Pergamon

0277-5387(94)00419-6

Polyhedron Vol. 14, No. 11, pp. 1419–1423, 1995
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0277-5387/95 $9.50+0.00

PREPARATION AND CRYSTALLOGRAPHIC CHARACTERIZATION OF [MoCo(CO)$_5$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)]

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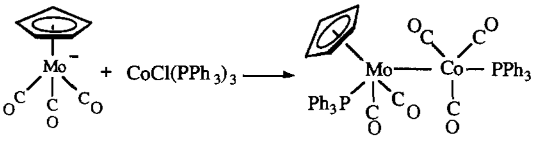
(*Received* 18 *August* 1994; *accepted* 7 *October* 1994)

Abstract—Reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] with CoCl(PPh$_3$)$_3$ in tetrahydrofuran yielded an unusual heterobimetallic compound [MoCo(CO)$_5$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**1**). Compound **1** was characterized by mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. The X-ray crystal structure of **1** was determined. The cobalt centre has picked up three carbonyl groups and one molybdenum carbonyl group has been replaced by the triphenylphosphine ligand.

The chemistry of heterometallic compounds has been extensively studied because of its potential in catalysis.[1] Heteronuclear metal complexes might offer the chance to observe cooperative effects of the different metal centres, thus enhancing its catalytic properties.[2] We now report the preparation and characterization of a heterobimetallic compound [MoCo(CO)$_5$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**1**).

RESULTS AND DISCUSSION

Reaction of [Mo(CO)$_3$(η^5-C$_5$H$_5$)] with CoCl(PPh$_3$)$_3$ in tetrahydrofuran yielded a unique heterobimetallic compound [MoCo(CO)$_5$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**1**) (Scheme 1). Compound **1** was characterized by mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra and supported by X-ray single crystal structural determination. The yield of **1** was 22.5%.



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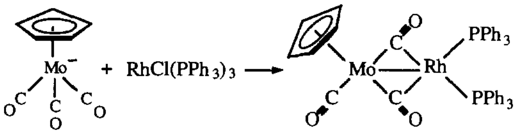
Scheme 1.

On the other hand, a closely related reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] with RhCl(PPh$_3$)$_3$ in tetrahydrofuran led to the formation of [MoRh(CO)(μ-CO)$_2$(PPh$_3$)$_2$] (**2**) with two bridge carbonyl groups bonding to Mo—Rh and two PPh$_3$ groups coordinating to rhodium (Scheme 2).[3] Compound **2** exhibited unsaturated character for the metal centres and catalytic property towards hydrogenation of cyclohexene.



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Scheme 2.

Interestingly, there are several notably different features in compound **1**. First, the structure of **1** (Fig. 1, Table 1) showed that one carbonyl group was replaced by a triphenylphosphine ligand from its molybdenum precursor and three carbonyl groups were picked up by its cobalt precursor. This might indicate that one carbonyl from the molybdenum centre migrated to the cobalt centre and then the unsaturated metal centre picked up one triphenylphosphine ligand during the formation of compound **1**. The cobalt centre also picked up extra carbonyl groups during the reaction. An example of unsaturated metal centre scavenging CO during reaction has been reported.[4] The 18-electron rule is obeyed by both metal centres of **1**, which is quite different from the product in which two metal cen-

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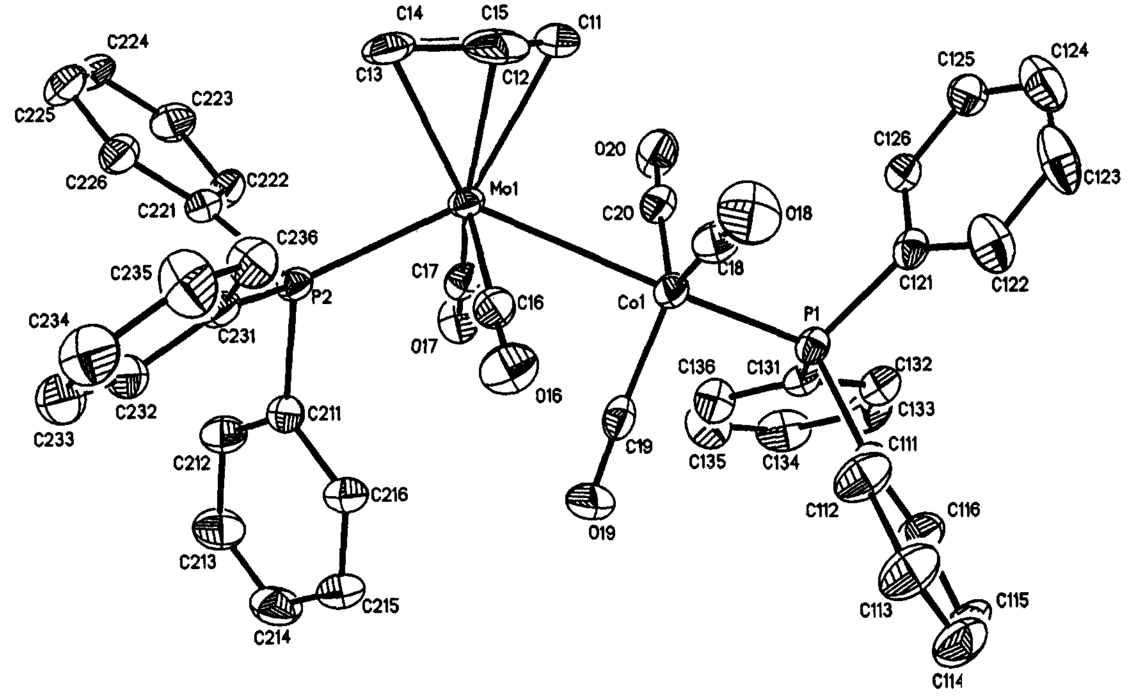

Fig. 1. ORTEP drawing with the numbering scheme of **1**. Hydrogen atoms are omitted for clarity.

tres are both unsaturated, shown in Scheme 2.[3]* The cobalt centre has a trigonal bipyramidal environment in **1**, while the molybdenum atom is part of a "four-legged piano stool" shape. The bond length of two metal centres is larger than most Mo—Co bonds in clusters, but it is within the typical Mo—Co single bond range (Table 1).[5] Furthermore, the triphenylphosphine ligand at the cobalt centre is in an axial position to avoid steric interaction with ligands from the molybdenum fragment.†

Compound **2** showed only one ^{31}P signal, which could be interpreted in terms of the mechanism for the fluxionality in solution. By contrast, there are two distinct ^{31}P NMR signals for **1**. In the off-resonance ^{31}P NMR spectrum, the downfield side peak, around 79.7 ppm, is a doublet and the upfield side peak, around 71.3 ppm, is a broad multiplet. Judging from their splitting patterns, the former and the latter peaks should correspond to the triphenylphosphines coordinating to molybdenum and cobalt, respectively. The broad peak of the latter is due to the coupling from phosphine ($I = 1/2$) and cobalt ($I = 7/2$). There were two sets of signals in the ^{13}C NMR spectra for carbonyl groups. They also showed a similar splitting pattern as in ^{31}P NMR. The downfield side peaks (doublet) correspond to the carbonyls which coordinate to molybdenum and the upfield side peaks (multiplet) correspond to the carbonyls which coordinate to cobalt. The IR spectra also showed two sets of peaks within the carbonyl region. No sign of bridging carbonyl groups was found.

Reaction of **1** with diphenylacetylene yielded a compound with one triphenylphosphine ligand being replaced by diphenylacetylene, probably at the molybdenum site. This product was completely converted to another compound in chloroform after several days. The newly formed compound showed simple ^{1}H and ^{13}C signal patterns and no ^{31}P signals. Further characterization of this compound is currently in progress.

Another reaction of $Na[W(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CoCl(PPh_3)_3$ in tetrahydrofuran was carried out as well. However, the yield of the expected compound, $[WCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$, was extremely low after purification.‡ The product showed the expected parent peaks from the mass spectrum, and the fragmentation pattern was similar to that of **1**. The ^{1}H NMR spectrum of the product showed one major Cp signal and peaks of phenyl groups. The product gradually decomposed during the taking of the ^{13}C NMR spectrum. Because of the low yield

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* A single plus a dative bond was proposed by the authors to accommodate the unusual short Mo—Rh bond length.

† The equatorial position without strong steric hindrance shall be favoured.

‡ The yield of $[WCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ was estimated as less than 1%.

Table 1. Selected bond distances (Å) and angles (°)

Mo(1)—Co(1)	2.951(1)	Mo(1)—P(2)	2.440(2)
Mo(1)—C(11)	2.371(8)	Mo(1)—C(12)	2.353(8)
Mo(1)—C(13)	2.325(9)	Mo(1)—C(14)	2.312(10)
Mo(1)—C(15)	2.352(12)	Mo(1)—C(16)	1.950(8)
Mo(1)—C(17)	1.968(8)	Co(1)—P(1)	2.178(2)
Co(1)—C(18)	1.769(9)	Co(1)—C(19)	1.770(8)
Co(1)—C(20)	1.756(8)	P(1)—C(111)	1.839(7)
P(1)—C(121)	1.819(7)	P(1)—C(131)	1.822(8)
P(2)—C(211)	1.830(8)	P(2)—C(221)	1.829(7)
P(2)—C(231)	1.848(7)	C(16)—O(16)	1.158(9)
C(17)—O(17)	1.157(10)	C(18)—O(18)	1.154(12)
C(19)—O(19)	1.144(10)	C(20)—O(20)	1.150(9)
Co(1)—Mo(1)—P(2)	132.0(1)	P(2)—Mo(1)—C(16)	80.5(2)
P(2)—Mo(1)—C(17)	78.3(2)	Mo(1)—Co(1)—P(1)	171.3(1)
Mo(1)—Co(1)—C(18)	87.3(3)	P(1)—Co(1)—C(18)	99.5(3)
Mo(1)—Co(1)—C(19)	89.7(2)	P(1)—Co(1)—C(19)	92.4(2)
C(18)—Co(1)—C(19)	114.3(4)	Mo(1)—Co(1)—C(20)	80.0(2)
P(1)—Co(1)—C(20)	91.9(3)	C(18)—Co(1)—C(20)	118.0(4)
C(19)—Co(1)—C(20)	125.8(4)		

and instability of the product, further characterization was not possible at this stage.

EXPERIMENTAL

Preparation of $CoCl(PPh_3)_3$

The synthesis of the title compound was done according to a procedure in the literature.[6]

Reaction of $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ *with* $CoCl(PPh_3)_3$

Into a 100 cm^3 round-bottomed flask equipped with a condenser and a magnetic stirrer were placed 1.45 g (5.50 mmol) of $Mo(CO)_6$ and anhydrous THF (30 cm^3). NaCp (6.58 mmol) was added and the reaction mixture was refluxed under dry N_2 for 12 h.[7] The reactor was cooled to room temperature and 4.83 g of $CoCl(PPh_3)_3$ (5.48 mmol), which was dissolved in 30 cm^3 of THF, was transferred into the reaction flask. The reaction was complete within 1 h. The mixture was filtered through silica gel and the solvent removed *in vacuo*.

The residue was dissolved in a small amount of CH_2Cl_2–hexane mixed solvent and was then loaded on to centrifugal thin layer chromography (CTLC) for separation. A dark red band was collected and identified as **1**. The separation in CTLC was under N_2. The yield of **1** was 22.5% (1.09 g).

Compound **1**. ^1H NMR (C_6D_6, δ/ppm): 4.96 (s, 5H, Cp), 6.98 (m, 18H), 7.78 (m, 12H). ^{13}C NMR ($CDCl_3$, δ/ppm): 92.778 (5C, Cp), 135.614 (3C, $J_{PC} = 71$ Hz), 133.553 (6C, $J_{PC} = 16$ Hz), 133.304 (6C, $J_{PC} = 18$ Hz), 132.138 (3C, $J_{Pc} = 16$ Hz), 129.978 (3C, $J_{Pc} = 58$ Hz), 128.662 (3C, $J_{PC} = 17$ Hz), 128.409 (6C, $J_{PC} = 16$ Hz), 128.172 (6C, $J_{PC} = 15$ Hz), 204.081 (m, 3CO), 238.106 (d, 2CO). ^{31}P NMR ($CDCl_3$, δ/ppm): 71.3 (m), 79.7 (d). Ir (Nujol): ν(CO) 1926, 1908, 1840 cm^{-1}. Mass spectrum: m/z 886 (P^+).

Apparatus and materials

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 CTLC, Chromatotron, Harrison model 8924. ^1H, ^{13}C and ^{31}P NMR were recorded on a Varian-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. Mass spectra were recorded on Jeol JMS-SX/SX 102A GC/MS/MS.

Crystal structure determination of **1**

A red crystal of **1** with size 0.2 × 0.6 × 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-K_α radiation, $\lambda = 0.71073$ Å. The positions of heavy atoms in the structure were determined by direct methods, and the remaining non-

Table 2. Crystal data of **1**

Formula	$C_{46}H_{35}CoMoO_5P_2$
Formula weight	884.6
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.367(2)
b (Å)	15.282(3)
c (Å)	26.117(5)
α (°)	74.96(3)
β (°)	89.81(3)
γ (°)	89.88(3)
V (Å^3)	3995.9(13)
Z	4
D_c (g cm^{-3})	1.470
λ (Mo-K_α) (Å)	0.71073
μ (mm^{-1})	0.855
Range (°)	3.0–45.0
Scan type	θ–2θ
No. of reflections collected	11088
No. of independent reflections	10405 (R_{int} = 3.70%)
No. of observed reflections	7373[$F > 4.0\sigma(F)$]
No. of refined parameters	991
R_f[a] for significant reflections	0.0469
R_w[b] for significant reflections	0.0574
GoF[c]	1.34

[a] $R_f = [\Sigma(F_0-F_c)/\Sigma F_0]$.

[b] $R_w = \Sigma w^{1/2}(F_0-F_c)/\Sigma w^{1/2}F_0$.

[c] $\mathrm{GoF} = [\Sigma w(F_0-F_c)^2/(N_{\mathrm{rflns}}-N_{\mathrm{params}})]^{1/2}$. $W^{-1} = \sigma^2(F)+0.0010F^2$.

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 of 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. The crystallographic data of the complex **1** are summarized in Table 2.

Supplementary material available: tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1**.

Acknowledgement—We thank the National Research Council of the R.O.C. (Grant NSC-84-2113-M-005-008) for support.

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