Inorganica Chimica Acta, 219 (1994) 93–97

The study of isolobal displacement reactions. Synthesis and structures of the heterobimetallic μ-alkyne cluster complexes η^5-$RC_5H_4(CO)_2M(\mu$-$R^1C_2R^2)Co(CO)_3$ (M = Mo, W; R = $CH_3C(O)$, CH_3O_2C)

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(Received December 14, 1993)

Abstract

η^5-$CH_3C(O)C_5H_4(CO)_2Mo(\mu$-$C_6H_5C_2C_6H_5)Co(CO)_3$ (**1a**), η^5-$CH_3C(O)C_5H_4(CO)_2Mo(\mu$-*p*-$CH_3C_6H_4C_2C_6H_5)Co(CO)_3$ (**1b**), η^5-$CH_3O_2CC_5H_4(CO)_2Mo(\mu$-$C_6H_5C_2C_6H_5)Co(CO)_3$ (**1c**), η^5-$CH_3C(O)C_5H_4(CO)_2W(\mu$-$C_6H_5C_2C_6H_5)Co(CO)_3$ (**1d**) and η^5-$CH_3O_2CC_5H_4(CO)_2W(\mu$-$C_6H_5C_2C_6H_5)Co(CO)_3$ (**1e**) were prepared by reactions of the corresponding sodium salts of functionally substituted cyclopentadienyl carbonyl molybdenum (tungsten) anions with $(CO)_3Co(\mu$-$C_6H_5C_2C_6H_5)Co(CO)_3$ or $(CO)_3Co(\mu$-*p*-$CH_3C_6H_5C_2C_6H_5)Co(CO)_3$, respectively. The compounds **1a**–**1e** were characterized by elemental analysis, IR, ^1H NMR and mass spectroscopy, while the structure of **1c** was further established by X-ray diffraction analysis. The compound crystallizes in the monoclinic space group $P2_1/n$ with $a = 8.503(1)$, $b = 26.721(7)$, $c = 11.033(2)$ Å; $\beta = 106.09(2)°$; $V = 2408$ Å^3; and $Z = 4$.

Key words: Crystal structures; Cobalt complexes; Alkyne complexes; Cluster complexes; Tungsten complexes; Molybdenum complexes

Introduction

Heterobimetallic μ-alkyne complexes containing the functionally substituted cyclopentadienyl VIB metal moiety and the isolobal displacement reaction between (μ-alkyne)hexacarbonyldicobalt and functionally substituted cyclopentadienyl VIB metal anions have not appeared in the literature so far, although a number of heterobimetallic μ-alkyne complexes have been reported and the isolobal displacement reactions were well documented [1–10]. In order to explore the reactivity of functionally substituted cyclopentadienyl VIB metal anions [11–21] and to prepare new complexes of this type, we have carried out the reactions of $RCpM(CO)_3Na$ (M = Mo, W; R = $CH_3C(O)$, CH_3O_2C) with $(CO)_3Co(\mu$-$R^1C_2R^2)Co(CO)_3$ ($R^1 = R^2 = C_6H_5$; $R^1 = C_6H_5$, $R^2 =$ *p*-$CH_3C_6H_4$). Herein we report the results concerning this study.

Results and discussion

The sodium salts of functionally substituted cyclopentadienyltricarbonylmolybdenum (tungsten), η^5-$RC_5H_4(CO)_3MNa$ (M = Mo, W; R = $CH_3C(O)$, CH_3O_2C), prepared from $M(CO)_6$ and η^5-RC_5H_4Na [13] were treated *in situ* with homobimetallic μ-alkyne compounds $(CO)_3Co(\mu$-$R^1C_2R^2)Co(CO)_3$ ($R^1 = C_6H_5$, $R^2 = C_6H_5$ [22] and $R^1 = C_6H_5$, $R^2 =$ *p*-$CH_3C_6H_4$ [23]) to give the expected compounds **1a**–**1e**, which could be regarded as a result of displacement of $Co(CO)_3$ (d^9ML_3) in $(CO)_3Co(\mu$-$R^1C_2R^2)Co(CO)_3$ by its isolobal metal fragments η^5-$RC_5H_4(CO)_2M$ (d^5ML_5) [10] (eqn. (1)).

The new compounds **1a**–**1e** were fully characterized by elemental analysis, IR, ^1H NMR and mass spectroscopy. In their IR spectra four to five peaks in the region 2050–1934 cm^{-1} were characteristic of the terminal carbonyls and one single peak at *c.* 1700 cm^{-1} was characteristic of the functional carbonyl group of the organic substituent on the cyclopentadienyl ring. In their ^1H NMR spectra two triplets appearing in the

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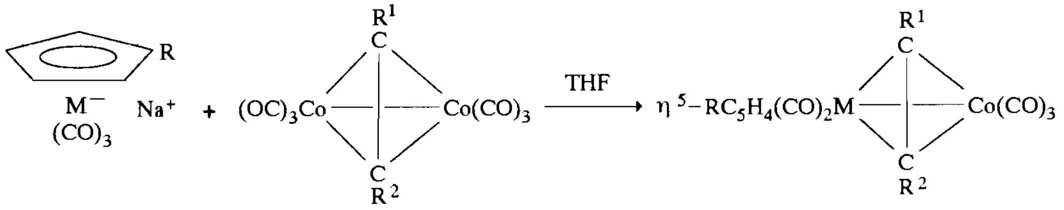

1a–1e

(1)

Compound	**1a**	**1b**	**1c**	**1d**	**1e**
M	Mo	Mo	Mo	W	W
R	$CH_3C(O)$	$CH_3C(O)$	CH_3O_2C	$CH_3C(O)$	CH_3O_2C
R^1	C_6H_5	C_6H_5	C_6H_5	C_6H_5	C_6H_5
R^2	C_6H_5	p-$CH_3C_6H_5$	C_6H_5	C_6H_5	C_6H_5

region δ 5–6 were assigned to four protons on the cyclopentadienyl ring; furthermore, the triplet upfield was assigned to H^3 and H^4, and the triplet downfield to H^2 and H^5. These assignments are in accord with those for compounds containing the same type of functionally substituted cyclopentadienyl ring [11–12]. It is noteworthy that the mass spectra of **1a**–**1e** all showed fragment ion peaks, such as those of alkyne $R^1C_2R^2$, cluster core C_2CoM, functional cyclopentadienyl RC_5H_4 and a series of molecular ion $- R^1 - R^2 - n$CO ($n = 0$–5); but only **1a** showed the molecular ion peak of **1a** in its mass spectrum.

In order to further establish the structures of **1a**–**1e**, a single crystal structure determination of **1c** was undertaken by the X-ray diffraction method. Table 1 lists the fractional coordinates and equivalent thermal parameters of non-hydrogen atoms. The bond lengths and bond angles are listed in Tables 2 and 3, respectively. Figure 1 shows its molecular structure.

In general, the structure of **1c** is quite similar to those previously described for η^5-$C_5H_5(CO)_2W(\mu$-$PhC_2CH_3)Co(CO)_3$ [7] and η^5-$C_5H_5(CO)_2Mo(\mu$-$CF_3C_2CF_3)Co(CO)_3$ [8]. **1c** has a quasi-tetrahedral core C_2CoMo, in which the C(17)–C(27) bond is equal to 1.347(5) Å and inclined at an angle θ of 88.3° to the Co–Mo(1) bond of 2.6873(6) Å. The average Co–C (μ-C_2) and Mo(1)–C bond lengths are 1.984(4) and 2.168(4) Å. These data are comparable to the corresponding values in η^5-$C_5H_5(CO)_2W(\mu$-$PhC_2CH_3)Co(CO)_3$ (C–C (μ-C_2) = 1.381(5), Co–W = 2.693(1) Å, θ = 87.7°, av. Co–C (μ-C_2) = 2.01(2), av. W–C (μ-C_2) = 2.14(2) Å) [7], and η^5-$C_5H_5(CO)_2Mo(\mu$-$CF_3C_2CF_3)Co(CO)_3$ (C–C

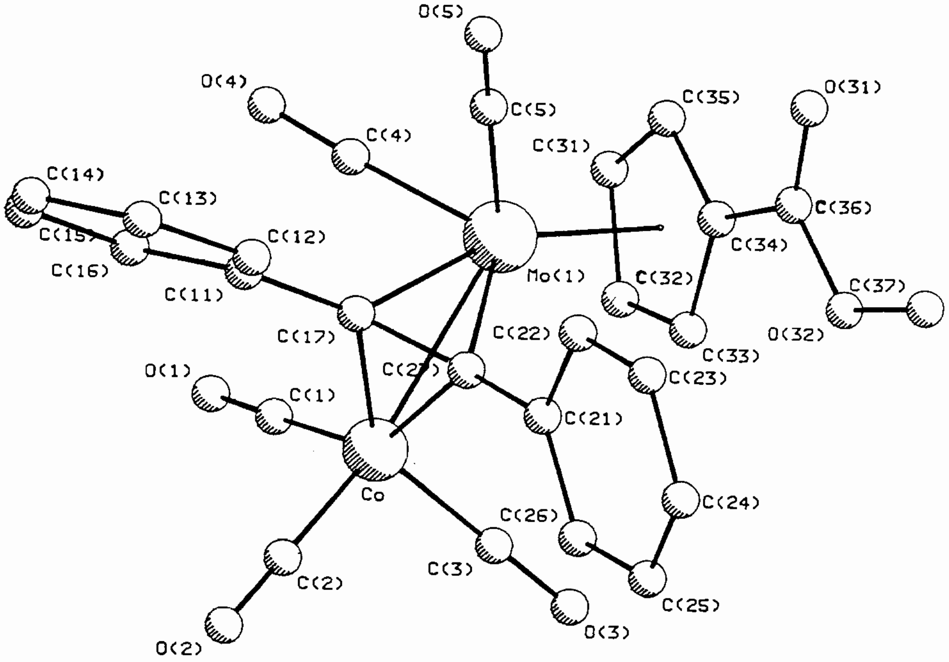

Fig. 1. Molecular structure of **1c**.

TABLE 1. Fractional coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms for **1c**

Atom	x	y	z	B_{eq} (Å^2)
Mo	0.33561(6)	0.37570(2)	0.38917(5)	2.480(8)
Co	0.0973(1)	0.30982(3)	0.28596(8)	2.58(2)
O(1)	0.1762(7)	0.3004(2)	0.0449(5)	6.1(1)
O(2)	−0.2492(6)	0.2853(2)	0.2150(6)	6.9(1)
O(3)	0.2416(7)	0.2200(2)	0.4249(5)	4.9(1)
O(4)	0.3264(7)	0.4165(2)	0.1224(5)	6.5(1)
O(5)	0.2809(7)	0.4875(2)	0.4518(6)	5.6(1)
O(31)	0.5290(7)	0.4304(2)	0.7361(5)	5.4(1)
O(32)	0.4470(6)	0.3525(2)	0.7686(4)	4.9(1)
C(1)	0.1448(8)	0.3036(2)	0.1377(6)	3.6(1)
C(2)	−0.1146(8)	0.2944(3)	0.2422(7)	4.1(2)
C(3)	0.1866(8)	0.2548(2)	0.3703(6)	3.4(1)
C(4)	0.3253(8)	0.4006(3)	0.2186(6)	3.7(1)
C(5)	0.3004(7)	0.4472(2)	0.4287(6)	3.2(1)
C(11)	−0.0489(7)	0.4181(2)	0.2384(6)	2.8(1)
C(12)	−0.1407(7)	0.4474(2)	0.2996(7)	3.6(1)
C(13)	−0.2573(9)	0.4813(3)	0.2278(9)	4.9(2)
C(14)	−0.281(1)	0.4858(3)	0.0996(9)	5.8(2)
C(15)	−0.190(1)	0.4571(3)	0.0404(8)	6.5(2)
C(16)	−0.072(1)	0.4226(3)	0.1086(7)	5.3(2)
C(17)	0.0700(6)	0.3821(2)	0.3128(5)	2.4(1)
C(21)	0.0508(6)	0.3571(2)	0.5409(5)	2.4(1)
C(22)	0.0540(7)	0.4018(3)	0.6091(6)	3.4(1)
C(23)	−0.0016(8)	0.4017(3)	0.7175(6)	4.0(2)
C(24)	−0.0602(8)	0.3568(3)	0.7568(6)	4.2(2)
C(25)	−0.0607(8)	0.3135(3)	0.6909(7)	4.5(2)
C(26)	−0.0051(8)	0.3128(3)	0.5810(6)	3.4(1)
C(27)	0.1059(6)	0.3583(2)	0.4247(5)	2.2(1)
C(31)	0.6128(7)	0.3572(3)	0.4105(7)	3.6(1)
C(32)	0.5352(7)	0.3115(3)	0.4277(6)	3.3(1)
C(33)	0.4781(7)	0.3173(2)	0.5383(6)	3.0(1)
C(34)	0.5210(7)	0.3663(2)	0.5856(6)	2.7(1)
C(35)	0.6039(7)	0.3915(2)	0.5057(6)	3.1(1)
C(36)	0.4986(7)	0.3875(3)	0.7037(6)	3.5(1)
C(37)	0.423(1)	0.3681(4)	0.8900(6)	6.8(2)

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as: $(4/3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

(μ-C_2) = 1.371(7), Co–Mo = 2.692(1) Å, θ = 88.5°, av. Co–C (μ-C_2) = 1.948(5), Mo–C (μ-C_2) = 2.127(5) Å) [8]. In addition, the two angles C(17)–C(27)–C(21) and C(27)–C(17)–C(11) in **1c** are equal to 139.3(4) and 140.1(4)°, which are somewhat larger than the corresponding values found in η^5-$C_5H_5(CO)_2W(\mu$-Ph-$C_2CH_3)Co(CO)_3$ (136.0(3) and 139.1(4)°) [7] and η^5-$C_5H_5(CO)_2Mo(\mu$-$CF_3C_2CF_3)Co(CO)_3$ (133.6(6) and 133.8(6)°) [8]. However, these values are in the typical range of angles 130–150 °C found for this type of bimetallic μ-alkyne cluster compounds [24].

Finally, it is worth pointing out that the diphenylacetylene ligand takes the usual *cis*-bent configuration and the bulky methoxycarbonylcyclopentadienyl ring is located in a position opposite to the diphenylacetylene, which is probably due to the intramolecular steric interactions between these two ligands.

TABLE 2. Bond distances (Å) between non-hydrogen atoms for **1c**[a]

Mo–Co	2.6873(6)	C(11)–C(17)	1.470(5)
Mo–C(4)	1.975(4)	C(12)–C(13)	1.412(6)
Mo–C(5)	2.000(4)	C(13)–C(14)	1.377(8)
Mo–C(17)	2.188(4)	C(14)–C(15)	1.376(9)
Mo–C(27)	2.147(4)	C(15)–C(16)	1.414(8)
Mo–C(31)	2.355(4)	C(17)–C(27)	1.347(5)
Mo–C(32)	2.366(4)	C(21)–C(22)	1.408(6)
Mo–C(33)	2.346(4)	C(21)–C(26)	1.394(7)
Mo–C(34)	2.313(4)	C(21)–C(27)	1.482(5)
Mo–C(35)	2.326(4)	C(22)–C(23)	1.402(7)
Mo–Cp[b]	2.002(4)	C(23)–C(24)	1.413(8)
Co–C(1)	1.798(5)	C(24)–C(25)	1.365(8)
Co–C(2)	1.781(5)	C(25)–C(26)	1.419(6)
Co–C(3)	1.793(4)	O(31)–C(36)	1.208(5)
Co–C(17)	1.976(4)	O(32)–C(36)	1.324(6)
Co–C(27)	1.992(4)	O(32)–C(37)	1.470(5)
O(1)–C(1)	1.130(5)	C(31)–C(32)	1.426(6)
O(2)–C(2)	1.127(5)	C(31)–C(35)	1.411(6)
O(3)–C(3)	1.136(6)	C(32)–C(33)	1.442(6)
O(4)–C(4)	1.145(6)	C(33)–C(34)	1.419(6)
O(5)–C(5)	1.129(5)	C(34)–C(35)	1.439(6)
C(11)–C(12)	1.404(6)	C(34)–C(36)	1.480(6)
C(11)–C(16)	1.396(6)		

[a] Numbers in parentheses are e.s.d.s in the least significant digits. [b] Cp is the center of the five-membered ring composed of the C(31)–C(35) atoms.

Experimental

All reactions were carried out under a dry nitrogen atmosphere. 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 Stream Chemicals Inc., $CH_3C(O)C_5H_4Na$, $CH_3O_2CC_5H_4Na$ [13], $(CO)_3Co(\mu$-$C_6H_5C_2C_6H_5)$-$Co(CO)_3$ [22], $(CO)_3Co(\mu$-p-$CH_3C_6H_4C_2C_6H_5)Co(CO)_3$ [23] were prepared according to literature 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 and ^{1}H NMR spectra were recorded on a NICOLET FT-IR 5DX spectrophotometer and a JEOL FX 90Q spectrometer. C/H analysis, MS and melting points data were obtained by using a 240C model analyzer, an HP 5988A spectrometer and a Yanako MP-500 instrument, respectively.

Preparation of 1a

A solution of 0.528 g (2.0 mmol) of $Mo(CO)_6$ and 0.26 g (2.0 mmol) of $CH_3C(O)C_5H_4Na$ in 20 ml of THF was stirred at reflux for 12 h. Upon cooling to room temperature, 0.464 g (1.0 mmol) of $(C_6H_5)_2C_2Co_2(CO)_6$ was added and the reaction mixture was stirred for an

TABLE 3. Bond angles (°) between non-hydrogen atoms for **1c**[a]

Co–Mo–C(4)	89.4(1)	C(16)–C(11)–C(17)	120.7(4)
Co–Mo–C(5)	125.2(1)	C(11)–C(12)–C(13)	119.0(5)
Co–Mo–C(17)	46.5(2)	C(12)–C(13)–C(14)	120.8(5)
Co–Mo–C(27)	47.0(2)	C(13)–C(14)–C(15)	119.8(6)
Co–Mo–Cp[b]	117.9(1)	C(14)–C(15)–C(16)	121.3(5)
C(4)–Mo–C(5)	85.2(2)	C(11)–C(16)–C(15)	118.6(5)
C(4)–Mo–C(17)	80.7(2)	Mo–C(17)–Co	80.3(1)
C(4)–Mo–C(27)	116.5(2)	Mo–C(17)–C(11)	137.9(3)
C(4)–Mo–Cp[b]	117.5(2)	Mo–C(17)–C(27)	70.3(2)
C(5)–Mo–C(17)	79.0(2)	Co–C(17)–C(11)	130.3(3)
C(5)–Mo–C(27)	88.2(2)	Co–C(17)–C(27)	70.7(2)
C(5)–Mo–Cp[b]	112.7(2)	C(11)–C(17)–C(27)	140.1(4)
C(17)–Mo–C(27)	36.2(1)	C(22)–C(21)–C(26)	120.6(4)
C(17)–Mo–Cp[b]	158.2(2)	C(22)–C(21)–C(27)	118.7(4)
C(27)–Mo–Cp[b]	123.2(2)	C(26)–C(21)–C(27)	120.7(4)
Mo–Co–C(1)	96.5(2)	C(21)–C(22)–C(23)	119.6(4)
Mo–Co–C(2)	148.6(2)	C(22)–C(23)–C(24)	119.6(4)
Mo–Co–C(3)	99.1(2)	C(23)–C(24)–C(25)	120.4(4)
Mo–Co–C(17)	53.3(2)	C(24)–C(25)–C(26)	121.0(5)
Mo–Co–C(27)	52.1(2)	C(21)–C(26)–C(25)	118.9(5)
C(1)–Co–C(2)	101.4(2)	Mo–C(27)–Co	81.0(1)
C(1)–Co–C(3)	103.1(2)	Mo–C(27)–C(17)	73.6(2)
C(1)–Co–C(17)	107.0(2)	Mo–C(27)–C(21)	133.2(3)
C(1)–Co–C(27)	142.2(2)	Co–C(27)–C(17)	69.6(2)
C(2)–Co–C(3)	101.7(3)	Co–C(27)–C(21)	134.3(3)
C(2)–Co–C(17)	96.5(2)	C(17)–C(27)–C(21)	139.3(4)
C(2)–Co–C(27)	100.3(2)	C(32)–C(31)–C(35)	109.6(4)
C(3)–Co–C(17)	140.7(2)	C(31)–C(32)–C(33)	107.3(4)
C(3)–Co–C(27)	102.4(2)	C(32)–C(33)–C(34)	107.3(4)
C(17)–Co–C(27)	39.7(2)	C(33)–C(34)–C(35)	109.0(4)
Co–C(1)–O(1)	178.9(4)	C(33)–C(34)–C(36)	126.4(5)
Co–C(2)–O(2)	179.2(4)	C(35)–C(34)–C(36)	124.4(4)
Co–C(3)–O(3)	178.9(4)	C(31)–C(35)–C(34)	106.8(4)
Mo–C(4)–O(4)	176.5(4)	O(31)–C(36)–O(32)	125.8(4)
Mo–C(5)–O(5)	179.5(6)	O(31)–C(36)–C(34)	123.7(5)
C(12)–C(11)–C(16)	120.4(4)	O(31)–C(36)–C(34)	110.5(5)
C(12)–C(11)–C(17)	119.1(4)	C(36)–O(32)–C(37)	116.3(4)

[a] Numbers in parentheses are e.s.d.s in the least significant digits. [b] Cp is the center of the five-membered ring composed of the C(31)–C(35) atoms.

additional 0.5 h. The solvent was removed at reduced pressure and the residue was extracted with CH_2Cl_2. The extracts were subjected to chromatographic separation on silica gel plates, using 2:1 CH_2Cl_2/petroleum ether as eluent to develop two bands. From the first band the unreacted starting material $(C_6H_5)_2C_2Co_2(CO)_6$ was removed. From the second orange band, **1a** was obtained (yield 0.336 g, 58%) as a dark red solid. m.p. 97–99 °C. *Anal.* Found: C, 53.31; H, 2.83. Calc. for $C_{26}H_{17}CoMoO_6$: C, 53.82; H, 2.95%. IR (KBr pellets, cm^{-1}): ν(C≡O), 2049(s), 2006(s), 1986(s), 1951(s); ν(C=O), 1682(m). ^1H NMR ($CDCl_3$, δ, ppm): 2.12 (s, 3H, CH_3), 5.46 (t, 2H, H^3, H^4), 5.84 (t, 2H, H^2, H^5), 7.31 (s, 10H, $2C_6H_5$). Mass spectrum (EI), *m/z* (Mo^{98}, relative intensity): 582 (M^+, 2.4%), 428 [$(M-2C_6H_5)^+$, 4.8], 400 [$(M-2C_6H_5-CO)^+$, 2.7], 372 [$(M-2C_6H_5-2CO)^+$, 10.9], 344 [$(M-2C_6H_5-3CO)^+$, 46.3], 316 [$(M-2C_6H_5-4CO)^+$, 3.4], 288 [$(M-2C_6H_5-5CO)^+$, 6.7], 181 [C_2CoMo^+, 0.5], 178 [$(C_6H_5)_2C_2^+$, 44.0], 107 [$CH_3C(O)C_5H_4^+$, 1.5].

Preparation of 1b and 1c

1b and **1c** are dark red solids, prepared using the same procedure as that for **1a**, but some of the starting materials were changed accordingly.

For preparing **1b**, 0.478 g (1.0 mmol) of $(p\text{-}CH_3C_6H_4)(C_6H_5)C_2Co_2(CO)_6$ was used instead of $(C_6H_5)_2C_2Co_2(CO)_6$. 0.37 g (62%) of **1b** was obtained as a dark red solid. m.p. 104–105 °C. *Anal.* Found: C, 54.72; H, 3.39. Calc. for $C_{27}H_{19}CoMoO_6$: C, 54.57; H, 3.22%. IR (KBr pellets, cm^{-1}): ν(C≡O), 2049(s), 2008(s), 1983(s), 1950(s); ν(C=O), 1680(s). ^1H NMR ($CDCl_3$, δ, ppm): 2.12 (s, 3H, $CH_3C(O)$), 2.33 (s, 3H, $p\text{-}CH_3$), 5.41 (t, 2H, H^3, H^4), 5.81 (t, 2H, H^2, H^5), 7.08–7.41 (m, 9H, C_6H_5, C_6H_4). Mass spectrum (EI) *m/z* (Mo^{98}, relative intensity): 484 [$(M-4CO)^+$, 3.4%], 456 [$(M-5CO)^+$, 16.7], 400 [$(M-p\text{-}CH_3C_6H_4-C_6H_5-CO)^+$, 14.8], 372 [$(M-p\text{-}CH_3C_6H_4-C_6H_5-2CO)^+$, 41.3], 344 [$(M-p\text{-}CH_3C_6H_4-C_6H_5-3CO)^+$, 17.3], 316 [$(M-p\text{-}CH_3C_6H_4-C_6H_5-4CO)^+$, 9.5], 288 [$(M-p\text{-}CH_3C_6H_4-C_6H_5-5CO)^+$, 9.4], 181 ($C_2CoMo^+$, 24.7), 192 ($p\text{-}CH_3C_6H_4C_6H_5C_2^+$, 34.6).

For preparing **1c**, 0.292 g (2.0 mmol) of $CH_3O_2CC_5H_4Na$ was used instead of $CH_3C(O)C_5H_4Na$. 0.34 g (57%) of **1c** was obtained as a dark red solid. m.p. 94–96 °C. *Anal.* Found: C, 52.31; H, 2.83. Calc. for $C_{26}H_{17}CoMoO_7$: C, 52.37; H, 2.87%. IR (KBr pellets, cm^{-1}): ν(C≡O), 2050(s), 2008(s), 1980(s), 1968(s), 1944(s); ν(C=O), 1728(m). ^1H NMR ($CDCl_3$, δ, ppm): 3.67 (s, 3H, CH_3), 5.40 (t, 2H, H^3, H^4), 5.89 (t, 2H, H^2, H^5), 7.30 (s, 10H, $2C_6H_5$). Mass spectrum (EI) *m/z* (Mo^{98}, relative intensity): 542 [$(M-2CO)^+$, 15.6%], 514 [$(M-3CO)^+$, 14.9], 458 [$(M-5CO)^+$, 81.7], 181 (C_2CoMo^+, 6.4), 178 [$(C_6H_5)_2C_2^+$, 100], 123 ($CH_3O_2CC_5H_4^+$, 18.0).

Preparation of 1d

A solution of 0.704 g (2.0 mmol) of $W(CO)_6$ and 0.26 g (2.0 mmol) of $CH_3C(O)C_5H_4Na$ in 20 ml of diglyme was stirred at reflux for 6 h. After the solvent was stripped at reduced pressure, 0.464 g (1.0 mmol) of $(C_6H_5)_2C_2Co_2(CO)_6$ and 20 ml of THF were added and the reaction mixture stirred for an additional 0.5 h. After the same workup as that for **1a**, 0.205 g (31%) of **1d** was obtained as a brick-red solid. m.p. 100–102 °C. *Anal.* Found: C, 46.61; H, 2.21. Calc. for $C_{26}H_{17}CoO_6W$: C, 46.74; H, 2.56%. IR (KBr pellets, cm^{-1}): ν(C≡O), 2050(s), 2004(s), 1983(s), 1977(s), 1945(s); ν(C=O), 1684(m). ^1H NMR ($CDCl_3$, δ, ppm): 2.16 (s, 3H, CH_3), 5.63 (t, 2H, H^3, H^4), 5.89 (t, 2H, H^2, H^5), 7.31 (s, 10H, $2C_6H_5$). Mass spectrum (EI) *m/z* (W^{184}, relative intensity): 528 [$(M-5CO)^+$, 7.3%], 458 [$(M-2C_6H_5-2CO)^+$, 6.3], 430 [$(M-2C_6H_5-$

$3CO)^+$, 4.3], 402 [$(M-2C_6H_5-4CO)^+$, 4.9], 374 [$(M-2C_6H_5-5CO)^+$, 11.3], 267 (C_2CoW^+, 29.7), 178 [$(C_6H_5)_2C_2^+$, 100].

Preparation of ***1e***

A solution of 0.704 g (2.0 mmol) of $W(CO)_6$ and 0.292 g (2.0 mmol) of $CH_3O_2CC_5H_4Na$ in 20 ml diglyme was stirred at reflux for 6 h. After the solution was stripped at reduced pressure, 0.464 g (1.0 mmol) of $(C_6H_5)_2C_2Co_2(CO)_6$ and 20 ml of THF were added and the reaction mixture stirred for an additional 0.5 h. After the same workup as that for **1a**, 0.338 g (49%) of **1e** was obtained as a dark red solid. m.p. 96–98 °C. *Anal.* Found: C, 45.88; H, 2.55. Calc. for $C_{26}H_{17}CoO_7W$: C, 45.64; H, 2.50%. IR (KBr pellets, cm^{-1}): $\nu(C\equiv O)$, 2049(s), 2000(s), 1967(s), 1934(s); $\nu(C=O)$, 1729(s). ^1H NMR ($CDCl_3$, δ, ppm): 3.69 (s, 3H, CH_3), 5.54 (t, 2H, H^3, H^4), 5.94 (t, 2H, H^2, H^5), 7.25 (s, 10H, $2C_6H_5$). Mass spectrum (EI), m/z (W^{184}, relative intensity): 628 [$(M-2CO)^+$, 22.1%], 600 [$(M-3CO)^+$, 38.6], 572 [$(M-4CO)^+$, 100], 544 [$(M-5CO)^+$, 46.5], 474 [$(M-2C_6H_5-2CO)^+$, 4.0], 418 [$(M-2C_6H_5-4CO)^+$, 2.7], 390 [$(M-2C_6H_5-5CO)^+$, 3.5], 267 (C_2CoW^+, 10.3), 178 [$(C_6H_5)_2C_2^+$, 90.4], 123 ($CH_3O_2CC_5H_4^+$, 1.4).

X-ray structural determination of ***1c***

Single crystals of **1c** were obtained by slowly evaporating its solution in 1:2 CH_2Cl_2/petroleum ether. A well-formed single crystal with the approximate dimensions $0.2\times0.2\times0.3$ mm was selected and mounted on the tip of a glass fibre. All X-ray data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation ($\lambda=0.71073$ Å). A total of 4516 independent reflections was collected in the range $2\leqslant\theta\leqslant24°$ with ω–2θ scan mode, of which 3169 reflections with $I\geqslant3\sigma(I)$ were considered to be observed and used for structural refinements. The intensity data were corrected for Lp and empirical absorption effects.

The crystal belongs to monoclinic space group $P2_1/n$. Cell parameters: $a=8.503(1)$, $b=26.721(7)$, $c=11.033(2)$ Å; $\beta=106.09(2)°$; $V=2408$ Å^3; $Z=4$; $D_x=1.64$ g/cm^3; $\mu=12.38$ cm^{-1}; $F(000)=1192$.

The structure was solved by the heavy-atom method. The Mo atom was first located by Patterson analysis and the other non-hydrogen atoms were found from successive difference-Fourier syntheses. The final refinement by the full-matrix least-squares method for the coordinates and the anisotropic thermal parameters of the non-hydrogen atoms converged to give the agreement factors $R=0.036$ and $R_w=0.044$. The highest residual electron density peak is equal to 0.75 e/Å^3 on the final difference Fourier map.

All calculations were performed on a PDP 11/44 computer using the SDP-PLUS program system.

Acknowledgements

We are grateful to the National Science Foundation of China and National Education Committee of China for financial support of this work.

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