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REACTIONS OF Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] TOWARDS CoCl(PPh$_3$)$_3$ AND CoCl(P(OMe)$_3$)$_5$: X-RAY CRYSTAL STRUCTURES OF [MoCo(CO)$_6$(PPh$_3$)(η^5-C$_5$H$_5$)] AND [Mo(CO)$_3$(P(OMe)$_3$)(η^5-C$_5$H$_5$)]$_2$

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Abstract—Reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] with CoCl(PPh$_3$)$_3$ in tetrahydrofuran under 1 atm of CO yielded two heterobimetallic compounds: [MoCo(CO)$_5$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**1a**) and [MoCo(CO)$_6$(PPh$_3$)(η^5-C$_5$H$_5$)] (**1b**). Both compounds were characterized by mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. The X-ray crystal structure of **1b** was determined. The cobalt centre of **1b** has acquired three carbonyl groups and released two triphenylphosphine ligands during the reaction. The only PPh$_3$ which remained on the cobalt centre was in the axial position of the trigonal bipyramidal structure, thus avoiding steric interaction with ligands from the molybdenum fragment. The molybdenum centre is in a 'four-legged piano stool' configuration. From the reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] and CoCl(P(OMe)$_3$)$_5$ in tetrahydrofuran, an unexpected bimetallic compound [Mo(CO)$_2$(P(OMe)$_3$)(η^5-C$_5$H$_5$)]$_2$ (**6**) was obtained which was characterized by mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra. The molecular structure of **6** was also determined by X-ray diffraction. The centrosymmetric complex is a typical four-legged piano-stool dimer. The M—M bond length (3.239 Å) is longer than the sum of the metal radii. Copyright © 1996 Elsevier Science Ltd

Our previous work had shown that the reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] with CoCl(PPh$_3$)$_3$ in tetrahydrofuran yielded unique heterobimetallic compound [MoCo(CO)$_5$(PPh$_3$)$_2$(η^5-C$_5$H$_5$)] (**1a**) (Scheme 1).[1] Compound **1a** was characterized by mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra and supported by X-ray single-crystal structural determination.

There are several interesting features of note in compound **1a**. First, the structure of **1a** showed that one carbonyl group was replaced by a triphenylphosphine ligand from its molybdenum precursor and three carbonyl groups were acquired by its cobalt precursor. This might indicate that one carbonyl from its molybdenum centre migrates to the cobalt centre and then the unsaturated metal centre picks up a triphenylphosphine ligand during the formation of compound **1a**. The cobalt centre also picked up extra carbonyl groups during the reaction. An example of unsaturated metal centre scavengers of CO during the reaction has been reported.[2]

Our previous work had also shown that the reaction of **1a** with excess phenylacetylene led to two compounds. Compound **2** was obtained first in excellent yield, (98%) under lower temperature (Scheme 2). Compound **3** was also obtained in rather high yield (92%) under higher reaction temperature (Scheme 3). Purified **2** can be converted completely to **3** at higher temperature.[3] These reactions demonstrated that **1a** is active enough to react with acetylene with accompanying loss of PPh$_3$ and CO ligands.

Compound **1a** has shown its potential as a useful reactant for many reactions. However, further

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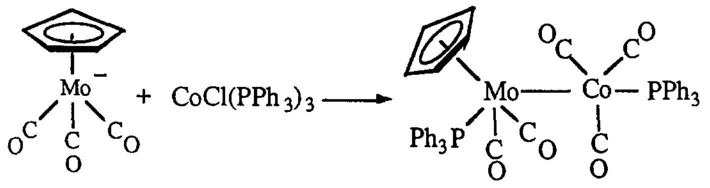
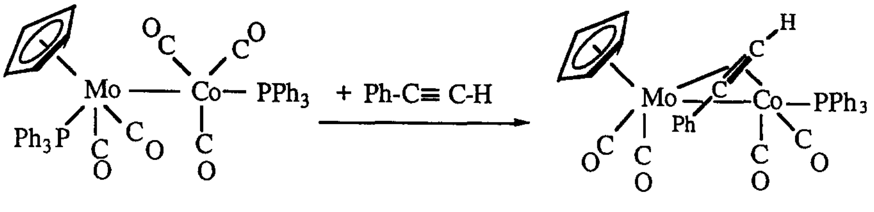


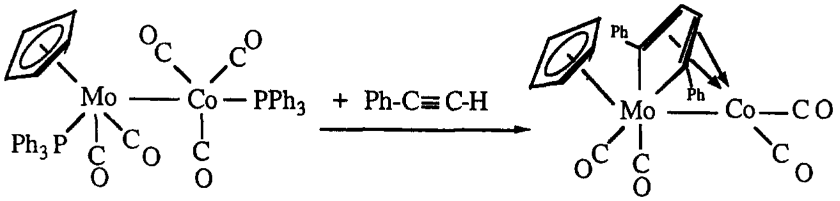
1a

Scheme 1.



1a **2**

Scheme 2.



1a **3**

Scheme 3.

research was limited by its relatively low yield (23%). Therefore, it is of interest to improve the yield of **1a**. It seems reasonable to do that by purging excess CO during the reaction, since it was shown that extra CO ligands were needed in the above reaction.

Efforts were made to produce some compounds closely related to **1a** by changing the metal in the reactant, $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$, to chromium and tungsten. Unfortunately, the results were discouraging. The yields were rather low and the compounds produced were unstable. Therefore, further characterizations were not possible. Nevertheless, the reaction of $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ with a modified cobalt-containing compound, $CoCl(P(OMe_3)_5$, was pursued. We now report the results of these reactions.

RESULTS AND DISCUSSION

The reaction of $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ with $CoCl(PPh_3)_3$ in tetrahydrofuran was carried out under similar condition as reported previously except for the purge of 1 atm of CO during reaction. Not quite as expected, the yield of **1a** was only increased slightly from 23% to 27%. However, another compound, **1b**, was obtained in larger quantity (38%). It was characterized later by mass, IR, ^1H, ^{13}C and ^{31}P NMR spectra. In the case of **1a**, the C_5H_5 group exhibits a doublet ($J_{PH} = 0.9$ Hz) due to long range coupling of a nucleus having $I = 1/2$, presumably ^{31}P. However, it disappears in **1b**, which implies that the PPh_3 ligand which attaches to molybdenum is absent. It was speculated that the site where the PPh_3 was released was replaced by a

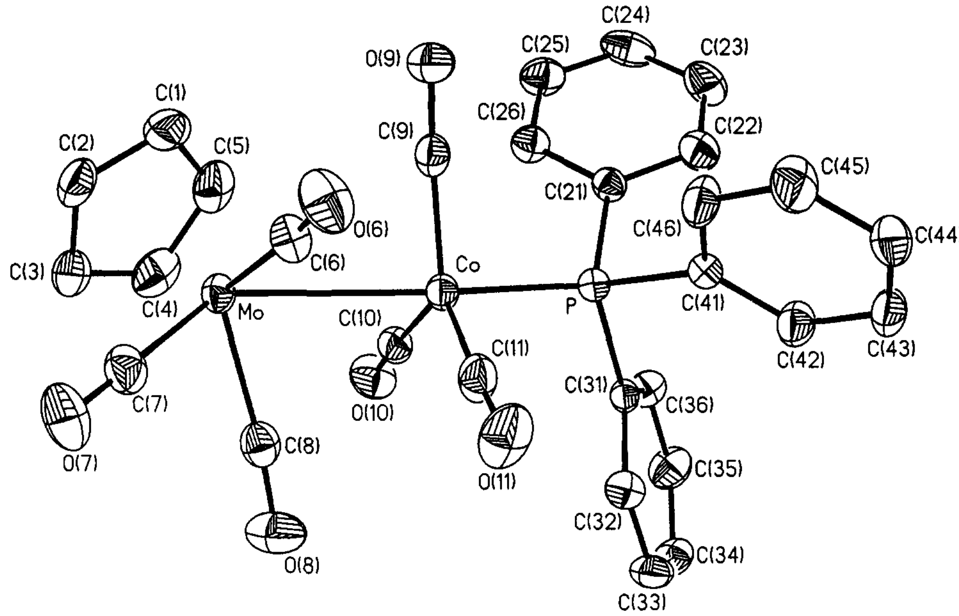
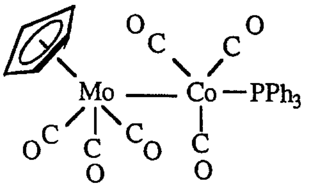


Fig. 1. ORTEP drawing with the numbering scheme of **1b**. Hydrogen atoms are omitted for clarity.

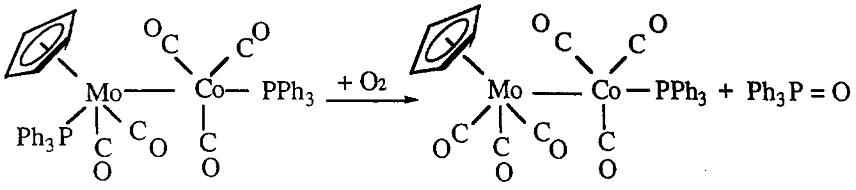
CO ligand. In order to be sure about the structure of this compound, the X-ray single-crystal structure of **1b** was determined. It shows a similar structure to **1a** except that the PPh$_3$ ligand, which was on the molybdenum centre, is replaced by one CO, as expected (Fig. 1). The only PPh$_3$ which remained on the cobalt centre was at the axial position of the trigonal bipyramidal structure, to avoid steric interaction with ligands from the molybdenum fragment. The molybdenum centre has an approximate 'four-legged piano stool' shape (Chart I). Molybdenum–cobalt bond lengths are 2.951 and 2.924 Å for **1a** and **1b**, respectively (Table 2). Compound **1b** was also obtained from the reaction of CoCl(CO)$_3$(PPh$_3$), which was obtained by bubbling CO into a tetrahydrofuran (THF) solution of CoCl(PPh$_3$)$_3$, with Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] under the same reaction conditions. No noticeable amount of **1a** was observed in this case. Compound **1b** can be converted to **1a** almost quantitatively by reacting **1b** with an excess of PPh$_3$ in THF solution around 60°C for 14 h.



1b

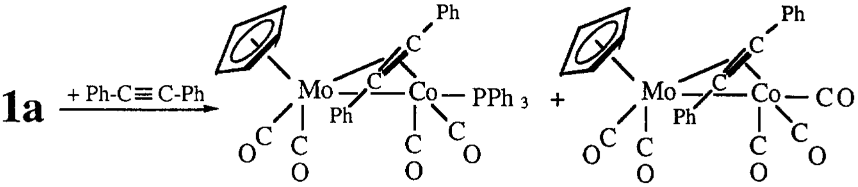
Chart I.

Our previous work had shown that **1a** reacts with phenylacetylene and produces two compounds. It was observed that the PPh$_3$ ligand attached to the molybdenum centre was removed first to form an unsaturated complex during the reaction. Therefore, we postulated that the Lewis acid, BH$_3$, might help to take out the PPh$_3$ ligand from the molybdenum centre to form a BH$_3$·PPh$_3$ adduct and the activated complex might react with excess BH$_3$ to form metallaboranes. The potential of using this small borane as boron source has recently been recognized by Fehlner and others.[4] This has proven to be an excellent way of providing boron fragment to a metal cluster. Unexpectedly, **1b** was obtained as the only separated product, with some decompositions. It was proposed that the Lewis acid, BH$_3$, removed the Lewis base, PPh$_3$, from the molybdenum centre and the activated complex either decomposed to provide a CO source or picked up released CO from other decomposed species to form **1b**. An attempt to synthesize a trinuclear cluster by reacting **1a** with Fe$_3$(CO)$_9$, which was considered as a good Fe(CO)$_3$ fragment source, again produced **1b**. Here, the Mo—PPh$_3$ bond of **1a** seems weak enough to break during the reaction and the activated complex picked up CO from the decomposed Fe$_3$(CO)$_9$ and formed **1b**. Another attempt to incorporate a conjugated double-bond-containing species to **1a** through π-bonding was carried out by its reaction with isoprene. However, this again produced **1b**. These results demonstrated that **1a** is a very reactive species. Unless the reactant is reactive enough, such as acetylene, the activated complex will either immediately pick up CO and form



1a **1b**

Scheme 4.



4 **5**

Scheme 5.

1b or decompose. It was also observed that **1a** will be gradually decomposed in THF solution at room temperature, but **1b** did not decompose under the same conditions. The above results demonstrate that **1b** is more stable than **1a**.

It was rather unexpected that the formation of **1b** was observed when a THF solution of **1a** was purged with pure O_2 at 50°C for about 4 h (Scheme 4).* It was proposed that the oxygen reacted with the PPh_3, forming $O{=}PPh_3$ and at the same time breaking the Mo—PPh_3 bond first, followed by decomposition of the activated complex or picking up of CO from other decomposed species to form **1b**. A similar reaction pattern to the conversion of **1a** to **1b** mentioned above was seen. Also, the formation of $O{=}PPh_3$ was observed from the ^{31}P NMR data.†

Our previous work has also shown that the reaction **1a** with excess phenylacetylene produced **2** and **3** (Schemes 2 and 3). The same products were also observed for the reaction of **1b** with excess phenylacetylene, as shown in Schemes 2 and 3, only yields were lower and higher reaction temperature was required. Even though no crystal structure was available, it is certain that **2** is an alkyne-bridged compound by comparing its spectroscopic data with those in the literature.[5] When **1a** was reacted with excess diphenylacetylene, **4** and **5** were obtained in yields of 70% and 20%, respectively (Scheme 5). The reaction pattern was similar to that shown in Scheme 2. Compound **4** was characterized spectroscopically. However, no tetraphenyl derivative of **3** was obtained from this reaction, as shown in Scheme 3, even with a higher reaction temperature and excess diphenylacetylene, which only caused more decomposition.

Interestingly, **4** was slowly converted to an unknown compound with the loss of only the PPh_3 ligand attached to the cobalt centre. An attempt to grow a single crystal was pursued. Unfortunately, only cell parameters were available from X-ray single-crystal structural determination because of the relatively small size of the crystal.‡ From the spectroscopic means available, such as ^{1}H, ^{13}C and the complete loss of the PPh_3 peak in ^{31}P NMR, as well as IR and mass spectra, it was proposed that the unknown compound, **5** has a similar structure to **4** except for the replacement of the PPh_3 ligand by CO. When **4** was reacted with pure O_2 in the THF, **5** was obtained along with a small amount of **1b**. It was proposed that only the PPh_3 attached to the cobalt centre of **4** reacted with oxygen to form $O{=}PPh_3$, then the activated complex either decomposed or picked up CO from other decomposed species and formed **5**. The formation of $O{=}PPh_3$ was observed from the ^{31}P NMR spectrum. The

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*The yield of the only separated compound (**1b**) is 68%.

†A peak at +28 ppm in the ^{31}P spectrum NMR in $CDCl_3$ was assigned as $O{=}PPh_3$.

‡Monoclinic, $C2/c$, $a = 17.803(32)$, $b = 30.952(65)$, $c = 8.716(35)$ Å, $\beta = 113.12(3)°$, $V = 4417(22)$ Å^3.

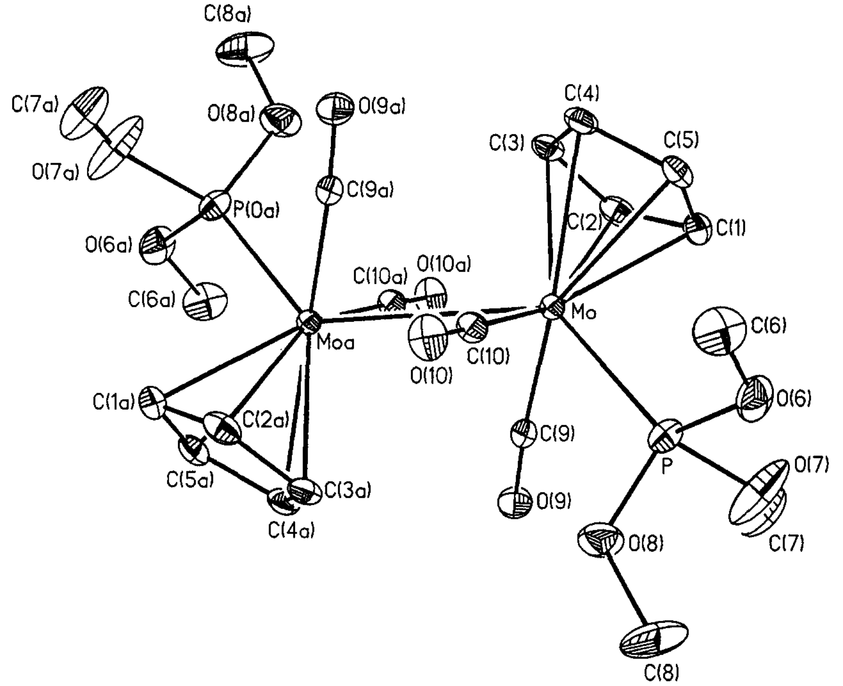

Fig. 2. ORTEP drawing with the numbering scheme of **6**. Hydrogen atoms are omitted for clarity.

conversion pattern of **4** to **5** is very similar to that of **1a** and **1b**. The formation of a small amount of **1b** in this reaction is noteworthy. It may be formed while the cleavage of bridged diphenylacetylene took place during oxidation and the unsaturated activated complex picked up two CO ligands. The π bridged bond of acetylene is known to be weaker than the normal σ bond. It is easy to break at high reaction temperatures or during an oxidation process. This again demonstrates that **1b** is relatively more stable than the other compounds.

We have made some efforts to synthesize similar compounds to **1a** in the past by changing the metal of the reactant, Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)], from molybdenum to chromium and tungsten. Unfortunately, the results were not encouraging.[1] The yields were rather low and the compounds produced were too sensitive to handle. Another effort involved modifying the cobalt centre. CoCl(P(OMe)$_3$)$_5$ was prepared according to a procedure in the literature.[6] Interestingly, the expected compound, the derivative of **1a** with two PPh$_3$ ligands replaced by two P(OMe)$_3$ ligands, was not obtained from the reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] with CoCl(P(OMe)$_3$)$_5$ in THF under similar reaction conditions. Instead, a molybdenum dimer, [Mo(CO)$_2$(P(OMe)$_3$)(η^5-C$_5$H$_5$)]$_2$ (**6**), was obtained in 30% yield. Compound **6** was characterized by mass, IR, ^{1}H, ^{13}C and ^{31}P NMR spectra and supported by X-ray single-crystal structural determination (Fig. 2). The structure of **6** shows that it is a centrosymmetric dimer with a typical four-legged piano stool shape for each metal centre. The production of **6** may come about via two possible pathways. First, the expected compound, the derivative of **1a** with two PPh$_3$ ligands replaced by two P(OMe)$_3$ ligands, did form during the reaction; however, it decomposed and recombined to form **6**, a much more stable compound. Second, the [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ dimer was formed first due to the oxidation of the reactant Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)], followed by the replacement of two CO ligands from the dimer by two P(OMe)$_3$ ligands.[7] From a separate experiment, a small amount of **6** could be obtained from the direct reaction of [(η^5-C$_5$H$_5$)Mo(CO)$_3$]$_2$ dimer with excess P(OMe)$_3$. However, the reaction rate was much slower.* The preparation of a closely related compound, [Mo(η^5-C$_5$H$_5$)(CO)$_2$(NC$_5$H$_4$PPh$_2$-2)]$_2$, has been reported.[8] The molybdenum–molybdenum metal bond in **6** is slightly shorter than that in [Mo(η^5-C$_5$H$_5$)(CO)$_2$(NC$_5$H$_4$PPh$_2$-2)]$_2$; however, it is longer than the sum of the metal radii, which is a common observation in this type of compound (Table 4).†

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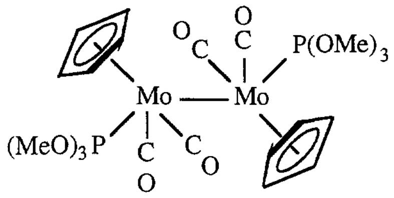
*Only quite a small amount of **6** was formed using the same reaction conditions judging by the ^{1}H NMR spectrum of the mixture.

†The metal–metal bond lengths of [Mo(CO)$_2$(P(OMe)$_3$)(η^5-C$_5$H$_5$]$_2$ and [Mo$_2$(η^5-C$_5$H$_5$)$_2$(CO)$_4$(NC$_5$H$_4$PPh$_2$-2)$_2$] are 3.239 and 3.276 Å, respectively.



6

Scheme 6.

EXPERIMENTAL

Apparatus and materials

All operations were performed in a nitrogen-flushed glove box or in a vacuum system. Freshly distilled solvents were used. All separations of products were performed by Centrifugal Thin Layer Chromatography (CTLC; Chromatotron, Harrison Model 8924). ^{1}H, ^{13}C and ^{31}P NMR spectra 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 instrument. Mass spectra were recorded on a Jeol JMS-SX/SX 102A GC/MS/MS spectrometer.

Preparation of $CoCl(PPh_3)_3$

The synthesis of the title compound was done according to a procedure in the literature.[9]

Reaction of $Na[Mo(CO)_3(\eta^5\text{-}C_5H_5)]$ *with* $CoCl(PPh_3)_3$ *under* 1 *atm of* CO

Into a 100 cm^3-round-bottomed flask equipped with a condenser and a magnetic stirrer was placed $Mo(CO)_6$ (250 mg, 0.95 mmol). NaCp (85 mg, 0.96 mmol) in 30 cm^3 of THF was added and the reaction mixture was refluxed under dry N_2 for 12 h.[10] The reactor was cooled to room temperature and $CoCl(PPh_3)_3$ (850 mg, 0.96 mmol), which was dissolved in 30 cm^3 of THF, was transferred into the reaction flask. The reaction mixture was bubbled with 1 atm of CO at room temperature for 2 h. The mixture was filtered through Celite and silica gel and the solvent removed *in vacuo*.

The residue was dissolved in a small amount of CH_2Cl_2 and was then loaded to CTLC for separation. Orange and dark red bands were collected through the elution of a mixture of solvents and were identified as **1b** and **1a**, respectively. The ratio of solvent mixture (CH_3Cl_2–hexanes) was changed from 1 : 20 to 1 : 4 as the separation proceeded. The separation in CTLC was under N_2. The yields of **1b** and **1a** were 37.5% (231 mg) and 27.3% (228.4 mg), respectively. The characterization of **1a**, including the X-ray crystal structural determination, has been reported.[1] Compound **1b** was crystallized from CH_2Cl_2–hexane (1 : 1) after storage at −15°C for a few days.

Compound **1b**. ^{1}H NMR (C_6D_6, δ/ppm): 5.43 (s, 5H, Cp), 7.46 (m, 15H, PPh_3). ^{13}C NMR ($CDCl_3$, δ/ppm): 92.2 (s, 5C, Cp), 134.6 (d, $J_{PC} = 46$ Hz, 3C, *ipso*), 133.2 (d, $J_{PC} = 11$ Hz, 6C, *ortho*), 130.6 (d, $J_{PC} = 2$ Hz, 3C, *para*), 128.7 (d, $J_{PC} = 10$ Hz, 6C, *meta*). ^{31}P NMR ($CDCl_3$, δ/ppm): 68.9 (m, Co—P). IR (CH_2Cl_2: ν(CO) 2028 (m), 1968 (s), 1942 (vs) cm^{-1}. Mass spectrum: *m*/*z* 652 (P^+).

Reaction of $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (**1a**) *with* PhC≡CPh

Into a 100 cm^3 round-bottomed flask equipped with a condenser and a magnetic stirrer were placed $[MoCo(CO)_5(PPh_3)_2(\eta^5\text{-}C_5H_5)]$ (108 mg, 0.122 mmol) and anhydrous THF (20 cm^3). Diphenylacetylene (26 mg, 0.147 mmol) was dissolved in 4 cm^3 THF and was then transferred to the reaction flask. The reaction mixture was heated under dry N_2 at 50–55°C for 14 h. The reactor was then cooled to room temperature and solvent was removed *in vacuo*.

The mixture was separated using CTLC via a procedure similar to that mentioned above. Yellow and orange bands were collected and identified as **5** and **4**, respectively. The yields of **5** and **4** were 19.5% (12.8 mg) and 70.0% (66.0 mg), respectively.

Compound **4**. ^{1}H NMR (C_6D_6, δ/ppm): 4.41 (s, 5H, Cp), 6.60 (m, 15H, PPh_3), 7.05 (m, 6H, Ph_2C_2), 7.15 (m, 4H, Ph_2C_2). ^{31}P NMR (C_6D_6, δ/ppm): 50.6 (m, Co—P). IR (CH_3Cl): ν(CO) 2062 (m), 2002 (vs), 1977 (vs), 1953 (vs), 1923 (s) cm^{-1}. Mass spectrum: *m*/*z* 774 (P^+).

Compound **5**. ^{1}H NMR ($CDCl_3$, δ/ppm): 5.37 (s, 5H, Cp), 7.20–7.34 (m, 10H, Ph_2C_2). ^{13}C NMR ($CDCl_3$, δ/ppm): 91.4 (5C, Cp), 126.6 (2C, *para*), 128.3 (4C, *meta*), 129.3 (4C, *ortho*), 141.9 (2C, *ipso*), 203.3 (m, Co—CO), 225.1 (s, Mo—CO). IR (CH_3Cl): ν(CO) 2060 (s), 2008 (vs), 1948 (m) cm^{-1}. Mass spectrum: *m*/*z* 540 (P^+).

Preparation of $CoCl(P(OMe)_3)_5$

The synthesis of the title compound was carried out according to a procedure in the literature.[11]

Reaction of Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] *with* CoCl(P(OMe)$_3$)$_5$

Na[Mo(CO)$_3$(η^5-C$_5$H$_5$)] (255 mg, 0.95 mmol) was prepared by the procedure shown above. It was then placed in a 100 cm^3 round-bottomed flask which was equipped with a condenser and a magnetic stirrer with THF (20 cm^3) and the solution was kept around 0°C. CoCl(P(OMe)$_3$)$_5$ (679 mg, 0.95 mmol) was dissolved in a small amount of CH$_2$Cl$_2$ then transferred into the reaction flask. The reaction mixture was stirred under dry N$_2$ for 3 h and the colour of the solution changed to dark red. The mixture was filtered through Celite and silica gel and washed with diethyl ether. Several red crystals were obtained from a mixture of CH$_2$Cl$_2$–hexane (2 : 1) after storage at −15°C for several days. The yield was 30% (207 mg, 0.28 mmol).

Table 1. Crystal data for **1b**

Formula	C$_{29}$H$_{20}$CoMoO$_6$P
Formula weight	650.3
Crystal system	Orthorhombic
Space group	*Pbca*
a (Å)	17.342(2)
b (Å)	16.974(2)
c (Å)	18.728(2)
V (Å^3)	5512.9(7)
Z	8
D_c (g cm^{-3})	1.567
λ(Mo-K_α) (Å)	0.71073
μ (mm^{-1})	1.155
Range (°)	4.0–45.0
Scan type	θ–2θ
No. of reflections collected	4650
No. of independent reflections	3619 (R_{int} = 1.28%)
No. of observed reflections	2729 [$F > 4.0\sigma$(F)]
No. of refined parameters	343
Rf[a] for significant reflections	0.0290
Rw[b] for significant reflections	0.0338
GoF[c]	1.06

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

Compound **6**. ^{1}H NMR (CDCl$_3$, δ/ppm): 5.05 (d, 5H, Cp, J_{PH} = 1.4 Hz), 3.73 (d, 18H, OCH$_3$, J_{PH} = 11.4 Hz). ^{13}C NMR (CDCl$_3$, δ/ppm): 51.0 (s, 6C, OCH$_3$), 90.9 (s, 5C, Cp), 215.8 (m, 4C, CO). ^{31}P NMR (CDCl$_3$, δ/ppm): −38.9 [s, 2P, P(OMe)$_3$]. IR (CHCl$_3$) :ν(CO) 1976 (s), 1884 (s) cm^{-1}. Mass spectrum: *m/z* 642 (P$^+$).

Crystal structure determination of **1b** *and* **6**

A red crystal of **1b** of size of 0.2 × 0.6 × 0.7 mm^3 and a red plate crystal of **6** of size of 0.04 × 0.8 × 0.8 mm^3 were used for X-ray diffraction measurements. The intensities were collected on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo-K_α 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 of 0.96 Å, and the temperature factors

Table 2. Selected bond distances (Å) and angles (°) for **1b**

Mo—Co	2.924(1)	Mo—C(1)	2.349(5)
Mo—C(2)	2.302(5)	Mo—C(3)	2.308(4)
Mo—C(4)	2.347(5)	Mo—C(5)	2.392(5)
Mo—C(6)	1.987(5)	Mo—C(7)	1.972(5)
Mo—C(8)	1.987(5)	Co—P	2.191(1)
Co—C(9)	1.773(5)	Co—C(10)	1.781(5)
Co—C(11)	1.783(5)	P—C(21)	1.834(4)
O—C(31)	1.832(4)	P—C(41)	1.829(4)
C(6)—O(6)	1.146(6)	C(7)—O(7)	1.149(6)
C(8)—O(8)	1.143(6)	C(9)—O(9)	1.151(6)
C(10)—O(10)	1.141(6)	C(11)—O(11)	1.136(6)
Mo—Co—P	172.6(1)	Mo—Co—C(9)	83.5(1)
P—Co—C(9)	95.5(1)	Mo—Co—C(10)	82.4(1)
P—Co—C(10)	92.0(1)	C(9)—(Co—C(10)	122.7(2)
Mo—Co—C(11)	91.9(1)	P—Co—C(11)	95.1(2)
C(9)—Co—C(11)	116.0(2)	C(10)—Co—C(11)	119.7(2)

Table 3. Crystal data for **6**

Empirical formula	$C_{10}H_{14}MoO_5P$
Formula weight	341.1
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.157(2)
b (Å)	7.949(2)
c (Å)	16.080(3)
β (°)	99.38(2)
V (Å^3)	1280.9(3)
Z	4
D_c (g cm^{-3})	1.769
λ (Mo-K_α) (Å)	0.71073
μ (mm^{-1})	1.154
Range (°)	3.0–50.0
Scan type	θ–2θ
No. of reflctions collctd	4886
No. of independent reflctions	2273 ($R_{\rm int}$ = 3.04%)
No. of observed reflctions	2021 [$F > 4.0\sigma(F)$]
No. of refined parameters	154
Rf^a for significant reflctions	0.0353
Rw^b for significant reflctions	0.0470
GoF^c	1.21

$^aR_f = [\Sigma(F_o - F_c)/\Sigma F_o]$.

$^bR_w = \Sigma w^{1/2}(F_o - F_c)/\Sigma w^{1/2}F_o$.

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

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 softward package on a Micro VAX 3100 computer.

Table 4. Selected bond distances (Å) and angles (°) for **6**

Mo—P	2.364(1)	Mo—C(1)	2.319(4)
Mo—C(2)	2.356(4)	Mo—C(3)	2.383(4)
Mo—C(4)	2.355(4)	Mo—C(5)	2.328(4)
Mo—C(9)	1.965(4)	Mo—C(10)	1.966(4)
P—O(6)	1.597(3)	P—O(7)	1.589(5)
P—O(8)	1.578(4)	C(1)—C(2)	1.401(6)
C(1)—C(5)	1.418(6)	C(2)—C(3)	1.395(6)
C(3)—C(4)	1.417(5)	C(4)—C(5)	1.392(5)
C(6)—O(6)	1.439(7)	C(7)—O(7)	1.303(8)
O(8)—C(8)	1.457(6)	O(9)—C(9)	1.157(5)
O(10)—C(10)	1.148(5)		
P—Mo—C(10)	78.6(1)	P—Mo—C(9)	79.0(1)
C(9)—Mo—C(10)	104.3(2)	Mo—P—O(6)	120.0(1)
Mo—P—O(7)	121.6(2)	Mo—P—O(8)	112.4(1)
P—O(6)—C(6)	120.8(3)	P—O(7)—C(7)	131.8(4)
P—O(8)—C(8)	123.3(4)		

The crystallographic data of the complexes **1b** and **6** are summarized in Tables 1 and 3.

Supplementary material available

Tables of atomic coordinates and thermal parameters, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **1b** and **6**.

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