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Reactions of molybdenum–cobalt complex with phenylacetylene: X-ray crystal structure of $[MoCo(CO)_4\{CPhCHCHCPh\}(\eta^5\text{-}C_5H_5)]$

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Abstract

Reaction of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (1) with phenylacetylene in tetrahydrofuran at 60°C produced a heterobimetallic compound, $[MoCo(CO)_4\{CPhCHCHCPh\}(\eta^5\text{-}C_5H_5)]$ (2), in high yield. Compound 2 was characterized by mass, infrared and ^1H, ^{13}C and ^{31}P NMR spectra. The X-ray crystal structure of 2 was determined: orthorhombic, P_{bca}, $a = 12.479(3)$, $b = 15.975(3)$, $c = 21.570(3)$ Å, $V = 4299.8(15)$ Å^3 and $Z = 8$, $R_w(F) = 4.00\%$ for 2143 ($F > 4\sigma(F)$) observed reflections. In 2, the cobalt fragment is at apical and the molybdenum fragment is at basal position of the pseudo-pentagonal pyramidal structure. $[MoCo(CO)_4\{\mu\text{-}PhC_2H\}(PPh_3)(\eta^5\text{-}C_5H_5)]$ (3) was obtained in excellent yield from the reaction of 1 with phenylacetylene at lower temperature. Compound 3 can be quantitatively converted into 2 by reaction with excess phenylacetylene at 60°C.

Keywords: Molybdenum; Cobalt

1. Introduction

The ability of alkynes to use one or both sets of filled π orbitals in bonding to one, two, three or four metal atoms is well known [1]. Complexes of this type are usually obtained by the reaction of metal complexes with alkynes. The formation of metallacyclopentadiene rings in reactions with excess alkynes is also well documented [2]. This occurs through the linkage of two alkynes with the metal center.

We recently reported the synthesis of a heterobimetallic compound, $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**1**), from the reaction of $NaCpMo(CO)_3$ with $CoCl(PPh_3)_3$ [3]. Initial studies showed that **1** is a latent catalyst for the hydroformylation of styrene under CO/H_2 pressure [4]. The reactivity of bimetallic compounds with alkynes has long been known [5]. Here we report the investigation of how this heterobimetallic compound behaved toward phenylacetylene.

2. Results and discussion

Reaction of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**1**) with excess phenylacetylene in tetrahydrofuran at 60°C yielded a heterobimetallic compound, $[MoCo(CO)_4\{CPhCHCHCPh\}(\eta^5\text{-}C_5H_5)]$ (**2**) in 94% yield. The ^1H NMR spectrum of **2** exhibited one resonance assigned to Cp at δ 4.84. Vinyl protons in alkenyl species resonate at 6.81 ppm, which may be caused by the deshielding effect from the adjacent phenyl rings [6]. There are broad multiplets in the region of δ 7.16–7.35 due to the phenyl protons. The ^{13}C NMR spectrum showed one sharp line at δ 236, which was assigned to the carbonyl carbon atom bonded to Mo atom. The signal of the carbonyl groups bonded to quadrupolar cobalt are often difficult to detect owing to line broadening. Fortunately, we were able to observe a broad multiplet at δ 202 after a long cumulation period. These spectral properties are consistent with a compound having a pseudo-pentagonal pyramidal structure. Nevertheless, it was difficult to establish which metal was engaged in the ring from these data alone. Therefore, an X-ray structure determination was carried out

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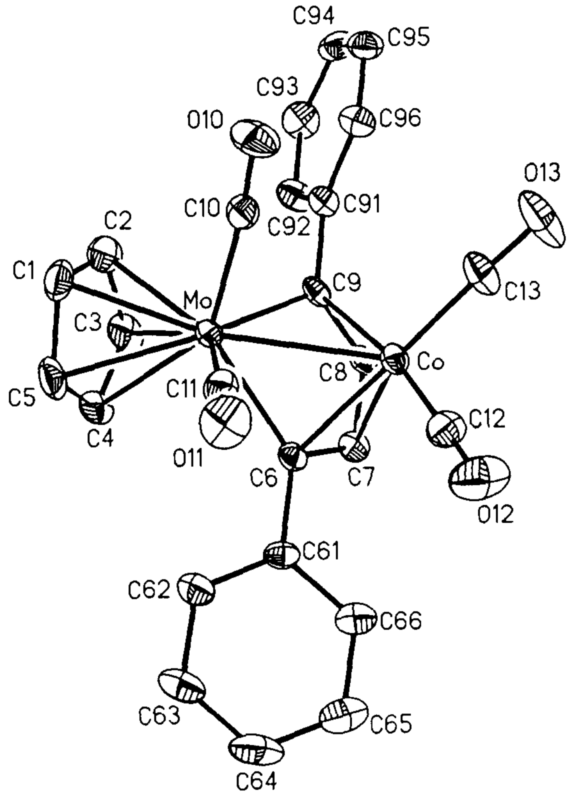
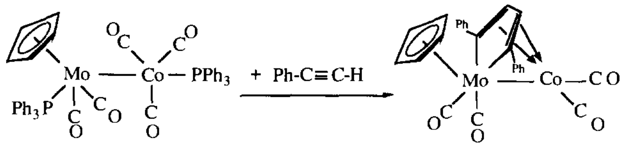


Fig. 1. ORTEP drawing with the numbering scheme of **2**. Hydrogen atoms are omitted for clarity.

on **2**. Single-crystal X-ray determination revealed that this compound indeed has a pseudo-pentagonal pyramidal structure as shown in Fig. 1. Two alkynes link with molybdenum to form a metallacyclopentadiene complex.

This structure can be viewed as a sandwich compound with η^5-MC_4 ligand π-bonded to the second metal (Scheme 1). The cobalt and the molybdenum fragment are at apical and basal positions of the pentagonal pyramidal structure, respectively. It is regarded as a *nido* structure according to Wade's electron counting rule [7]. Also, both metal centers obey the 18-electron rule. The Mo–Co bond is within the normally observed cobalt–molybdenum single bond range [8]. However, it is shorter in **2** than in **1** [9]. The fact that the C(7)–C(8) bond is shorter than that of C(6)–C(7) and C(8)–C(9) bonds is consistent with the normal observation for compounds with this type of structure (Table 1). Several closely related complexes analogous to **2** have been reported and prepared using alternative synthetic pathways [10].



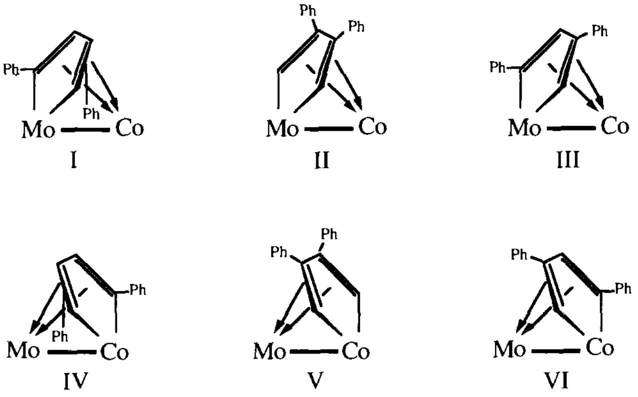
1 **2**

Scheme 1.

Table 1
Selected bond distances and angles

Bond distances (Å)			
Mo–Co	2.698(1)	Mo–C(1)	2.300(6)
Mo–C(2)	2.294(7)	Mo–C(3)	2.325(6)
Mo–C(4)	2.348(5)	Mo–C(5)	2.351(6)
Mo–C(6)	2.191(5)	Mo–C(9)	2.172(5)
Mo–C(10)	1.997(6)	Mo–C(11)	2.016(6)
Co–C(6)	2.089(5)	Co–(7)	2.107(5)
Co–C(8)	2.111(5)	Co–C(9)	2.060(5)
Co–C(12)	1.741(7)	Co–C(13)	1.745(6)
O(10)–C(10)	1.148(7)	O(11)–C(11)	1.136(7)
O(12)–C(12)	1.143(8)	O(13)–C(13)	1.134(8)
C(6)–C(7)	1.421(7)	C(7)–C(8)	1.398(7)
C(8)–C(9)	1.416(7)	C(6)–C(61)	1.513(7)
C(9)–C(91)	1.489(7)		
Bond angles (°)			
C(6)–Mo–C(9)	73.5(2)	C(10)–Mo–C(11)	80.0(2)
Mo–Co–C(6)	52.6(1)	Mo–Co–C(7)	79.3(1)
C(6)–Co–C(7)	39.6(2)	Mo–Co–C(8)	78.7(1)
C(6)–Co–C(8)	68.9(2)	C(7)–Co–C(8)	38.7(2)
Mo–Co–C(9)	52.2(1)	C(6)–Co–C(9)	78.0(2)
C(7)–Co–C(9)	69.7(2)	Mo–C(6)–C(7)	116.6(3)
Co–C(7)–C(8)	70.8(3)	C(6)–C(7)–C(8)	114.9(5)
Co–C(8)–C(7)	70.5(3)	Co–C(8)–C(9)	68.2(3)
C(7)–C(8)–C(9)	115.6(5)	Mo–C(9)–Co	79.2(2)
Mo–C(9)–C(8)	116.9(3)	Co–C(9)–C(8)	72.1(3)
Mo–C(10)–O(10)	174.2(5)	Mo–C(11)–O(11)	178.4(5)
Co–C(12)–O(12)	177.5(6)	Co–C(13)–O(13)	177.3(6)

In principle, there are several possible combinations of the two linked phenylacetylenes from **I** to **VI**, as shown in Scheme 2. However, it is strikingly noteworthy that only one isomer, out of many possible ones, is obtained for **2**. A crystal structure determination confirmed the head-to-head structure shown in Fig. 1 in which the carbon atoms bearing the phenyl groups are

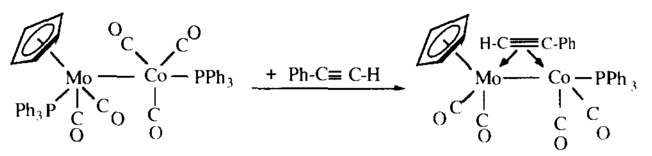


I, II, III: Co = $Co(CO)_3$; Mo = $Mo(CO)(\eta^5\text{-}C_5H_5)$
IV, V, VI: Co = $Co(CO)_2$; Mo = $Mo(CO)_2(\eta^5\text{-}C_5H_5)$

Scheme 2.

both bonded to the molybdenum atom. Therefore, structure **I** best represents **2**. There are precedents for the observed head-to-head linkage of the two PhC_2H ligands [10b,11]. Thermolysis of complex **I** did not produce **IV** even on reflux in toluene. Fragmentation of **I** was observed after prolonged heating. The activation energy between these two isomers may be too large to prevent the conversion. In this case, **I** is the kinetically favored isomer and **II** or **III** are the more thermodynamically stable isomers. In contrast, intramolecular rearrangement did take place for a closely related compound in which a head-to-tail structure changed to a head-to-head structure [10a]. The reason why structure **I** is more predominant than **IV** is unknown. Probably the fact that the molybdenum–carbon σ-bond is stronger than the cobalt–carbon bond is a key factor.

Reaction of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**1**) with phenylacetylene in tetrahydrofuran at 47°C yielded a major product, $[MoCo(CO)_4\{\mu\text{-}PhC_2H\}(PPh_3)(\eta^5\text{-}C_5H_5)]$ (**3**) (Scheme 3), with a trace amount of **2**. The yield of **3** was 98%. The ^1H NMR spectrum of **3** showed one resonance, assigned to Cp at δ 5.28. Vinyl protons in alkenyl species resonate at δ 4.86 (d, J_{PH} = 8.7 Hz) ppm. There are broad multiplets in the regions of δ 6.87–6.98(m, 5H, PhC_2H) and δ 7.17–7.32(m, 15H, PPh_3) due to the phenyl protons. The ^{13}C NMR spectrum showed two distinct signals for two carbonyls which are attached to molybdenum owing to the asymmetric nature of **3**. Again, the signals of the carbonyl groups bonded to quadrupolar cobalt are broadened. It is proposed that one triphenylphosphine ligand being replaced by a phenylacetylene was probably at the molybdenum site during the reaction; then the coordinated phenylacetylene moved to the top of the heterometallic bond and a carbonyl was knocked out from the cobalt center. The singlet instead of doublet Cp signal suggested that the triphenylphosphine ligand remained at the cobalt site. The distance between the Cp and the triphenylphosphine ligand is too long to allow observable coupling. The alkyne methine proton, nevertheless, exhibits a small coupling to the triphenylphosphine ligand (J_{PH} = 8.7 Hz). In the case of **1**, the C_5H_5 group exhibits a doublet, J_{PH} = 0.9 Hz, due to a long-range coupling of a nucleus having $I = 1/2$, presumably ^{31}P. Although the crystal structure is not available, all these spectroscopic data when compared with the literature indicated that it is an alkyne-bridged complex [6,12]. Further reaction of **3** with excess phenylacetylene at 60°C afforded **2**. The conversion is quantitative.



1 **3**

Scheme 3.

3. Experimental section

All operations were performed in a nitrogen-flushed glove-box or in a vacuum system. Freshly distilled solvents were used. All processes of separation of products were performed by centrifugal thin-layer chromatography (CTLC) on a Harrison Chromatotron Model 8924 System. ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Varian Model 300 spectrometer at 300, 75.46 and 121.44 MHz, respectively. Chemical shifts are reported in ppm downfield from internal TMS. IR spectra were recorded in CH_2Cl_2 on a Hitachi 270-30 spectrometer. Mass spectra were recorded on a JEOL JMS-SX/SX 102A GC/MS/MS System. Elemental analyses of the complexes were performed using a Heraeus CHN-O-RAPID instrument.

3.1. Preparation of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (1)

The compound was synthesized according to a procedure in the literature [3].

3.2. Reaction of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (1) with $HC \equiv CPh$

Into a 100 ml round-bottomed flask equipped with a condenser and a magnetic stirrer were placed 120 mg (0.14 mmol) of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**1**) and anhydrous tetrahydrofuran (30 ml). Excess phenylacetylene (0.15 ml, 1.37 mmol) was added and the reaction mixture was heated under dry nitrogen at 60°C for 15 h. The solvent was removed in vacuo.

The residue was dissolved in a small amount of CH_2Cl_2–hexane and then was loaded into the CTLC system for separation. The CTLC separation was carried out under nitrogen. A yellow band was collected and identified as **2**, with a yield of 94% (69 mg). It was brown when dried, and was a fairly thermally and air-stable compound.

Similarly, 122 mg (0.14 mmol) of **1** and anhydrous tetrahydrofuran (30 ml) were placed in a 100 ml round-bottomed flask, excess phenylacetylene (0.15 ml, 1.37 mmol) was added and the reaction mixture was heated under dry nitrogen at 47°C for 15 h. A similar purification procedure was applied. An orange band was collected and identified as **3**, with a yield of 98% (94 mg). It was dark brown when dried, and was a fairly thermally stable compound.

2: ^1H NMR ($CDCl_3$, δ/ppm): 4.84 (s, 5H, Cp), 6.81 (s, 2H, PhC_2H), 7.16–7.35 (m, 10H, PhC_2H). ^{13}C NMR ($CDCl_3$, δ/ppm) [13]: 90.7 (Cp), 119.8 (C(7), C(8)), 126.3 (C(64), C(94)), 127.2 (C(63), C(65), C(93), C(95)), 128.0 (C(62), C(66), C(92), C(96)), 153.2 (C(61), C(91)), 171.9 (C(6), C(9)), 202.4 (Co–COs), 236.4 (Mo–COs). IR (CH_2Cl_2): ν (CO) 2032(s), 1978(vs), 1922(m) cm^{-1}. Mass spectrum: m/z 538 (P^+). Anal. Calc. for $C_{25}H_{17}CoMoO_4$: C, 55.99; H, 3.19. Found: C, 55.42; H, 3.36%.

3: ^1H NMR ($CDCl_3$, δ/ppm): 5.28 (s, 5H, Cp), 4.86 (d, J_{PH} = 8.7 Hz, PhC_2H), 6.87–6.98 (m, 5H, PhC_2H), 7.17–7.32 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$, δ/ppm): 57.8(m). IR ($CHCl_3$): ν (CO) 2004(s), 1968(vs), 1940(s), 1862(m) cm^{-1}. Mass spectrum: m/z 698 (P^+).

3.3. Crystal structure determination of 2

An red parallelepiped crystal of **2** with size of 0.2 × 0.4 × 0.7 mm was used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation, λ = 0.71073 Å. The positions of heavy atoms in the structure were determined by direct methods, and the remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were considered to ride on carbon atoms with a C–H bond length 0.96 Å, and the temperature factors were fixed at 0.08 Å. The hydrogen atoms were included for structure factor calculation in the final cycles. All refinements and calculations were carried out with the Siemens SHELXTL PLUS software package on a Micro VAX 3100 computer.

Table 2
Crystal data of **2**

Formula	$C_{25}H_{17}CoMoO_4$
Formula weight	536.3
Cryst system	Orthorhombic
Space group	*Pbca*
a (Å)	12.479(3)
b (Å)	15.975(3)
c (Å)	21.570(3)
V ($Å^3$)	4299.(15)
Z	8
D_c (g cm^{-3})	1.657
λ (Mo Kα) (Å)	0.71073
μ (mm^{-1})	1.384
Range (°)	4.0–45.0
Scan type	$\theta/2\theta$
No. of reflections collctd	3644
No. of independt reflections	2809 (R_{int} = 1.55%)
No. of observed reflections	2143 ($F > 4.0\sigma(F)$)
No. of refined parameters	280
R_f [a] for significant reflctns	0.0324
R_w [b] for sigft reflctns	0.0400
G_oF [c]	1.00

[a] $R_f = [\Sigma(F_o - F_c)/\Sigma F_o]$.
[b] $R_w = \Sigma w^{1/2}(F_o - F_c)/\Sigma w^{1/2}F_o$.
[c] $G_oF = [\Sigma w(F_o - F_c)^2/(N_{rflns} - N_{params})]^{1/2}$. $W^{-1} = \sigma^2(F) + 0.0010F^2$.

Table 3
Atomic coordinates (×10^4) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U(eq)
Mo	1386(1)	3592(1)	926(1)	28(1)
Co	−486(1)	2853(1)	1229(1)	31(1)
O(10)	2358(4)	1828(3)	1239(2)	63(2)
O(11)	1530(4)	3709(3)	2382(2)	66(2)
O(12)	−1179(5)	3010(3)	2498(2)	88(2)
O(13)	−998(5)	1097(3)	1245(2)	92(2)
C(1)	3109(5)	3944(4)	653(3)	58(2)
C(2)	2566(5)	3700(4)	115(3)	56(2)
C(3)	1763(5)	4284(3)	3(3)	50(2)
C(4)	1799(5)	4888(3)	472(3)	47(2)
C(5)	2649(5)	4682(4)	879(3)	54(2)
C(6)	−185(4)	4134(3)	1137(2)	31(2)
C(7)	−1044(4)	3907(3)	738(2)	34(2)
C(8)	−810(4)	3266(3)	318(2)	33(2)
C(9)	227(4)	2913(3)	369(2)	31(2)
C(10)	1954(4)	2451(3)	1116(3)	39(2)
C(11)	1468(4)	3658(3)	1859(3)	42(2)
C(12)	−927(5)	2949(3)	1991(3)	50(2)
C(13)	−783(6)	1786(4)	1226(3)	53(2)
C(61)	−443(4)	4816(3)	1601(2)	34(2)
C(62)	314(5)	5402(3)	1768(3)	49(2)
C(63)	68(6)	6062(4)	2158(3)	68(3)
C(64)	−947(7)	6149(4)	2387(3)	74(3)
C(65)	−1722(6)	5576(4)	2235(3)	68(3)
C(66)	−1479(5)	4913(4)	1840(3)	50(2)
C(91)	504(4)	2264(3)	−101(2)	36(2)
C(92)	490(5)	2498(3)	−721(3)	48(2)
C(93)	719(5)	1928(4)	−1179(3)	55(2)
C(94)	945(5)	1096(4)	−1037(3)	52(2)
C(95)	972(5)	864(3)	−432(3)	46(2)
C(96)	780(5)	1439(3)	34(3)	43(2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The crystallographic data of the complex **2** are summarized in Table 2.

4. Supplementary Material Available

Atomic coordinates are given in Table 3; tables of thermal parameters, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates for **2**, are available from the authors.

Acknowledgement

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