



Synthesis of $\text{Mo}(\text{CO})_2(\eta^3\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{C}(=\text{O})\text{H})_2$ and its reaction with C_{60}

Chi-Shian Chen, Cha-Shie Lin, Wen-Yann Yeh*

Center for Nanoscience and Nanotechnology, National Sun Yat-Sen University, 70 Lien-Hai Road, Kaohsiung 804, Taiwan

ARTICLE INFO

Article history:

Received 6 December 2010

Received in revised form

15 January 2011

Accepted 18 January 2011

Keywords:

Molybdenum complex

Fullerene complex

Aldehyde complex

Aldehyde coupling

ABSTRACT

Reaction of $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ and $\text{PPh}_2(o\text{-C}_6\text{H}_4)\text{C}(=\text{O})\text{H}$ (abbreviated as PCHO) at room temperature affords $\text{Mo}(\text{CO})_2(\eta^3\text{-PCHO})_2$ (**1**), while compound **1** and the phosphine-imine complex $\text{Mo}(\text{CO})_4(\eta^2\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{CH}=\text{NMe})$ (**2**) are obtained by using $\text{Mo}(\text{CO})_3(\eta^3\text{-(MeNCH}_2)_3)$ as the reactant. Thermal reaction of **1** with C_{60} products $\text{Mo}(\text{CO})_2(\eta^4\text{-(PPh}_2(o\text{-C}_6\text{H}_4)\text{CH})_2)(\eta^2\text{-C}_{60})$ (**3**) in low yield, apparently through coupling of the formyl moieties. The structures of **1** and **3** have been determined by an X-ray diffraction study. The two aldehyde groups of **1** and C_{60} ligand of **3** are coordinated to the molybdenum atom in a π -fashion.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Chelating ligands containing “soft” phosphorus and “hard” nitrogen or oxygen donor atoms can alter the reactivity or metal centers and may be of interest in design and development of new homogeneous catalytic systems [1–5]. The *o*-(diphenylphosphino) benzaldehyde molecule ($\text{PPh}_2(o\text{-C}_6\text{H}_4)\text{C}(=\text{O})\text{H}$; abbreviated as PCHO) is one of the simplest bidentate P,O-chelating agents [6]. Usually, the phosphine center is coordinated to the metal in advance of the aldehyde group and can serve as a monodentate $\eta^1\text{-P}$ donor [7,8]. On the other hand, the PCHO ligand can act as a chelating phosphine–aldehyde, with the aldehyde moiety bonded to the metal in a σ -fashion through the oxygen atom [9,10], or in a π -fashion through the $\text{C}=\text{O}$ double bond [11,12]. Recently, synthesis of fullerene-bound organometallic complexes has been a focal point of many research topics, due to their potential application in biological, magnetic, electronic, catalytic and optical devices [13–16]. In this paper, we present a new molybdenum complex bearing π -bonded formyl groups and show its reaction with C_{60} .

2. Results and discussion

Previously, reactions of the triazacyclohexane complex $\text{W}(\text{CO})_3(\eta^3\text{-(MeNCH}_2)_3)$ with PCHO were shown to give $\text{W}(\text{CO})_3(\eta^3\text{-PCHO})(\eta^1\text{-PCHO})$ and $\text{W}(\text{CO})_2(\eta^3\text{-PCHO})_2$ [12], with the aldehyde groups coordinating in a unique π -fashion. The analogous reaction of $\text{Mo}(\text{CO})_3(\eta^3\text{-(MeNCH}_2)_3)$ with two equivalents of PCHO at ambient temperature afforded $\text{Mo}(\text{CO})_2(\eta^3\text{-PCHO})_2$ (**1**) in 30% yield. Interestingly, an orange side-product was also isolated, characterized as $\text{Mo}(\text{CO})_4(\eta^2\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{CH}=\text{NMe})$ (**2**; 35%). In contrast, treating the acetonitrile complex $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ with PCHO produced **1** in 35% yield without the formation of **2**. The results are summarized in Scheme 1.

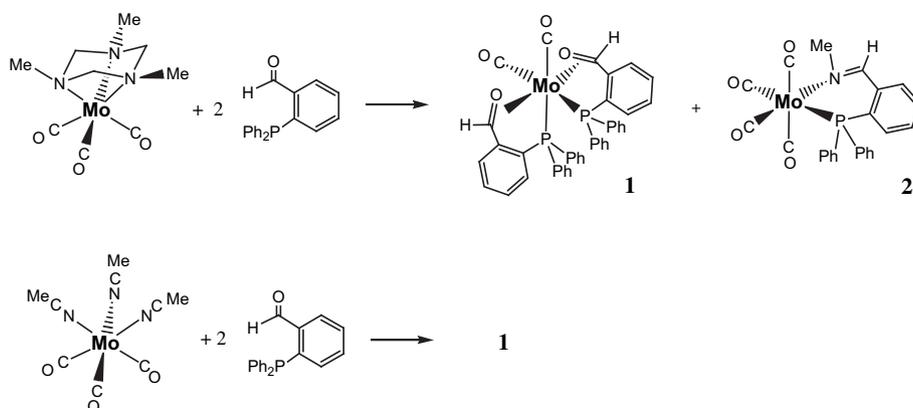
Compound **1** forms air-stable, bright yellow crystals. The FAB mass spectrum gives the molecular ion at m/z 734 (^{98}Mo), corresponding to a $\text{Mo}(\text{CO})_2$ segment plus two PCHO molecules. The IR spectrum displays two CO absorptions at 1976 and 1918 cm^{-1} , suggesting a *cis*-arrangement for the two carbonyl ligands. The free PCHO ligand presents a ^{31}P resonance at -11.37 ppm for the phosphorus atom and an ^1H resonance at 10.50 ppm for the formyl proton, while compound **1** displays one ^{31}P resonance at 18.04 ppm and the formyl proton resonance is shift upfield to 5.38 ppm. These spectral data suggest a same coordination mode for the two PCHO ligands.

The molecular structure of **1** is depicted in Fig. 1. The Mo center is coordinated by two terminal carbonyl ligands and two PCHO ligands. Taking the centers of the aldehyde $\text{C}=\text{O}$ bond, the phosphorus atoms and the carbonyl groups, the coordination about the Mo atom can be described as a distorted octahedron. The two carbonyl ligands are in *cis* positions, with the $\text{C}1\text{--Mo--C}2$ angle of $86.3(2)^\circ$. The average Mo–CO length is 1.99 Å, and the average Mo–C–O angle is 175.5° . The two PCHO ligands are coordinated to the Mo atom in an η^3 -fashion. The two P atoms are *cis* to each other, with Mo–P1 and Mo–P2 distances of 2.5652(9) and 2.593(1) Å, respectively, and the

The molecular structure of **1** is depicted in Fig. 1. The Mo center is coordinated by two terminal carbonyl ligands and two PCHO ligands. Taking the centers of the aldehyde $\text{C}=\text{O}$ bond, the phosphorus atoms and the carbonyl groups, the coordination about the Mo atom can be described as a distorted octahedron. The two carbonyl ligands are in *cis* positions, with the $\text{C}1\text{--Mo--C}2$ angle of $86.3(2)^\circ$. The average Mo–CO length is 1.99 Å, and the average Mo–C–O angle is 175.5° . The two PCHO ligands are coordinated to the Mo atom in an η^3 -fashion. The two P atoms are *cis* to each other, with Mo–P1 and Mo–P2 distances of 2.5652(9) and 2.593(1) Å, respectively, and the

* Corresponding author. Fax: +886 7 5253908.

E-mail address: wenyann@mail.nsysu.edu.tw (W.-Y. Yeh).

Scheme 1. Preparation of **1** and **2**.

P1–Mo–P2 angle is $100.12(3)^\circ$. The *trans* angles P1–Mo–C2 $167.2(1)^\circ$ and P2–Mo–C1 $165.3(1)^\circ$ are deviated significantly from linearity (180°) and could be attributed to steric congestion surrounding the Mo atom. The two aldehyde groups are in *trans* positions and are π -bonded to the Mo atom, with the distances C3–Mo $2.215(4)$, O3–Mo $2.088(2)$, C22–Mo $2.232(4)$, and O4–Mo $2.086(2)$ Å. The angles C4–C3–O3 $118.4(3)^\circ$ and C23–C22–O4 $120.5(3)^\circ$ are close to the ideal value of 120° for an sp^2 hybrid C atom. However, the distances C3–O3 $1.335(4)$ Å and C22–O4 $1.323(4)$ Å are *ca.* 0.1 Å longer than the pendant formyl distance founded in $W(CO)_3(\eta^3\text{-PCHO})(\eta^1\text{-PCHO})$ [12], suggesting a significant π back-donation from

Mo to the π^* orbital of the C=O double bond. The C3–O3 and C22–O4 vectors, which are bent away from the adjacent arene planes by an average of 54° , are approximately perpendicular to each other (88°), presumably to obtain better π back-donation from separate filled d orbitals of the Mo metals.

The IR spectrum of **2** in the carbonyl region shows three stretching absorptions at 2016, 1903, and 1855 cm^{-1} , with the pattern resemble to a *cis*-M(CO)₄LL' composition [17,18]. The ^{31}P { ^1H } NMR spectrum shows a downfield signal at 36.3 ppm, while the ^1H NMR spectrum presents a 1H singlet at 8.21 ppm, a multiplet (14H) in the range 7.54–6.85 ppm, and a 3H singlet at 3.74 ppm. Because of the absence of diagnostic spectral features to reveal its structure, a single-crystal X-ray diffraction study was performed. An ORTEP drawing of **2**, shown in Fig. 2, consists of a Mo(CO)₄ fragment bonded with an iminophosphine group. It turns out that compound **2** (and its crystal structure) is known [19], previously prepared from Mo(CO)₄(piperidine)₂ and the $\text{PPh}_2(o\text{-C}_6\text{H}_4)\text{CH}=\text{NMe}$ ligand directly. Yet the origin of MeN fragment in **2** remains interesting. Since PCHO does not react with free $(\text{MeNCH}_2)_3$

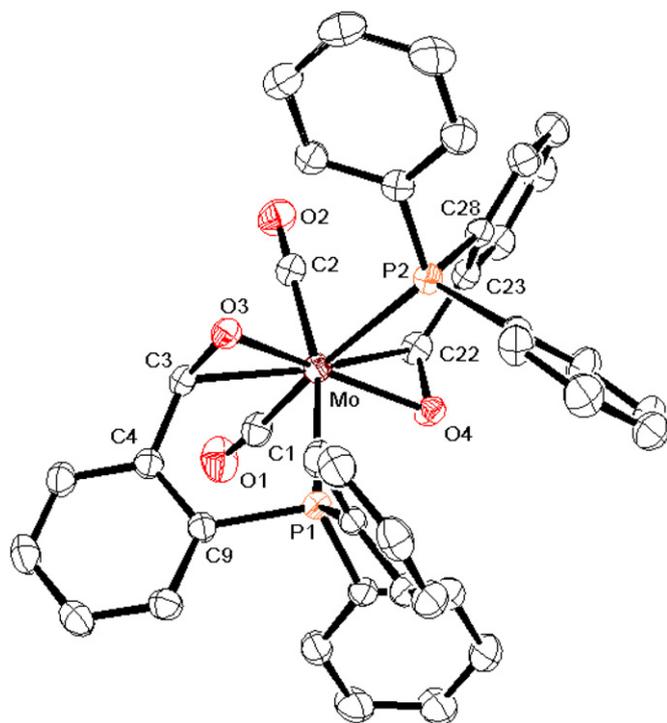


Fig. 1. Molecular structure of **1**. Selected bond distances (Å) and bond angles ($^\circ$): Mo–P1 $2.5652(9)$, Mo–P2 $2.593(1)$, Mo–C1 $1.995(5)$, Mo–C2 $1.988(4)$, Mo–C3 $2.215(4)$, Mo–O3 $2.088(2)$, Mo–C22 $2.232(4)$, Mo–O4 $2.086(2)$, C3–O3 $1.335(4)$, C22–O4 $1.323(4)$ and P1–Mo–C2 $167.2(1)$, P2–Mo–C1 $165.3(1)$, C3–Mo–C22 $153.3(1)$, C3–Mo–O3 $36.0(1)$, O3–Mo–O4 $155.7(1)$, O4–Mo–C22 $35.5(1)$, C9–P1–Mo $101.5(1)$, C28–P2–Mo $99.7(1)$, C23–C22–O4 $120.5(3)$, C4–C3–O3 $118.4(3)$, O1–C1–Mo $175.2(4)$, O2–C2–Mo $175.8(4)$.

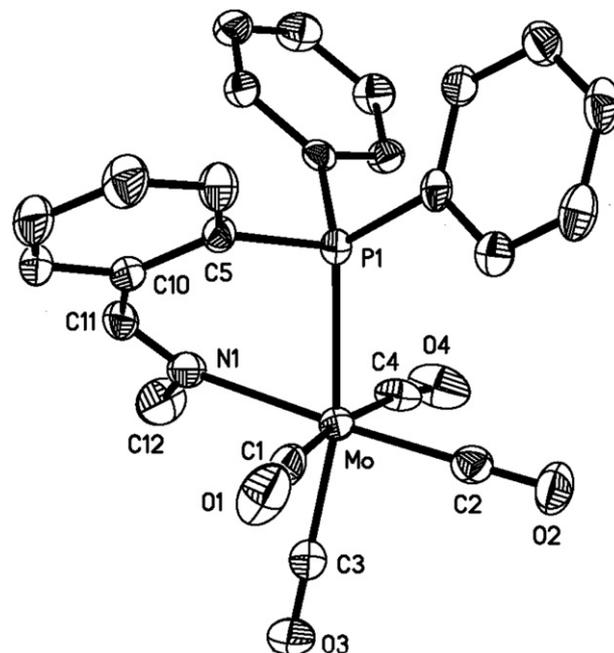


Fig. 2. ORTEP diagram of **2**. This structure is identical to that previously determined [19].

molecule at room temperature and the reaction of $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ with PCHO does not produce **2**, the iminophosphine ligand of **2** is apparently generated by a Mo-mediated Schiff-base condensation [20–22] and rearrangement reactions of PCHO and $(\text{MeNCH}_2)_3$ species, though the mechanism is still unclear. Fragmentation of $(\text{MeNCH}_2)_3$ molecule to generate an amidino $[\text{CH}(\text{NMe})_2]$ ligand has been observed in the triosmium system [23,24].

The attachment of C_{60} to organometallic complexes is an important area within fullerene chemistry. Compound **1** was therefore reacted with C_{60} in refluxing chlorobenzene to generate a new fullerene complex $\text{Mo}(\text{CO})_2(\eta^4\text{-}(\text{PPh}_2(o\text{-C}_6\text{H}_4)\text{CH})_2)(\eta^2\text{-C}_{60})$ (**3**) (Scheme 2), but in low yield. Most of **1** decomposes under such harsh conditions, and there are no reactions with the temperatures below 100°C . The MALDI mass spectrum of **3** displays the highest ion peak at m/z 1390 (^{98}Mo), corresponding to the $[\text{M}^+ - \text{CO}]$ fragment, and the isotope distribution matches the calculated pattern. The ^1H NMR spectrum shows a multiplet (24H) in the range 7.83–6.99 ppm and a triplet signal (2H, $J_{\text{P-H}} = 6$ Hz) at 4.30 ppm, and the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum presents one signal at 52.59 ppm.

The molecular structure of **3** is illustrated in Fig. 3, in which the molybdenum atom is bonded to two terminal CO, a C_{60} , and a $(\text{PPh}_2(o\text{-C}_6\text{H}_4)\text{CH})_2$ ligand in a distorted octahedral fashion. The two phosphine and the two carbonyl groups are *trans* to each other, with the angle C1-Mo-C2 $177.6(3)^\circ$ being close to linearity, while the P1-Mo-P2 angle ($154.05(6)^\circ$) shows a substantial distortion (Fig. 4) and may be attributed to steric interactions with the bulky C_{60} group. The bond lengths Mo-P1 2.516(2) and Mo-P2 2.512(1) Å are 0.06 Å shorter than those observed for **1**, while the M–CO distances (2.038(6) and 2.023(7) Å) are 0.04 Å longer, consistent with the stronger net π -accepting capacity of the CO ligand compared with $\text{P}(\text{aryl})_3$. The C_{60} moiety is bound to the molybdenum atom in an η^2 -fashion through a 6:6-ring junction with Mo-C41 2.283(6) Å and Mo-C42 2.288(5) Å. The distance C41-C42 1.497(8) Å is elongated (*ca.* 0.12 Å) in comparison with other unperturbed 6:6-double bonds and is attributed to π back-donation from the molybdenum atom. The most striking feature is the formation of *trans*- $\text{PPh}_2(o\text{-C}_6\text{H}_4)\text{CH}=\text{CH}(o\text{-C}_6\text{H}_4)\text{PPh}_2$ species which is likely from coupling of two PCHO ligands concomitant with loss of two oxygen atoms; the results are analogous to the organic McMurry reaction [25]. The $\text{C21}=\text{C22}$ unit is π -bonded to the molybdenum atom with Mo-C21 2.317(6) Å and Mo-C22 2.335(5) Å, which are *ca.* 0.04 Å longer than the opposite Mo-C_{60} bonds. The C20-C21-C22-C23 atoms are not coplanar to have the torsional angle 139.1° . The $(\text{Mo}, \text{C21}, \text{C22})$ and $(\text{Mo}, \text{C41}, \text{C42})$ planes are about orthogonal, giving a dihedral angle of $85.2(5)^\circ$.

In conclusion, we have prepared compound **3** and presented its reactivity toward C_{60} . The structure of **1** closely resembles the tungsten analogue $\text{W}(\text{CO})_2(\eta^3\text{-PCHO})_2$ with the bond lengths and angles differing to within 0.04 Å and 2° , respectively. This is due to the lanthanide contraction, leading to comparable Mo and W radii.

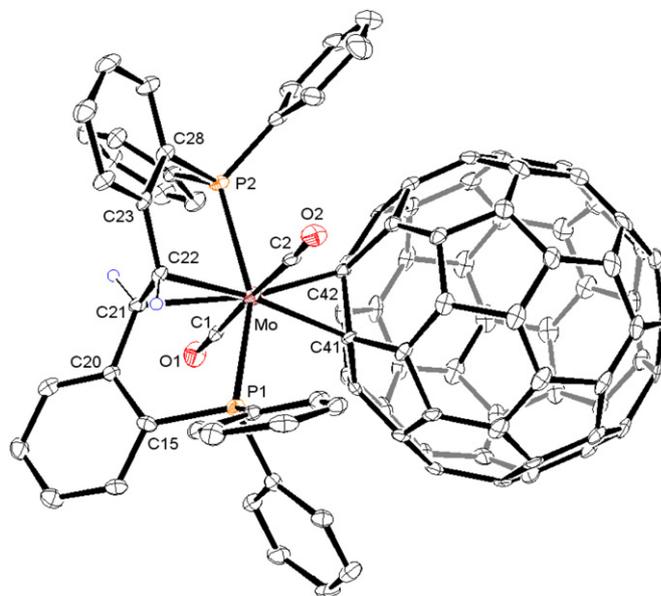


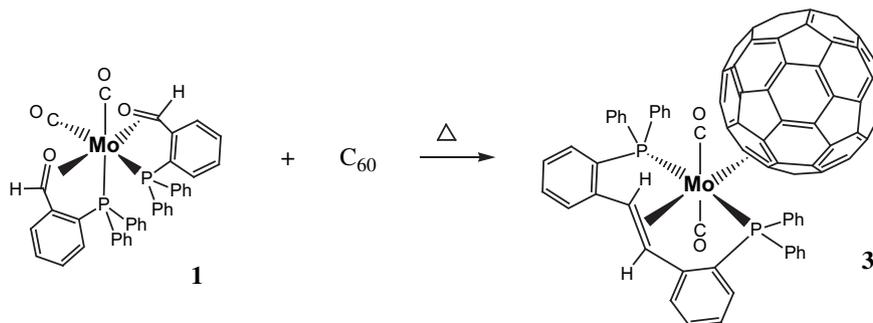
Fig. 3. Molecular structure of **3**. Selected bond distances (Å) and bond angles ($^\circ$): Mo-P1 2.516(2), Mo-P2 2.512(1), Mo-C1 2.038(6), Mo-C2 2.023(7), Mo-C21 2.317(6), Mo-C22 2.335(5), Mo-C41 2.283(6), Mo-C42 2.288(5), C1-O1 1.153(6), C2-O2 1.141(6), C21-C22 1.418(7), C41-C42 1.497(8) and Mo-C1-O1 $176.0(5)^\circ$, Mo-C1-O2 $177.5(6)^\circ$, Mo-P1-C15 $103.8(2)^\circ$, Mo-P2-C28 $104.0(2)^\circ$, P1-Mo-P2 $154.05(6)^\circ$, P1-Mo-C1 $90.4(2)^\circ$, P1-Mo-C2 $89.3(2)^\circ$, C1-Mo-C2 $177.6(3)^\circ$, P2-Mo-C1 $93.5(2)^\circ$, P2-Mo-C2 $87.8(2)^\circ$, C21-C22-C23 $120.0(6)^\circ$, C22-C21-C20 $118.5(5)^\circ$.

On the other hand, $\text{Mo}(\text{CO})_3(\eta^3\text{-}(\text{MeNCH}_2)_3)$ and **1** show higher chemical reactivity than their tungsten analogues, consistent with the characteristic that the second-row transition metal complexes are usually more reactive than either of those containing first- or third-row elements [26]. Finally, despite the low yield of **3**, the reaction of **1** and C_{60} leads to coupling of PCHO ligands is unique within metal-fullerene chemistry.

3. Experimental

3.1. General methods

All manipulations were carried out under an atmosphere of purified dinitrogen with standard Schlenk techniques. $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ [27], $\text{Mo}(\text{CO})_3(\eta^3\text{-}(\text{MeNCH}_2)_3)$ [28], and PCHO [6] were prepared as described in the literature. C_{60} (99%) was purchased from Bulky USA. Solvents were dried over appropriate reagents under dinitrogen and distilled immediately before use. Preparative thin-layer chromatographic (TLC) plates were prepared from silica gel (Merck). Infrared spectra were recorded on a Jasco FT/IR-4100 IR



Scheme 2. Reaction of **1** and C_{60} .

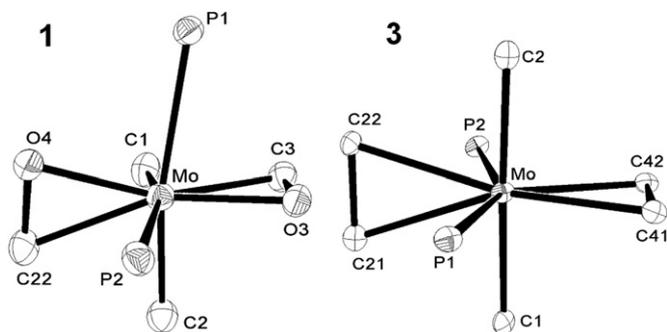


Fig. 4. The coordination environment of molybdenum atom in **1** and **3**.

spectrometer. ^1H and ^{31}P NMR spectra were obtained on a Varian Unity INOVA-500 spectrometer at 500 and 202.5 MHz, respectively. Fast-atom-bombardment (FAB) mass spectra and Matrix-assisted laser desorption ionization (MALDI) mass spectra were recorded on a JEOL JMS-SX102A and Bruker Microflex-LT mass spectrometer, respectively. Elemental analyses were performed at the National Science Council Regional Instrumentation Center at National Cheng-Kung University, Tainan, Taiwan.

3.2. Reaction of $\text{Mo}(\text{CO})_3(\eta^3\text{-MeNCH}_2)_3$ and PCHO

$\text{Mo}(\text{CO})_3(\eta^3\text{-MeNCH}_2)_3$ (120 mg, 0.388 mmol) and PCHO (280 mg, 0.965 mmol) were placed in an oven-dried 100 ml Schlenk flask under a dinitrogen atmosphere. Dichloromethane (40 ml) was introduced into the flask via a syringe and the mixture was stirred at room temperature for 24 h, resulting in an orange-red solution. The solvent was removed on a rotary evaporator and the residue was subjected to TLC, with dichloromethane/*n*-hexane (1:1, v/v) as eluant. Isolation of the material forming the second orange band afforded $\text{Mo}(\text{CO})_4(\eta^2\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{CH}=\text{NMe})$ (**2**; 70 mg, 35%). Isolation of the material forming the fourth pale yellow band afforded air-stable, yellow crystals of $\text{Mo}(\text{CO})_2(\eta^3\text{-PCHO})_2$ (**1**; 85 mg, 30%).

3.2.1. Compound **1**

Anal. Calc. for $\text{C}_{40}\text{H}_{30}\text{MoO}_4\text{P}_2$: C, 65.58; H, 4.13. Found: C, 65.18; H, 4.43%. MS (FAB): m/z 734 (M^+ , ^{98}Mo), 734–28 n ($n = 1, 2$). IR (CH_2Cl_2 , ν_{CO}): 1976s, 1918s cm^{-1} . ^1H NMR (CD_2Cl_2 , 22 °C): 5.38 (s, 2H, CHO), 7.69–6.93 (m, 28H, Ph) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 22 °C): 18.04 (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 24 °C): 215.2 (dd, $J_{\text{P-C}} = 17, 58$ Hz, CO), 155.0–127.2 (Ph), 88.5 (s, $\eta^2\text{-CHO}$) ppm.

3.2.2. Compound **2**

Anal. Calc. for $\text{C}_{24}\text{H}_{18}\text{NM}_2\text{O}_4\text{P}$: C, 56.38; H, 3.55; N, 2.74. Found: C, 56.56; H, 3.62; N, 2.73%. MS (MALDI): m/z 513 (M^+ , ^{98}Mo). IR (CH_2Cl_2 , ν_{CO}): 2016s, 1903s, 1855s cm^{-1} . ^1H NMR (CDCl_3 , 24 °C): 8.21 (s, 1H, CH=N), 7.54–6.85 (m, 14H, Ph), 3.74 (s, 3H, NMe) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3 , 24 °C): 36.27 (s) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 24 °C): 221.0 (d, $J_{\text{P-C}} = 8$ Hz, CO), 216.6 (d, $J_{\text{P-C}} = 33$ Hz, CO), 207.8 (d, $J_{\text{P-C}} = 9$ Hz, CO), 168.5 (d, $J_{\text{P-C}} = 3$ Hz, CH=N), 137.6 (d, $J_{\text{P-C}} = 15$ Hz, C_6H_4), 134.4 (d, $J_{\text{P-C}} = 7$ Hz, C_6H_4), 133.5 (d, $J_{\text{P-C}} = 14$ Hz, $o\text{-C}_6\text{H}_5$), 133.1 (d, $J_{\text{P-C}} = 33$ Hz, $ipso\text{-C}_6\text{H}_5$), 131.9 (d, $J_{\text{P-C}} = 25$ Hz, C_6H_4), 131.7 (d, $J_{\text{P-C}} = 4$ Hz, C_6H_4), 131.2 (s, C_6H_4), 130.2 (s, $p\text{-C}_6\text{H}_5$), 130.1 (s, C_6H_4), 128.7 (d, $J_{\text{P-C}} = 15$ Hz, $m\text{-C}_6\text{H}_5$), 61.7 (d, $J_{\text{P-C}} = 2$ Hz, CH_3) ppm.

3.3. Reaction of $\text{Mo}(\text{CO})_3(\text{NCMe})_3$ and PCHO

$\text{Mo}(\text{CO})_3(\text{NCMe})_3$ (120 mg, 0.396 mmol) and PCHO (287 mg, 0.99 mmol) were placed in an oven-dried 100 ml Schlenk flask under a dinitrogen atmosphere. Dichloromethane (40 ml) was

Table 1
Crystal data for **1** and **3**.

	1	3
Formula	$\text{C}_{40}\text{H}_{30}\text{MoO}_4\text{P}_2$	$\text{C}_{100}\text{H}_{30}\text{MoO}_2\text{P}_2 \cdot 2\text{CS}_2$
Crystal system	Monoclinic	Monoclinic
Formula weight	732.52	1573.38
T (K)	295(2)	200(2)
Space group	$P2_1/n$	$P2_1/n$
a (Å)	9.4464(1)	15.175(2)
b (Å)	16.9229(2)	18.471(3)
c (Å)	21.3523(3)	23.684(3)
α (°)	90	90
β (°)	101.5918(8)	99.169(3)
γ (°)	90	90
V (Å ³)	3343.77(7)	6554.0(16)
Z	4	4
D_{calc} (Mg/m ³)	1.455	1.595
μ (mm ⁻¹)	0.53	0.440
R_1/wR_2	0.050/0.136	0.0666/0.1096
GOF on F^2	1.006	0.961

introduced into the flask via a syringe and the solution was stirred at room temperature for 24 h. The solvent was removed on a rotary evaporator and the residue was subjected to TLC, with dichloromethane/*n*-hexane (1:1, v/v) as eluant. Compound **1** was isolated from the major pale yellow band (100 mg, 35%).

3.4. Thermal reaction of **1** and C_{60}

Compound **1** (30 mg, 0.041 mmol) and C_{60} (29 mg, 0.044 mmol) were placed in an oven-dried 100 ml Schlenk flask, equipped with a reflux condenser, and chlorobenzene (10 ml) was introduced into the flask via a syringe. The mixture was refluxed under dinitrogen for 30 min, resulting a brownish green solution. The solvent was removed under vacuum, and the residue was subjected to TLC, with CS_2 as eluant. The first purple band recovered C_{60} (19 mg) in 66%. Isolation of the material forming the second green band afforded $\text{Mo}(\text{CO})_2(\eta^4\text{-PPh}_2(o\text{-C}_6\text{H}_4)\text{CH}_2)(\eta^2\text{-C}_{60})$ (**3**; 2 mg, 3%). MS (MALDI): m/z 1390 ($\text{M}^+ - \text{CO}$, ^{98}Mo), 1362 ($\text{M}^+ - 2\text{CO}$), 642 ($\text{M}^+ - 2\text{CO} - \text{C}_{60}$). IR (CS_2 , ν_{CO}): 1926s cm^{-1} . ^1H NMR (CDCl_3 , 24 °C): 7.83–6.99 (m, 24H, Ph), 4.30 (t, $J_{\text{P-H}} = 6$ Hz, 2H, CH=CH) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 24 °C): 52.59 (s) ppm.

3.5. Structure determination of **1** and **3**

The crystals of **1** and **3** found suitable for X-ray analysis were each mounted in a thin-walled glass capillary and aligned on the Nonius Kappa CCD diffractometer, with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The θ range for data collection is 1.6–27.5° for **1** and 1.74–25.03° for **3**. Of the 32,008 and 44,688 reflections collected for **1** and **3**, 7652 and 11,560 reflections were independent, respectively. All data were corrected for Lorentz and polarization effects and for the effects of absorption. The structure was solved by the direct method and refined by least-square cycles. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the SHELXTL-97 package [29]. The data collection and refinement parameters are presented in Table 1.

Acknowledgements

This work was financially supported by the National Science Council of Taiwan. We thank Mr. Ting-Shen Fuo (National Taiwan Normal University, Taipei) and Mr. Gene-Hsiang Lee (National Taiwan University, Taipei) for X-ray diffraction analysis.

Appendix A. Supplementary material

CCDC 801640 for **1**, and 801641 for **3** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

References

- [1] G.R. Newkome, *Chem. Rev.* 93 (1993) 2067–2089.
- [2] H.-F. Klein, A. Bickelhaupt, T. Jung, G. Cordier, *Organometallics* 13 (1994) 2557–2559.
- [3] J.-C. Hierro, R. Amardeil, E. Bentabet, R. Broussier, B. Gautheron, P. Meunier, P. Kalck, *Coord. Chem. Rev.* 236 (2003) 143–206.
- [4] J.W. Faller, T. Friss, J. Parr, *J. Organomet. Chem.* 695 (2010) 2644–2650.
- [5] H.-F. Dai, W.-Y. Yeh, *Inorg. Chim. Acta* 363 (2010) 925–929.
- [6] J.E. Hoots, T.B. Rauchfuss, D.A. Wroblewski, *Inorg. Synth.* 21 (1982) 175–179.
- [7] H. Schumann, H. Hemling, V. Ravindar, Y. Badrieh, J. Blum, *J. Organomet. Chem.* 469 (1994) 213–219.
- [8] R. El Mail, M.A. Garralda, R. Hernández, L. Ibarlucea, *J. Organomet. Chem.* 648 (2002) 149–154.
- [9] T.B. Rauchfuss, *J. Am. Chem. Soc.* 101 (1979) 1045–1047.
- [10] X. Chen, F.J. Femia, J.W. Babich, J. Zubieta, *Inorg. Chim. Acta* 315 (2001) 147–154.
- [11] C.P. Lenges, M. Brookhart, P.S. White, *Angew. Chem. Int. Ed.* 38 (1999) 552–555.
- [12] W.-Y. Yeh, C.-S. Lin, S.-M. Peng, G.-H. Lee, *Organometallics* 23 (2004) 917–920.
- [13] A.L. Balch, M.M. Olmstead, *Chem. Rev.* 98 (1998) 2123–2165.
- [14] A. Hirsch, M. Brettreich, *Fullerenes*. Wiley-VCH, Weinheim, 2005, pp. 231–250.
- [15] Y. Matsuo, E. Nakamura, *Chem. Rev.* 108 (2008) 3016–3028.
- [16] W.-Y. Yeh, K.-Y. Tasi, *Organometallics* 29 (2010) 604–609.
- [17] S.C.N. Hsu, W.-Y. Yeh, *J. Chem. Soc. Dalton Trans.* (1998) 125–132.
- [18] C.-C. Yang, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, *J. Organomet. Chem.* 598 (2000) 353–358.
- [19] G. Sánchez, J.L. Serrano, C.M. López, J. García, J. Pérez, G. López, *Inorg. Chim. Acta* 306 (2000) 168–173.
- [20] P.A. Vigato, S. Tamburini, *Coord. Chem. Rev.* 248 (2004) 1717–2128.
- [21] W.-Y. Yeh, S.-C. Hsiao, S.-M. Peng, G.-H. Lee, *Organometallics* 24 (2005) 3365–3367.
- [22] C.-S. Chen, W.-Y. Yeh, *Chem. Commun.* 46 (2010) 3098–3100.
- [23] Y.-C. Liu, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, *Organometallics* 22 (2003) 4163–4166.
- [24] Y.-C. Liu, W.-Y. Yeh, G.-H. Lee, S.-M. Peng, *J. Organomet. Chem.* 690 (2005) 163–167.
- [25] B.P. Mundy, M.G. Eller, F.G. Favaloro Jr., *Name Reactions and Reagents in Organic Synthesis*. Wiley, New Jersey, USA, 2005.
- [26] G.O. Spessard, G.L. Miessler, *Organometallic Chemistry*. Oxford University Press, Oxford, 2010.
- [27] D.P. Tate, W.R. Knipple, J.M. Augl, *Inorg. Chem.* 1 (1962) 433–434.
- [28] M.V. Baker, M.R. North, *J. Organomet. Chem.* 565 (1998) 225–230.
- [29] G.M. Sheldrick, SHELXTL-97. University of Göttingen, Germany, 1997.