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Syntheses and characterization of tri-metal cluster compounds; X-ray structure determination of $[Co_2Mo(\mu_3\text{-}CC_6H_5)Br(CO)_8(bipy)]$ (bipy = α,α-dipyridyl)

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Abstract

The carbyne compound $[Br(CO)_2(Py)_2Mo(\equiv CC_6H_5)]$ (1) (Py = pyridine) reacts with $Co_2(CO)_8$, $Fe_2(CO)_9$ and $Mn_2(CO)_{10}$ to give the tetrahedral tri-metal cluster compounds $Co_2Mo(\mu_3\text{-}CC_6H_5)Br(CO)_8(Py)_2$ (3), $Fe_2Mo(\mu_3\text{-}CC_6H_5)Br(CO)_9(Py)_2$ (4) and $Mn_2Mo(\mu_3\text{-}CC_6H_5)Br(CO)_{10}(Py)_2$ (5), respectively. The tri-metal cluster compound $Co_2Mo(\mu_3\text{-}CC_6H_5)Br(CO)_8(bipy)$ (6) is prepared in a similar reaction sequence from $[Br(CO)_2(bipy)Mo(\equiv CC_6H_5)]$ (2) and $Co_2(CO)_8$. IR, ^1H and ^{13}C NMR spectral data of these compounds are reported and discussed. The crystal structure of compound 6 has been determined by X-ray diffraction. It belongs to the monoclinic space group, $P2_1/c$, $z = 4$ $a = 9.711(1)$, $b = 17.358(2)$, $c = 17.809(2)$ Å, $\beta = 97.70(1)°$, $R = 0.096$ for 3185 unique reflections with $|I| > 3\sigma(I)$. The molecule consists of a Co_2Mo isosceles triangle of metal atoms (Mo–Co = 2.778(4) and Co–Co = 2.478(5) Å) capped by a triply bridging phenylmethylidyne ligand (Mo–C = 2.048(2) and Co–C = 1.942(2) Å). Two carbonyls attached to the molybdenum atom are terminal but each of these two carbonyl ligands is semi-bridging to one of the cobalt atoms. The other six carbonyls are all terminal.

Introduction

The metal carbyne compounds of general type $[M(\equiv CR)(CO)_2L]$ [1–3] (M = Cr, Mo, W; R = alkyl or aryl), where L = η^5-C_5H_5, η^5-C_5Me_5, or $HB(Pz)_3$ (Pz-pyrazol-1-yl) have been shown to be good precursors for syntheses of metal cluster compounds. The structure of the resulting clusters and the reactivity of the starting carbyne compounds with metal carbonyl compounds or the compounds containing metal–metal multiple bonds are very dependent on the nature of the L and R groups. We therefore, considered it of interest to study the reactivity of carbyne

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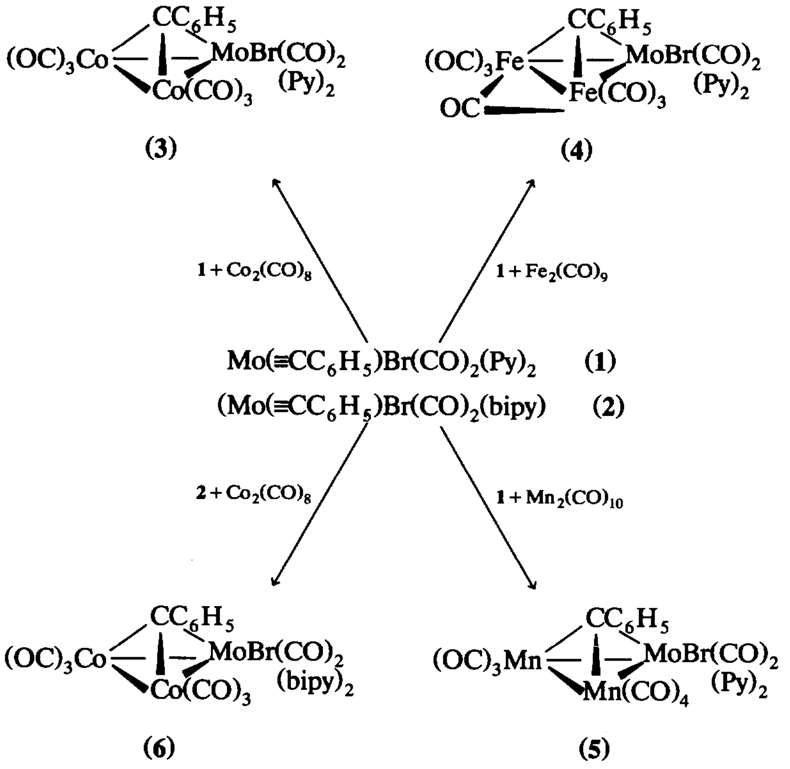

Scheme 1.

compounds [Mo(≡CC_6H_5)Br$(CO)_2$L] (L = $(Py)_2$ or bipy) with metal carbonyl compounds and $(C_5H_5)(CO)_2$Mo≡Mo$(CO)_2(C_5H_5)$. In the present work, we report the synthesis, structures, properties and spectral data of tri-metal cluster compounds **3**, **4**, **5** and **6** together with the X-ray structural data of **6**.

Results and discussion

The carbyne compounds **1** and **2** reacted with metal carbonyl compounds to give tri-metal cluster compounds as shown in Scheme 1.

Compared with **1** and **2**, compounds **3–6** are more stable. The latter could be handled and operated in air for a short period of time. The carbyne compounds **1** and **2** did not react with $(C_5H_5)(CO)_2$Mo≡Mo$(CO)_2(C_5H_5)$ [7].

Analytical and spectroscopic data are given in Tables 1 and 2.

The presence of the capping μ_3-C atoms in **3**, **4**, **5** and **6** are indicated by the appearance in the ^{13}C NMR spectra of signals in the range δ 230–240 ppm [1,5]. The IR spectra bands of **3**, **4**, and **6** in the range of $\nu(CO)$ 1750–1850 cm^{-1} indicated the presence of species with bridging or semi-bridging CO ligands. The tetrahedral structures of compounds **3**, **4**, **5** and **6** are in accord with ^1H NMR, ^{13}C NMR and IR spectra listed in Tables 1 and 2.

Table 1

Physical properties, elemental analyses and IR spectra of compounds **1–6**

Compound	Colour	Yield (%)	ν(CO) [a] (cm^{-1})	Elemental analysis (%) [b]		
				C	H	N
1	Yellow	75	1905s, 1955s	47.81 (47.63)	3.51 (3.13)	5.89 (5.85)
2	Red	70	2000s, 1919s	47.79 (47.80)	2.70 (2.73)	5.69 (5.87)
3	Green	97	2098w, 2080s, 2041vs, 2025s, 1910s, 1838w	39.55 (39.25)	2.00 (1.98)	4.07 (3.66)
4	Brown	64	2002s, 1923s, 1920s, 1833w, 1755m	39.81 (39.69)	1.90 (1.91)	3.61 (3.56)
5	Yellow	73	2047m, 2010s, 1990m, 1923s, 1905s	40.10 (39.89)	2.14 (1.84)	3.95 (3.45)
6	Black	95	2106m, 2066vs, 2056vs, 1977w, 1858s	36.82 (37.07)	1.62 (1.77)	3.24 (3.30)

[a] Measured in CH_2Cl_2. [b] Calculated values are given in parentheses.

Table 2

^{1}H NMR and ^{13}C NMR spectra [a] of compounds

^{1}H NMR δ (ppm)	^{13}C NMR δ (ppm)
1 9.04 (d, 4H, *o*-Py)	275.68 (CPh), 222.32 (CO)
7.72 (t, 2H, *p*-Py)	153.04, 138.09, 124.67 (C_5H_5N)
7.48 (m, br, 9H, *m*-Py, C_6H_5)	145.24, 128.78, 128.34 (C_6H_5)
2 9.22 (d, 2H, 2,2′-bipy)	278.36 (CPh), 223.73 (CO)
8.22 (d, 2H, 5,5′-bipy)	154.52, 154.07, 139.41
8.03 (t, 2H, 4,4′-bipy)	125.92, 122.72 (bipy)
7.53 (t, 2H, 3,3′-bipy)	145.80, 129.04, 128.48
7.30–7.15 (m, 5H, C_6H_5)	127.92 (C_6H_5)
3 8.68 (d, 4H, *o*-Py),	232.09 (CPh), 208.32 (CO)
8.28 (t, 2H, *p*-Py)	150.22, 136.14, 123.31 (C_5H_5N)
7.46 (m, br, 9H, *m*-Py, C_6H_5)	140.83, 125.54, 125.02 (C_6H_5)
4 9.00 (d, 4H, *o*-Py)	241.27 (CPh), 211.59 (CO)
8.14–7.02 (m, br, 11H)	152.11–128.04 (C_5H_5N, C_6H_5)
5 9.05 (d, 4H, *o*-Py)	243.91 (CPh), 212.06, 211.94 (CO)
8.18 (t, 2H, *p*-Py)	152.98–128.00 (C_5H_5N, C_6H_5)
7.47–7.08 (m, br, C_6H_5)	
6 8.80 (d, 2H, 2,2′-bipy)	231.04 (CPh), 199.73 (CO)
8.60 (d, 2H, 5,5′-bipy)	157.96, 154.16, 126.55
7.82 (d, 2H, 4,4′-bipy)	122.61 (bipy)
7.72 (t, 2H, 3,3′-bipy)	153.23, 138.45, 127.25–125.85
6.91–6.30 (5H, C_6H_5)	125.04 (C_6H_5)

[a] Measured in $CDCl_3$.

Table 3

Positional parameters with their estimated standard deviations in parentheses (fractional coordinates)

Atom	*x*	*y*	*z*	*B* (Å^2)
Mo	0.25618(9)	0.22716(5)	0.78668(5)	2.36(2)
Br	0.5009(2)	0.2730(1)	0.75397(9)	6.18(4)
Co1	0.0053(2)	0.26427(9)	0.83569(9)	3.72(3)
Co2	−0.0003(2)	0.16265(9)	0.73757(8)	3.61(3)
O1	0.200(1)	0.2291(7)	0.6097(5)	6.9(3)
O2	0.199(1)	0.4034(5)	0.7649(7)	7.5(3)
N1	0.3720(9)	0.1168(6)	0.7978(5)	3.5(2)
N2	0.380(1)	0.2259(6)	0.9011(5)	4.0(2)
C1	0.211(1)	0.2253(7)	0.6761(7)	4.3(3)
C2	0.212(1)	0.3383(7)	0.7764(7)	4.3(3)
C3	−0.132(1)	0.2249(8)	0.8865(8)	4.6(3)
C4	0.066(2)	0.3287(7)	0.9125(7)	4.8(3)
C5	−0.092(2)	0.3356(8)	0.7743(9)	5.4(3)
C6	−0.146(1)	0.1146(8)	0.7674(8)	5.4(3)
C7	0.049(1)	0.0817(8)	0.6863(7)	5.1(3)
C8	−0.083(1)	0.2181(8)	0.6580(7)	5.3(3)
C9	0.110(1)	0.1687(6)	0.8368(6)	2.8(2)
C10	0.125(1)	0.1087(6)	0.8974(6)	2.7(2)
C13	0.176(1)	−0.0023(8)	1.0121(7)	4.8(3)
C16	0.375(1)	0.0639(7)	0.7412(8)	4.5(3)
C18	0.507(2)	−0.0252(9)	0.826(1)	4.5(3)
C20	0.440(1)	0.0991(7)	0.8678(7)	4.1(3)
C21	0.448(1)	0.1598(7)	0.9254(6)	3.8(3)
C23	0.528(2)	0.214(1)	1.0461(8)	6.9(4)
C25	0.391(2)	0.2890(9)	0.9500(8)	6.1(3)
Solvent molecule				
C11	0.298(1)	0.5947(6)	0.0639(5)	16.4(3)
C12	0.312(1)	0.5333(5)	−0.0838(4)	15.1(3)
C26	0.241(4)	0.534(2)	0.002(1)	22(1)

The results of the X-ray work are summarized in Tables 3 and 4. The molecular structure of **6** is shown in Fig. 1. As expected, the molecule comprises a Co_2Mo isosceles triangle (within the accuracy of this determination) of metal atoms (Mo–Co(1) 2.771(5), Mo–Co(2) 2.764(4), Co–Co 2.478(5) Å) capped by a triply bridging phenylidyne ligand (Mo–C 2.048(2), Co–C 1.942(2) Å). The dipyridyl ligates as a bidentate donor to the molybdenum atom. The molecule possesses mirror symmetry; it is defined (Fig. 1) by the atoms Mo, Br, C(9), C(10) and C(13). The plane of the phenyl ligand lies perpendicular to the mirror plane. Each cobalt atom is bonded with three terminal carbonyls and one semi-bridging carbonyl which is, terminal to the molybdenum atom. Two of the CO ligands [CO(3), CO(4) and CO(6), CO(7)] on each cobalt atom are approximately equatorial with respect to the metal atom plane.

Experimental

All experiments were carried out using Schlenk tube techniques under a dry oxygen-free nitrogen atmosphere. The solvents were dried and distilled under

Table 4

Selected interatomic distances (Å) and bond angles (deg)

Mo–Co1	2.771(5)	Mo–Co2	2.764(4)	Co–Co	2.478(5)
Co–C9	1.943(2)	Mo–C9	2.048(2)	Mo–Br	2.644(5)
Mo–N	2.221(2)	C9–C10	1.493(3)	Mo–C1	1.959(3)
Mo–C2	1.979(3)	Co1–C2	2.712(3)	Co2–C1	2.681(3)
Co1–C3	1.837(4)	Co2–C6	1.783(4)	O1–C1	1.763(3)
O3–C3	1.116(4)	C10–C11	1.399(3)	N1–C20	1.336(3)
C20–C21	1.466(4)	C19–C20	1.395(4)		
Mo–Co1–Co2	63.25(1)	Mo–Co2–Co1	63.55(1)		
Co2–Co1–C9	50.32(6)	Co1–Co2–C9	50.36(7)		
Mo–Co2–C9	47.75(7)	Co2–Mo–C9	44.55(6)		
Co1–Mo–C9	44.45(6)	Mo–Co1–C9	47.60(7)		
Co2–Co1–C3	97.66(9)	Co2–Co1–C5	95.7(2)		
Co1–Co2–C6	93.9(2)	Co1–Co2–C8	98.0(2)		
Co1–Co2–C7	160.60(8)	Co2–Co1–C4	161.8(2)		
Co2–Mo–C1	66.67(9)	Co1–Mo–C2	67.21(9)		
Mo–Co1–C2	42.31(6)	Mo–Co2–C1	42.14(6)		
N1–Mo–N2	72.75(8)	Br–Mo–Co1	148.59(1)		
Br–Mo–Co2	148.29(1)	Co1–Mo–N2	96.00(6)		
Co2–Mo–N1	95.93(5)	Mo–C1–O1	171.1(3)		
Co1–C3–O3	175.5(3)	Co2–C6–O6	178.3(3)		

nitrogen prior to use. Silica gel (100–200 m) was pumped on a vacuum line (10^{-3} mmHg) for 15 h, and flushed with nitrogen. Elemental analyses were recorded on a Carlo Erba 1106 elemental analyzer. The NMR measurements were made with Bruker AM400 instrument and IR spectra recorded with a Nicolet FT-10DX spectrometer. $(CO)_5Mo[C(OEt)C_6H_5]$, $[Br(CO)_2(Py)_2Mo(\equiv CC_6H_5)]$ and $[Br(CO)_2(bipy)Mo\equiv CC_6H_5)]$ were prepared as described previously [8,9].

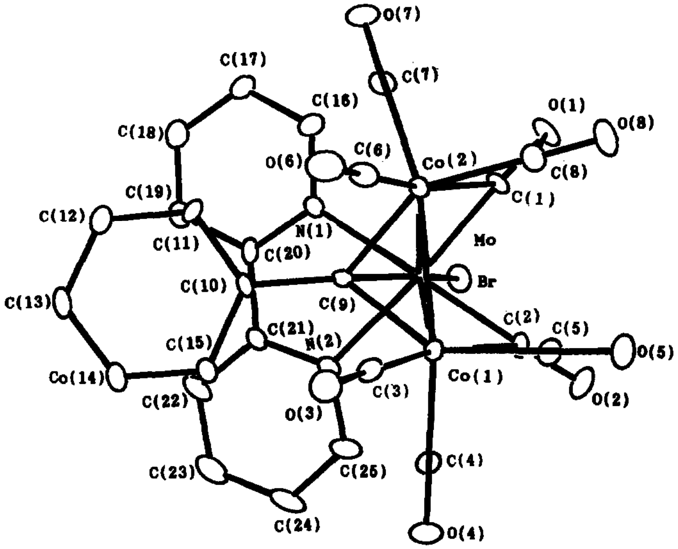

Fig. 1. Molecular structure of $[Co_2Mo(\mu_3\text{-}CC_6H_5)Br(CO)_8(bipy)]$ (6).

Synthesis of [$Co_2Mo(\mu_3$-$CC_6H_5)Br(CO)_8(Py)_2$ (3)

The compound [$Br(CO)_2(Py)_2Mo(\equiv CC_6H_5)$] (**1**) (0.48 g, 1.0 mmol) in CH_2Cl_2 (10 cm^3) was treated with $Co_2(CO)_8$ (0.34 g, 1.0 mmol), with CO evolution and the formation of a deep green solution. After stirring for 2 h, some of the solvent was removed *in vacuo* and the product was obtained as green needle crystals by the addition of petroleum ether (2–3 cm^3) and cooled to -20°C (0.74 g, 97%).

Syntheses of [$Fe_2Mo(\mu_3$-$CC_6H_5)Br(CO)_9(Py)_2$ (4)

A mixture of **1** (0.2 g, 0.55 mmol) and $Fe_2(CO)_9$ (0.6 g, 1.6 mmol) in toluene (20 cm^3) was stirred at room temperature for 5 h. Solvent was removed *in vacuo*. The residue was dissolved in CH_2Cl_2 (2 cm^3) and chromatographed on silica gel, eluting with CH_2Cl_2 and petroleum ether (1 : 4) to remove unreacted $Fe_2(CO)_9$. The eluting solution was changed to CH_2Cl_2 and petroleum ether (1 : 1) to remove the red-brown band which was collected and concentrated to about 10 cm^3; petroleum ether (5 cm^3) was added, giving a deep brown solid of **4** (0.05 g, 64%).

Syntheses of [$Mn_2Mo(\mu_3$-$CC_6H_5)Br(CO)_{10}(Py)_2$ (5)

A solution of **1** (0.48 g, 1.0 mmol) and $Mn_2(CO)_{10}$ (0.39 g, 1.0 mmol) in THF (10 cm^3) was stirred at room temperature overnight. Solvent was removed, and the residue was dissolved in CH_2Cl_2 and chromatographed on silica gel. The light-brown band was collected and concentrated. Compound **5** was obtained as a yellow-brown solid (0.59 g, 73%).

Syntheses of [$Co_2Mo(\mu_3$-$CC_6H_5)Br(CO)_8$(bipy) (6)

The procedure was similar to that described for **3** (yield 95%).

X-Ray data collection and structure solution of 6

Single crystals suitable for X-ray diffraction were grown by recrystallization from dichloromethane and petroleum ether. A black crystal with dimensions of $0.52 \times 0.37 \times 0.15$ mm^3, which was sealed in a capillary, was used for collection of intensity data. Diffraction data were collected at 295 K with an Enraf–Nonius CAD-4 four-circle diffractometer using graphite-monochromated Mo-K_α radiation (0.71073 Å). The unit cell parameters were derived from least-squares refinement of 25 well-centred reflections ($26° < 2\theta < 40°$).

Crystal data. [$Co_2Mo(\mu_3$-$CC_6H_5)Br(CO)_8$(bipy), $M = 848.04$, monoclinic, $P2_1/c$, $a = 9.711(1)$, $b = 17.358(2)$, $c = 17.809(2)$ Å, $\beta = 97.70(1)°$, $U = 2974.7$ Å^3, $Z = 4$, $D_c = 1.893$ g cm^{-3}, $F(000) = 1656$, μ(Mo-K_α) = 30.7 cm^{-1}. Intensity data were collected by the ω–2θ scan technique in the range $1 \leqslant 2\theta \leqslant 48°$. The intensities of three standard reflections measured every hour showed no significant variations. Lorentz and polarization corrections and a ψ (maximum and minimum transmission 99.95 and 72.22%, respectively) empirical absorption correction were applied. The 5008 reflections were measured and 3158 independent reflections with $|I| > 3\sigma(I)$ were used in the calculation. The structure was solved by the heavy-atom method and refined by the minimum function $\Sigma w(|F_o| - |F_c|)^2$; $w = 1$. Refinement converged at $R = 0.096$ ($R_w = 0.089$) and $(\Delta/\sigma) = 0.19$. The R value is a little large, this is due to the intense X-ray absorption by the capillary. The final electron density maps showed maximum residual peaks 1.686 e Å^{-3} close to the Mo atom. Atomic scattering factors and anomalous dispersion terms were taken from ref. 10. All calculations were carried out on a PDP11/44 computer using the SDP package.

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