2, H^5)]. MS (EI), *m/z*(W^{184}, rel. int.): 714 (P^+-6CO, 2.1%), 520 [$SFeW_2(C_5H_4)^+$, 0.2]. **2e**, m.p. 144–145°C. Found: C, 29.2; H, 1.6. Calc. for $C_{21}H_{14}FeO_9SW_2$: C, 29.1; H, 1.6%. IR (KBr, disc): $\nu(C{\equiv}O)$, 2041s, 1975s, 1893m, 1836m cm^{-1}; $\nu(C{=}O)$, 1680s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 2.36 [s, 6H, 2C(O)CH_3], 5.20–5.36, 5.48–5.62 [m, m, 4H, 2(H^3, H^4)], 5.68–5.92 [m, 4H, 2(H^2, H^5)]. MS (EI), *m/z* (W^{184}, rel. int.): 698(P^+-6CO, 0.2%), 670 (P^+-7CO, 0.2), 668 [$SFeW_2(C_5H_4)_2(CO)_2^+$, 0.2]. **3**, m.p. 117–118°C. Found: C, 27.9; H, 1.5. Calc. for $C_{21}H_{14}FeO_{11}SW_2$: C, 28.1; H, 1.6%. IR (KBr, disc): $\nu(C{\equiv}O)$, 2041s, 1975s, 1893s, 1836m cm^{-1}; $\nu(C{=}O)$, 1721s cm^{-1}. ^1H NMR ($CDCl_3$, δ, ppm): 3.82 (s, 6H, $2CO_2CH_3$), 5.24, 5.48 [q, q, 4H, 2(H^3, H^4)], 5.66–6.02 [m, 4H, 2(H^2, H^5)], MS (EI), *m/z*(W^{184}, rel. int.):730 (P^+-6CO, 2.0%), 612 [$SFeW_2(C_5H_4)_2(CO)^+$, 0.9].

RESULTS AND DISCUSSION

When tetrahedral MFeCoS cluster complexes of the type [(η^5-RC_5H_4)$(CO)_2$M]Fe$(CO)_3$Co$(CO)_3$(μ_3-S) (R = CO_2Me, CO_2Et; M = Mo, W) were treated with group 6 metal anions η^5-$R'C_5H_4(CO)_3M'^-$ (R = H, Me, C(O)Me, CO_2Me; M′ = Mo, W) in refluxing THF for several hours, four tetrahedral MM′FeS cluster complexes [(η^5-RC_5H_4)$(CO)_2$M][η^5-$R'C_5H_4(CO)_2M'$]Fe$(CO)_3$(μ_3-S) (**1a–d**) were obtained via the isolobal displacement reaction of a d^9 ML_3 unit Co$(CO)_3$[23] in the starting cluster complexes by the d^5 ML_5 fragment η^5-$R'C_5H_4(CO)_2M'$[23] generated from the starting anions, along with four tetrahedral M′M′FeS cluster complexes [(η^5-$R'C_5H_4$)$(CO)_2M']_2$Fe$(CO)_3$(μ_3-S) (**2a–d**) as shown in Scheme 1. Although **1a–d** are products derived from the well-known d^9 ML_3/d^5 ML_5 isolobal displacement reaction,[1–16] **2a–d** are generated through an unknown process involving another type of isolobal displacement reaction between two different d^5ML_5 fragments both having the same basic structure i.e. Cp*$(CO)_2$M.

For the reactions involving two types of isolobal displacement mentioned above, a possible pathway can be suggested, as shown in Scheme 2.

According to the pathway described above the group 6 metal anions η^5-$R'C_5H_4(CO)_3M'^-$ may attack, from either the back of Co$(CO)_3$ or the back of η^5-$RC_5H_4(CO)_2M$, at the starting cluster compounds [(η^5-RC_5H_4)$(CO)_2$M]Fe$(CO)_3$Co$(CO)_3$(μ_3-S) to form two anionic intermediates $\mathbf{m_1}$ and $\mathbf{m_2}$. Then, if the intermediate $\mathbf{m_1}$ loses an anion $(CO)_4Co^-$, formally as formed from the displaced Co$(CO)_3$, one CO and one negative charge from η^5-$R'C_5H_4(CO)_3M'^-$, products **1a–d** will be produced. Actually this is the result of the well-known d^9 ML_3/d^5 ML_5 isolobal displacement reaction. However, if the intermediate $\mathbf{m_2}$ loses an anion η^5-$RC_5H_4(CO)_3M^-$, formally as formed from the displaced η^5-$RC_5H_4(CO)_2M$, one CO and one negative charge from η^5-$R'C_5H_4(CO)_3M'^-$, the analogues of starting cluster compounds $\mathbf{m_3}$ would be formed. It is this step in which an isolobal displacement reaction between two different d^5 ML_5 fragments η^5-$RC_5H_4(CO)_2M$ and η^5-$R'C_5H_4(CO)_2M'$ was involved. Finally, products **2a–d** are produced by further isolobal displacement of a d^9 ML_3 Co$(CO)_3$ in $\mathbf{m_3}$ by a d^5 ML_5 η^5-$R'C_5H_4(CO)_2M'$ generated

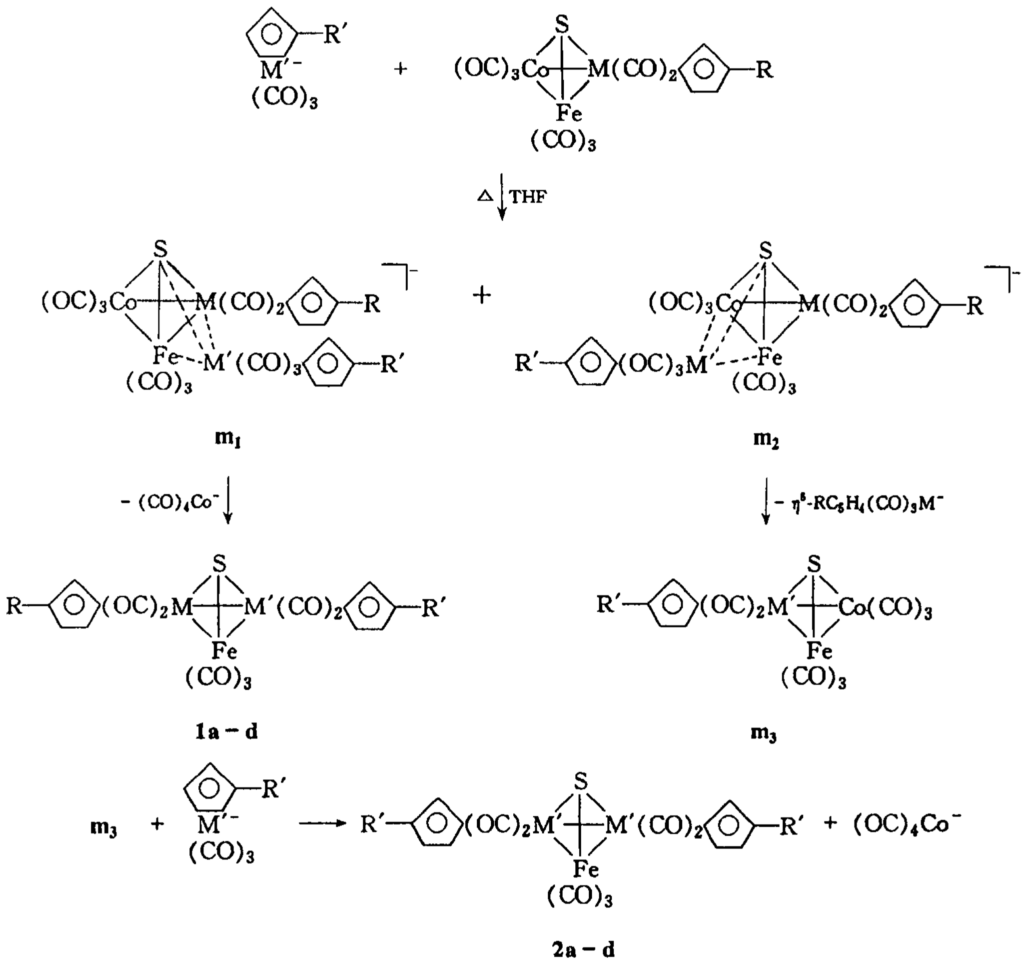


1a–d **2a–d**

	1a	**1b**	**1c**	**1d**
M	W	W	W	Mo
R	CO_2Et	CO_2Me	CO_2Me	CO_2Et
M′	Mo	Mo	Mo	W
R′	H	C(O)Me	CO_2Me	Me

	2a	**2b**	**2c**	**2d**
M′	Mo	Mo	Mo	W
R′	H	C(O)Me	CO_2Me	Me

Scheme 1.

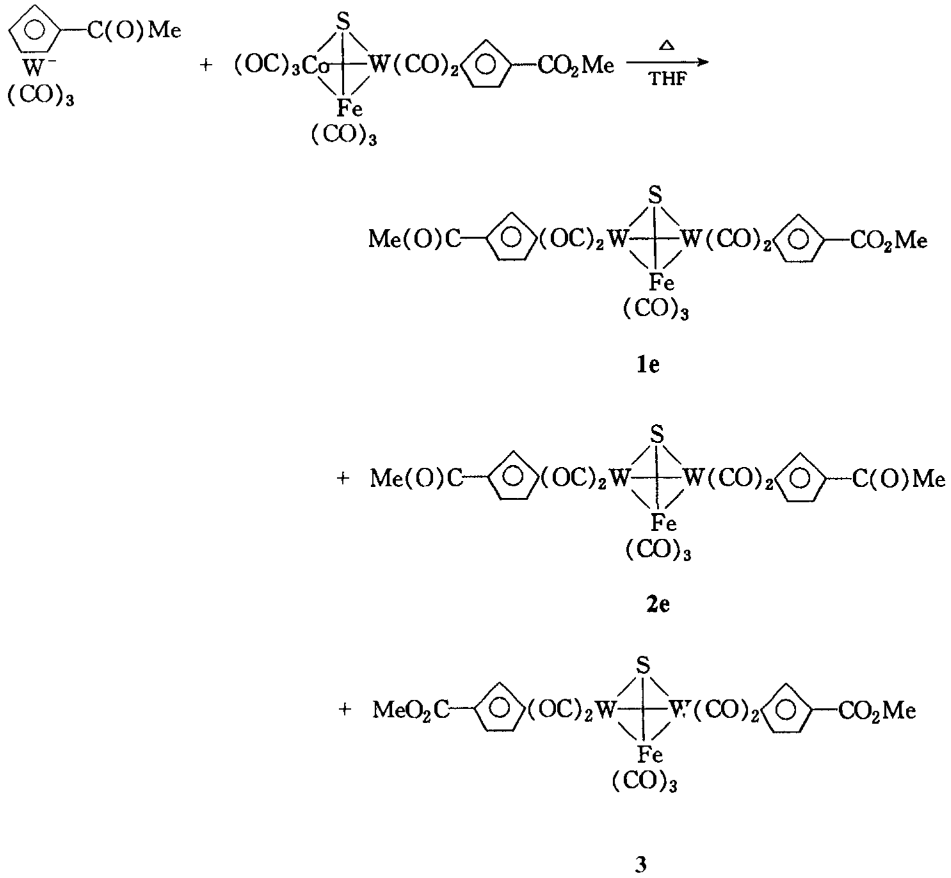


Scheme 2.

from η^5-R'$C_5H_4(CO)_3M'^-$. We initially supposed that **2a–d** might be produced by isolobal displacement between products **1a–d** and the isolobal displacement reagents η^5-R'$C_5H_4(CO)_3M'^-$. However, our experiments showed that it was not the case. When a reaction of **1c** with η^5-$MeO_2CC_5H_4(CO)_3Mo^-$ was completed, no supposed **2c** was formed and only 85% of starting material **1c** was recovered.

Further experiment showed that the reaction of η^5-MeC(O)$C_5H_4(CO)_3W^-$ with $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3\text{-}S)$, which is different from those reactants mentioned above by having same group 6 metal, i.e. tungsten, gave products **1e**, **2e** and **3**, as shown in Scheme 3. This result is consistent with the pathway described in Scheme 2 and provides additional evidence to support the pathway shown in Scheme 2. This is because the formation of **3** can be attributed to the isolobal displacement reaction of $Co(CO)_3$ in the starting cluster $[(\eta^5\text{-}MeO_2CC_5H_4)(CO)_2W]Fe(CO)_3Co(CO)_3(\mu_3\text{-}S)$ by the fragment of η^5-$MeO_2CC_5H_4(CO)_2W$ produced from the anion η^5-$MeO_2CC_5H_4(CO)_3W^-$ generated *in situ* through the proceeding isolobal displacement reaction in formation of **2e**. However, up to now, we still do not know why the isolobal displacement between different d^5 ML_5 fragments with general formula $Cp^*M(CO)_2(M = Mo, W)$ could occur only in the cluster system in which the unit $Co(CO)_3$ should be present.

Except **2a**[23] the compounds **1a–e**, **2b–e** and **3** were all new and fully characterized by elemental analysis, IR, ^1H NMR and mass spectroscopy. In their IR spectra terminal carbonyl absorption bands in the range of 2065–1901 cm^{-1} were packed. The bridging carbonyls[24] might also exist due to one to three absorption bands present between 1893 and 1835 cm^{-1}. The IR spectra of **1a–e**, **2b–c**, **2e** and **3** also showed one or two absorption bands at *ca* 1700 cm^{-1}, which were characteristic of the corresponding functional carbonyl group of the organic substituent on the cyclopentadienyl ring. It is worth pointing out the ^1H NMR spectral features for **1a–e**, **2b–e**, and **3**. The protons on the cyclo-



Scheme 3.

pendadienyl ring of **2b–c**, **2e**, and **3** all exhibited three sets of multiplets, the two upfield quartets (or multiplets) being assigned to H^3, H^4 remote from the substituent and the downfield triplet (or quartet, or multiplet) assigned to H^2, H^5 close to the substituent. These assignments are in accord with those for the tetrahedral clusters $[(\eta^5\text{-RC}_5H_4)(CO)_2M]Fe(CO)_3Co(CO)_3(\mu_3\text{-S})$ (M = Mo, W) which contain the same type of functionally substituted cyclopentadienyl ring.[16] In view of **1a–e** either having two different cyclopentadienyl rings or having two different group 6 metals (or both) the ^{1}H NMR spectra of their protons on the cyclopentadienyls are much more complicated. Generally, these protons exhibited two to four sets of multiplets. For the mass spectra of compounds **1a–e**, **2b–e** and **3**, only **1a** showed its molecular ion peak. However, for all these compounds four types of fragment peaks were usually observed in their mass spectra. That is, (i) (P^+-nCO), the fragments by successive loss of carbonyl from molecular ion; (ii) $SFeMoW(C_5H_4)_2(CO)_{7-n}^+$ or $SFeM_2(C_5H_4)_2(CO)_{7-n}^+$(M = Mo, W), fragments by successive loss of carbonyl and substituent R (or R′) from molecular ion, (iii) $SFeMoW(C_5H_4)(CO)_{7-n}^+$ or $SFeM_2(C_5H_4)(CO)_{7-n}^+$(M = Mo, W), fragments by successive loss of carbonyl, substituent R (or R′) and one C_5H_4 ring from molecular ion; (iv) $SFeMoW(CO)_{7-n}^+$ or $SFeM_2(CO)_{7-n}^+$ (M = Mo, W), fragments by successive loss of carbonyl and two substituted cyclopentadienyls from molecular ion.

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