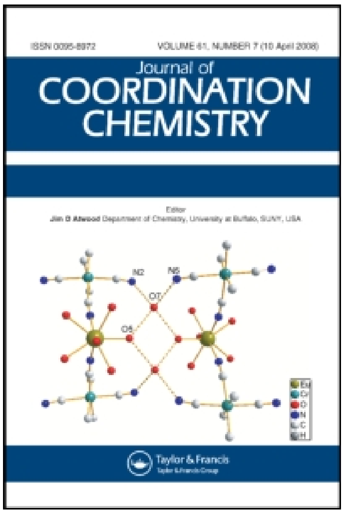

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Reactions of *trans*-Carbonyl(Chloro)-[Bis(Triphenylphosphine)]Rhodium(I) with Substituted Cyclopentadienyl Tricarbonyl Molybdenum Anions

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REACTIONS OF *trans*-CARBONYL(CHLORO)-[BIS(TRIPHENYLPHOSPHINE)]RHODIUM(I) WITH SUBSTITUTED CYCLOPENTADIENYL TRICARBONYL MOLYBDENUM ANIONS

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Reactions of *trans*-carbonyl(chloro)[bis(triphenylphosphine)]rhodium(I): *trans*-$ClRh(CO)(PPh_3)_2$ with substituted cyclopentadienyl tricarbonyl molybdenum anions, $[Mo(CO)_3(\eta^5\text{-}C_5H_4R)]^-$ (R=H; $COCH_3$) in tetrahydrofuran (THF) at 55°C for 24 h yielded two monometallic complexes as by-products: $[Rh(CO)(PPh_3)(\eta^5\text{-}C_5H_4R)]$ (R = H (**1a**); $COCH_3$ (**2a**)) and two main heterobimetallic compounds: $[RhMo(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_4R)]$ (R = H (**1b**); $COCH_3$ (**2b**)). These compounds were characterized by elemental analysis, IR and ^{1}H NMR spectra. The molecular structure of (**2a**) was determined by X-ray diffraction.

Keywords: Heterobimetallic compound; Crystal structure; Rhodium; Molybdenum

INTRODUCTION

Asymmetric catalysis induced by a metal cluster that contains a chiral tetrahedral metal framework is still one of the challenges of organometallic chemistry [1]. Our previous work has shown that bimetallic carbonyl complexes react readily with asymmetric alkynes to give tetrahedral compounds containing a $M_2C^1C^2$ core, which can be changed into chiral tetrahedral products $M^1M^2C^1C^2$ by a metal-exchange reaction and indicated that such chiral bimetallic tetrahedral compounds possessed asymmetric catalytic activity in the addition of diethylzinc to benzaldehyde [2]. Rhodium is implicated in a number of catalytic organic reactions [3] and the effects of the early transition metals Mo or W on the reactivity of these elements is of interest [4]. Furthermore, it has also been reported that $CoMoCp(CO)_5(PPh_3)_2$ reacts with $PhC{\equiv}CH$ to give a bimetallic tetrahedral product [5]. All of these prompted us to hope to obtain a series of chiral bimetallic tetrahedral compounds containing the

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$RhMoC^1C^2$ core and attempt to resolve their enantiomers to further investigate their activities for asymmetric catalysis. We report now the synthesis and characterization of two monometallic complexes $[Rh(CO)(PPh_3)(\eta^5\text{-}C_5H_4R)]$ (R=H (**1a**); $COCH_3$ (**2a**)) and two heterobimetallic compounds $[RhMo(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_4R)]$ (R=H (**1b**); $COCH_3$ (**2b**)).

EXPERIMENTAL

Preparative work was carried out under an atmosphere of pure nitrogen by using standard Schlenk or vacuum-line techniques. Freshly distilled solvents were used. Column chromatography was carried out by using a silica-gel column of 160 ~ 200 mesh. Thin-layer chromatography (TLC) was performed on commercial Merck plates coated with a 0.20 mm layer of silica gel. $Mo(CO)_6$ was purchased from Aldrich. *trans*-$ClRh(CO)(PPh_3)_2$ [6] and $Na(C_5H_4R)]$ (R=H; $COCH_3$) [7] were prepared according to published methods. Infrared spectra were recorded on a Bruker 120 HR FTIR spectrophotometer. ^{1}H NMR spectra were measured on a Bruker AM-400 MHz spectrometer; Elemental analyses (C, H) were performed on a Carlo-Erba 1106 type analyzer.

Syntheses of Compounds 1a and 1b

Into a 100 mL three-necked flask equipped with a condenser and magnetic stirrer were placed 0.264 g (1.0 mmol) of $Mo(CO)_6$ and anhydrous THF (20 mL). NaCp (1.0 mmol) was added and the mixture was refluxed for 12 h. The reactor was cooled to room temperature and 0.691 g of *trans*-$ClRh(CO)(PPh_3)_2$ (1.0 mmol), which was dissolved in 10 mL of THF, was transferred into the reaction flask. The mixture was heated at 55°C for 24 h. After THF was removed, the residue was extracted with a small amount of CH_2Cl_2 and transferred to the top of a 2.5 cm × 40 cm silica-gel column. Elution with CH_2Cl_2–petroleum ether (2 : 1) afforded the first orange product (**1a**) (0.083 g, 36.2%) and the second orange-red band (**1b**) (0.268 g, 59.4%). Calcd. for $C_{24}H_{20}OPRh$ (**1a**) (%): C, 62.88; H, 4.40. Found: C, 62.57; H, 4.26. IR (KBr disk) $\tilde{\nu}$ (cm^{-1}): 3049 (w, ArH), 1964 (vs, CO). ^{1}H NMR ($CDCl_3$, δ): 7.76–7.37 (m, 15H, $3C_6H_5$), 5.31 (s, 5H, C_5H_5).

Calcd. for $C_{45}H_{35}O_4P_2MoRh$ (**1b**) (%): C, 59.87; H, 3.91. Found: C, 59.65; H, 3.78. IR (KBr disk) $\tilde{\nu}$ (cm^{-1}): 3051 (w, ArH), 2047 (m, CO), 1982 (vs), 1853 (vs), 1794 (s), 1743 (s). ^{1}H NMR ($CDCl_3$, δ): 8.05–7.37 (m, 30H, $6C_6H_5$), 5.31 (s, 5H, C_5H_5).

Syntheses of Compounds 2a and 2b

To a solution of $Na(C_5H_4COCH_3)$ (0.130 g, 1.0 mmol) in anhydrous THF (20 mL), $Mo(CO)_6$ (0.264 g, 1.0 mmol) was added. The mixture was heated under reflux for 15 h and cooled to room temperature. A solution of 10 mL *trans*-$ClRh(CO)(PPh_3)_2$ (0.691 g, 1.0 mmol) in THF was added to the reaction flask and heated at 55°C for 24 h with stirring. Removal of the solvent under vacuum and purification of the residue by chromatography on silica gel using CH_2Cl_2–petroleum ether (5 : 2) as an eluent gave the first orange product (**2a**) (0.077 g, 30.8%), which crystallized from a 1:1 mixture of CH_2Cl_2–*n*-hexane at −20°C and the second orange-red band (**2b**) (0.287 g, 60.8%). Calcd. for $C_{26}H_{22}O_2PRh$ (**2a**) (%): C, 62.39; H, 4.43. Found: C, 62.24; H, 4.69.

IR (KBr disk) $\tilde{\nu}$ (cm^{-1}): 3069 (w, ArH), 1969 (vs, CO), 1649 (m, C=O). ^{1}H NMR (CDCl$_3$, δ): 7.66–7.28 (m, 15H, 3C$_6$H$_5$), 5.41–5.20 (d, 4H, C$_5$H$_4$), 2.50 (s, 3H, CH$_3$)

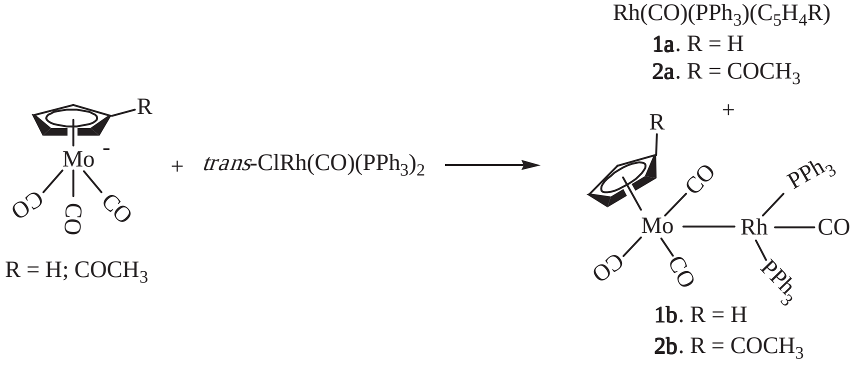
Calcd. for $C_{47}H_{37}O_5P_2MoRh$ (**2b**) (%): C, 59.74; H, 3.95. Found: C, 59.56; H, 3.77. IR (KBr disk) $\tilde{\nu}$ (cm^{-1}): 3056 (w, ArH), 2051 (m, CO), 1987 (vs), 1849 (vs), 1790 (s), 1738 (s), 1677 (m, C=O). ^{1}H NMR (CDCl$_3$, δ): 7.73–7.39 (m, 30H, 6C$_6$H$_5$), 5.50–5.28 (d, 4H, C$_5$H$_4$), 2.59 (s, 3H, CH$_3$). ^{31}P NMR (CDCl$_3$, δ): 35.49 (d, 2P, 2PPh$_3$).

Crystallography of 2a

A suitable orange-red block crystal of Compound **2a** was obtained from CH$_2$Cl$_2$–hexane at $-20°$C. All diffraction data were collected on a Bruker CCD APEX diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K by the φ–ω scan mode ($1.74 < \theta < 28.29°$). A total of 6693 reflections were collected with 4836 unique reflections ($R_{(\mathrm{int})} = 0.0464$). The intensity data were corrected for absorption with Bruker/Siemens area detector absorption and other corrections (SADABS). The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added by the geometrical method. The final cycle of full-matrix least-squares refinement was based on 4836 unique reflections and 348 variable parameters and converged with unweighted and weighted agreement factors. The final $R = 0.0362$, $wR = 0.0798$ for 4131 observed reflections [$I > 2\sigma(I)$]. The minimum and maximum final electron densities were -0.832 and 0.867 e Å^{-3}. All the calculations were performed using the SHELXL-97 crystallographic program package [8].

RESULTS AND DISCUSSION

The work described in this article is summarized in Scheme 1. Reactions of *trans*-ClRh(CO)(PPh$_3$)$_2$ with [Mo(CO)$_3$(η^5-C$_5$H$_4$R)]$^-$ (R=H; COCH$_3$) in THF proceed similarly with displacement of the chloride ligand to yield the unexpected monometallic complex, [Rh(CO)(PPh$_3$)(η^5-C$_5$H$_4$R)] (R=H (**1a**); COCH$_3$ (**2a**)) and the desired heterobimetallic complex, [RhMo(CO)$_4$(PPh$_3$)$_2$(η^5-C$_5$H$_4$R)] (R=H (**1b**); COCH$_3$ (**2b**)). Complexes **1a** and **2a** are stable to air in the solid state, but Complexes **1b** and **2b**



SCHEME 1

are slightly sensitive to air in both the solid state and solution. They have been characterized by elemental analysis and spectroscopic techniques.

All IR spectra of these compounds showed a weak absorption band in the region 3069–3049 cm^{-1}, characteristic of the phenyl rings of triphenylphosphine ligands. In the IR spectra of **1b** and **2b**, the absorption bands around 2051 and 1982 cm^{-1} and 1853 and 1738 cm^{-1} are caused by the carbonyl ligands coordinated to rhodium and molybdenum, respectively, similar to $(CO)_4MoRh(CO)(\mu\text{-dppm})(S_2CNEt_2)$ [4b] and the bimetallic complexes, reported by Carlton *et al.* [4a]. The absorption bands at 1677 and 1649 cm^{-1} can be assigned to ketonic carbonyl bonded to the cyclopentadienyl ring in **2a** and **2b**.

^{1}H NMR spectra of all these compounds exhibited multiplets at $\delta = 8.05$–7.28 for the protons of the phenyl rings of the triphenylphosphine ligand. For Complexes **2a** and **2b**, the doublets at $\delta = 5.50$–5.20 are assigned to four protons of the substituted cyclopentadienyl ligand and the singlets at $\delta = 2.59$–2.50 are assigned to the methyl protons of the acetyl group. The singlets at $\delta = 5.31$ can be assigned to the protons of the cyclopentadienyl ring for Complexes **1a** and **1b**. The ^{31}P NMR spectrum of **2b** has a doublet at 35.49 ppm, assigned to the phosphorus bonded to rhodium not to molybdenum [4b].

For **1b** and **2b**, the structures are indicated as $[RhMo(CO)_4(PPh_3)_2(\eta^5\text{-}C_5H_4R)]$, in which one carbonyl and two phosphorus ligands bond to rhodium [9] while the other ligands coordinate to molybdenum. An additional Rh → Mo dative interaction provides 16- and 18-electron environments for the metals.

The molecular structure of **2a** was determined by X-ray diffraction. Crystal data and experimental details for **2a** are collected in Table I. Table II give the selected bond lengths and angles and the atomic coordinates are listed in Table III. Figure 1 shows the molecular structure of **2a**.

TABLE I Summary of crystal and refinement data for Compound **2a**

Empirical formula	$C_{26}H_{22}O_2PRh$
Formula weight	500.32
Crystal system	Triclinic
Space group	*P*-1
$F(000)$	508
a (Å)	9.0069(7)
b (Å)	10.4240(8)
c (Å)	12.5945(10)
α (°)	110.035(10)
β (°)	101.1420(10)
γ (°)	82.2560(10)
V (Å^3)	1086.95(15)
Z	2
$D_{calc.}$ (g/cm^3)	1.529
Absorption coefficient (mm^{-1})	0.879
Temperature (°C)	20
Scan type	Φ–ω
θ_{max} (°)	28.29
Number of observations [$I > 2\sigma(I)$]	4131
Number of variables	348
Goodness-of-fit on F^2	0.945
R^a, R_w^b	0.0366, 0.0899

$^a R = \sum||F_0|-|F_c||/\sum|F_0|$; $^b R_w = \left[\sum\omega(|F_0|-|F_c|)^2/\sum\omega F_0^2\right]^{1/2}$

TABLE II Selected bond lengths (Å) and angles (°) for compound **2a**

Rh–C(1)	1.823(3)	P–C(15)	1.839(3)	C(6)–C(7)	1.465(5)
Rh–C(5)	2.248(3)	O(1)–C(1)	1.140(4)	C(7)–C(8)	1.504(6)
Rh–P	2.2476(7)	O(2)–C(7)	1.224(4)	C(9)–C(14)	1.378(4)
Rh–C(2)	2.269(3)	C(2)–C(6)	1.415(4)	C(9)–C(10)	1.392(4)
Rh–C(3)	2.275(3)	C(2)–C(3)	1.425(5)	C(10)–C(11)	1.380(5)
Rh–C(4)	2.299(3)	C(3)–C(4)	1.385(5)	C(11)–C(12)	1.366(6)
Rh–C(6)	2.311(3)	C(4)–C(5)	1.415(5)	C(12)–C(13)	1.359(6)
P–C(9)	1.826(3)	C(5)–C(6)	1.421(5)	C(13)–C(14)	1.384(5)
P–C(21)	1.830(3)				
C(1)–Rh–P	89.70(9)	C(9)–P–C(21)	104.09(13)	C(9)–P–Rh	113.44(10)
C(5)–Rh–C(2)	60.44(12)	C(9)–P–C(15)	103.25(13)	C(21)–P–Rh	116.50(9)
C(3)–Rh–C(6)	60.10(12)	C(21)–P–C(15)	103.09(13)	C(15)–P–Rh	114.89(9)
C(4)–Rh–C(6)	60.01(13)	C(6)–C(2)–C(3)	107.9(3)	C(17)–C(16)–C(15)	120.3(3)
C(5)–Rh–C(3)	60.00(13)	C(5)–C(6)–C(7)	124.4(3)	C(24)–C(23)–C(22)	120.4(4)
C(2)–Rh–C(4)	59.98(13)	O(1)–C(1)–Rh	178.1(3)	C(12)–C(11)–C(10)	120.3(4)

TABLE III Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Compound **2a**

Atom	*x*	*y*	*z*	*U(eq)*
Rh	6770(1)	8187(1)	7397(1)	29(1)
P	8107(1)	6964(1)	8473(1)	27(1)
O(1)	7028(4)	10719(2)	9403(2)	70(1)
O(2)	8017(4)	9839(3)	5269(3)	76(1)
C(1)	6951(4)	9735(3)	8640(3)	45(1)
C(2)	6805(4)	6775(3)	5571(3)	42(1)
C(3)	5368(4)	6732(4)	5868(3)	45(1)
C(4)	4606(4)	8017(4)	6061(3)	45(1)
C(5)	5576(4)	8897(3)	5934(3)	44(1)
C(6)	6911(4)	8114(3)	5564(2)	41(1)
C(7)	8150(5)	8667(4)	5296(3)	53(1)
C(8)	9574(5)	7760(5)	5045(4)	70(1)
C(9)	10054(3)	6463(3)	8196(2)	31(1)
C(10)	10890(4)	7449(4)	8119(3)	44(1)
C(11)	12374(4)	7124(5)	7930(3)	55(1)
C(12)	13019(4)	5824(5)	7780(3)	57(1)
C(13)	12208(4)	4849(4)	7843(3)	54(1)
C(14)	10736(4)	5165(3)	8070(3)	42(1)
C(15)	7349(3)	5324(3)	8254(2)	29(1)
C(16)	7157(4)	4372(3)	7163(3)	40(1)
C(17)	6556(5)	3150(3)	6967(3)	48(1)
C(18)	6138(4)	2865(4)	7847(3)	49(1)
C(19)	6331(4)	3787(4)	8930(3)	47(1)
C(20)	6942(4)	5010(3)	9128(3)	38(1)
C(21)	8313(3)	7789(3)	10026(2)	29(1)
C(22)	9703(4)	7878(3)	10727(3)	41(1)
C(23)	9795(5)	8528(4)	11903(3)	52(1)
C(24)	8512(5)	9082(4)	12373(3)	48(1)
C(25)	7122(5)	8995(3)	11679(3)	46(1)
C(26)	7022(4)	8371(3)	10512(3)	38(1)

U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

As shown in Fig. 1, three ligands bond to rhodium: one carbonyl, one PPh_3 and one acetylcyclopentadienyl. The distance between the rhodium atom and the center of the cyclopentadienyl ring is 1.9385 Å. The mechanism of Cp group transfer from molybdenum to rhodium is not clear but may be similar to that

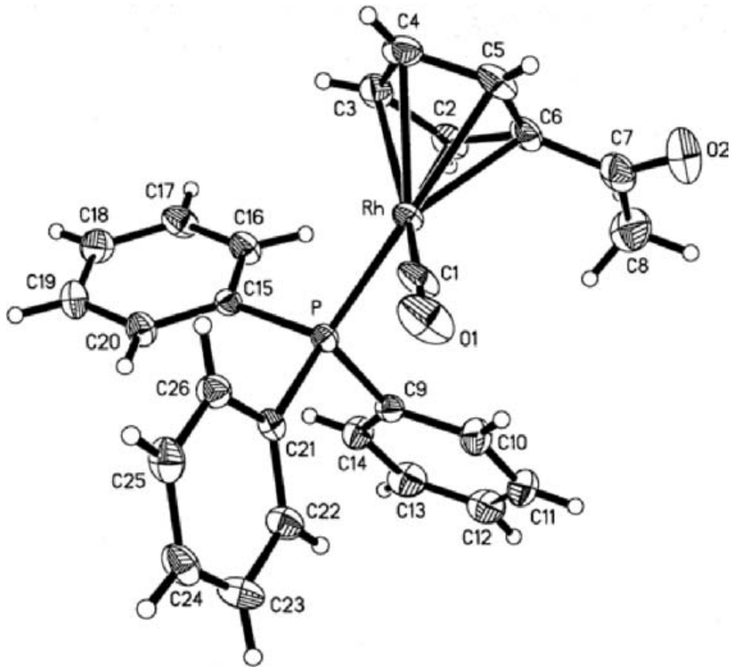


FIGURE 1 Molecular structure of Compound **2a**.

reported by Vahrenkamp *et al.* [10]. The bond lengths of Rh–P (2.2476(7) Å) and Rh–Cl (1.823(3) Å) are shorter and longer, respectively, than corresponding distances in *trans*-ClRh(CO)(PPh_3)$_2$ [11]. All atoms in the cyclopentadienyl ligand, together with C(7), O(2) and C(8) in the acetyl group, are located approximately in a plane (C(2)–C(6)–C(7)–C(8), −3.6(5)°; C(5)–C(6)–C(7)–C(8), 173.1(3)°; C(2)–C(6)–C(7)–O(2), 175.9(3)°; C(5)–C(6)–C(7)–O(2), −7.5(5)°) and the π system of the CH_3(O)C substituent is fully conjugated with the cyclopentadienyl π system, giving bond lengths of C(6)–C(7) (1.465(5) Å) and C(7)–C(8) (1.504(6) Å) shorter than normal C–C distances (1.54 Å) and indicating double-bond character.

Acknowledgment

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Supplementary Material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 190661 for Compound **2a**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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