Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 691 (2006) 1216–1222
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Synthesis and structure of some ruthenium–rhenium heterodinuclear complexes and their catalytic activity in the addition of carboxylic acids to phenylacetylene

Suming Ye [a], Weng Kee Leong [b,*]

[a] Institute of Chemical and Engineering Sciences, 1 Pesek Road, Jurong Island 627833, Singapore
[b] Department of Chemistry, National University of Singapore, Kent Ridge 119260, Singapore

Received 2 November 2005; received in revised form 23 November 2005; accepted 24 November 2005
Available online 4 January 2006

Abstract

The salt elimination reaction of $Na[Re(CO)_5]$ with Cp*Ru(dppm)Cl, CpRu(dppm)Cl or $CpRu(CO)_2Cl$ afforded the heterodinuclear species $Cp^*Ru(\mu\text{-}CO)_2(\mu\text{-}dppm)Re(CO)_3$, $Cp(CO)Ru(\mu\text{-}dppm)Re(CO)_4$, or $Cp(CO)_2RuRe(CO)_5$, respectively, in moderate yields. An orthometallated species, $Cp^*(CO)Ru(\mu\text{-}H)[\mu\text{-}PhP(C_6H_4)CH_2PPh_2]Re(CO)_3$, was also obtained from the first reaction. All these heterodinuclear products have been characterised crystallographically. They also showed good catalytic activity for the addition of carboxylic acids to phenylacetylene to afford the anti-Markovnikov products selectively.

Keywords: Rhenium; Ruthenium; Heterodinuclear; Catalysis; Anti-Markovnikov addition; Alkyne; Addition of carboxylic acid

1. Introduction

The possibility of cooperative reactivity of adjacent heterometallic centers, which may impart new reactivity patterns significantly different from those of the homobimetallic complexes, continues to be of great interest particularly with regards to catalysis [1]. One heterodinuclear system that has interested us is the ruthenium–rhenium dinuclear system. Synthetic routes to metal–metal bonded heterobimetallic complexes in general are very well documented [2]; one of the most commonly employed being the displacement of a halide ligand by an anionic metal fragment. Nevertheless, much of the work that has been carried out with complexes containing both ruthenium and rhenium has an interconnecting ligand between the metal centres. This included studies directed at synthesis [3], and electron or energy transfers [4]. The only known ruthenium–rhenium dinuclear complexes containing a metal–metal bond appear to be the 30-electron species $[(PPh_3)_2HRe(\mu\text{-}H)_3(\mu\text{-}CO)RuH(PPh_3)_2]$ and $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$; their syntheses and derivatives chemistry have been described [5]. In this paper, we present our syntheses of Ru–Re metal–metal bonded complexes via the reaction of Cp* or Cp complexes of ruthenium with the carbonylate $Na[Re(CO)_5]$ (**2**), and some preliminary investigations into their catalytic properties.

2. Results and discussion

The carbonylate **2** was obtainable by the reduction of $Re_2(CO)_{10}$ (**1**) with sodium amalgam [6]. It underwent a salt elimination reaction at 75 °C with the ruthenium chloro derivatives Cp*Ru(dppm)Cl (**3a**), CpRu(dppm)Cl (**3b**) or $CpRu(CO)_2Cl$ (**3c**), to afford the heterodinuclear species $Cp^*Ru(\mu\text{-}CO)_2(\mu\text{-}dppm)Re(CO)_3$ (**4a**), $Cp(CO)Ru(\mu\text{-}dppm)Re(CO)_4$ (**4b**), or $Cp(CO)_2RuRe(CO)_5$ (**4c**), respectively, in moderate yields. In the reaction with **3a**, another heterodinuclear species, $Cp^*(CO)Ru(\mu\text{-}H)[\mu\text{-}PhP(C_6H_4)CH_2PPh_2]Re(CO)_3$ (**5**), was also isolated. These

* Corresponding author.
E-mail address: chmlwk@nus.edu.sg (W.K. Leong).

0022-328X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2005.11.061

reactions are summarized in Scheme 1. The products **4a**–**c** and **5** have been characterized completely, including by single-crystal X-ray structural studies. The ORTEP diagrams, together with selected bond parameters, for **4a**–**c** and **5**, as well as that for **3b**, are shown in Figs. 1–5, respectively.

The formation of **4a** and **4b** from **3a** and **3b**, respectively, involved the rearrangement of the diphosphine ligands from a chelating mode to that of a bridge across the heterometallic bond. This was to be expected as such a rearrangement would lead to a release of the PRuPC ring strain in **3a** and **3b**. The reaction of **3c** also gave some $[CpRu(CO)_2]_2$ (**6**), which suggested that some redox process was also involved. Similar reactions with the dppe analogues Cp*Ru(dppe)Cl and CpRu(dppe)Cl gave mixtures of compounds which we have not been able to identify, as was also the case for the indenyl analogue (Ind)Ru(dppm)Cl. It may be expected a priori that **4a** was the precursor to **5**. However, we have found that the IR spectrum of a sample of **4a** remained unchanged even after heating for 2 d. Thus, it appeared that **5** was formed directly from the reaction of **2** with **3a** via a different pathway. Interestingly, the orthometallation in **5** is by the Re atom, a reflection of the greater tendency for the third row transition metals to do so.

The structure of **4a** exhibits two bridging carbonyl ligands. In contrast, the Cp analogue **4b** does not contain any bridging carbonyl ligands. This situation is similar to, for example, the homometallic analogues $[Cp^*Os(\mu\text{-}CO)(CO)]_2$ and $[CpOs(CO)_2]_2$ [7], and may be attributed to the greater electron-donating ability of the Cp* compared to the Cp ligand. The Ru–Re bond length is shortened by the bridging carbonyls (2.8596(5) Å in **4a** compared to 2.939(10) and 2.9239(6) Å in **4b** and **4c**, respectively), but is lengthened by a bridging hydride (3.2652(5) Å in **5**). The difference in the covalent radius between ruthenium and rhenium (1.25 and 1.28 Å, respectively) is manifested in the metal–phosphorus bond lengths,

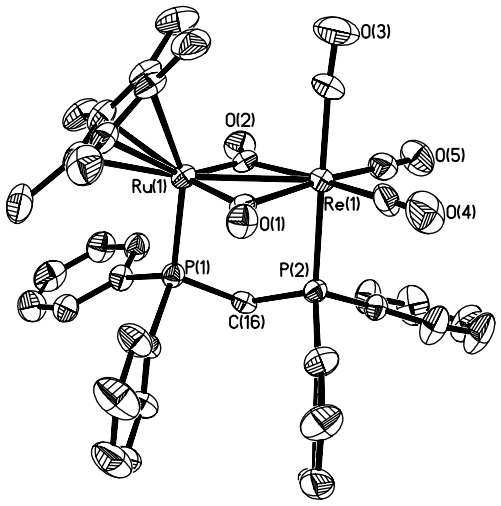
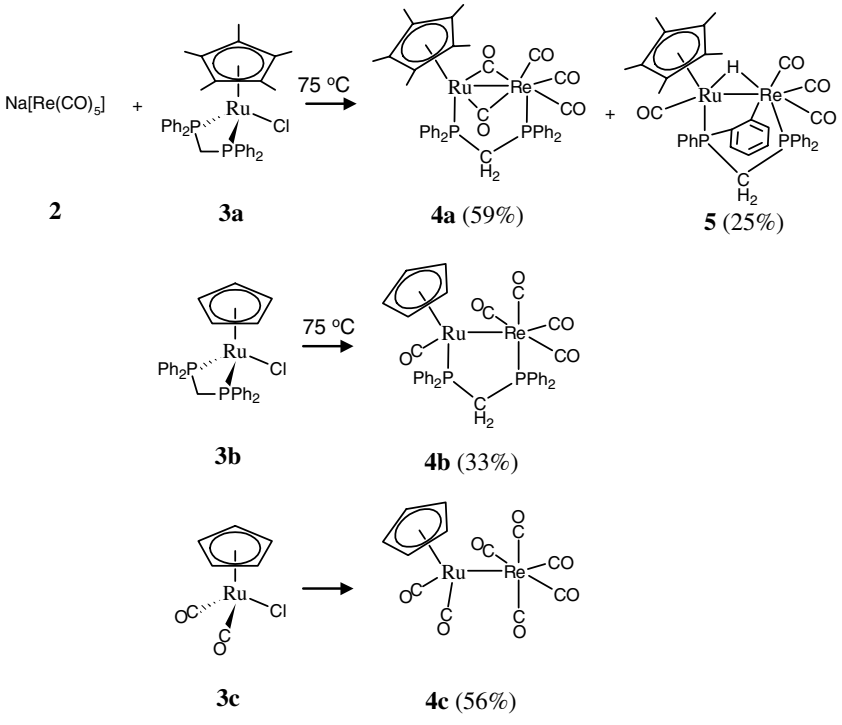


Fig. 1. ORTEP diagram showing the molecular structure (50% probability thermal ellipsoids), and selected bond parameters, of **4a**. Ru(1)–Re(1) = 2.8596(5) Å; Ru(1)–P(1) = 2.2985(16) Å; Re(1)–P(2) = 2.4544 (15) Å; Re(1)–C(1) = 2.262(6) Å; Ru(1)–C(1) = 1.968(6) Å; Re(1)–C(2) = 2.198(6) Å; Ru(1)–C(2) = 2.002(6) Å; Re(1)–C(3) = 1.937(7) Å; Re(1)–C(4) = 1.957(7) Å; Re(1)–C(5) = 1.936(7) Å; P(1)–C(16) = 1.838(6) Å; P(2)–C(16) = 1.830(6) Å; P(1)–Ru(1)–Re(1) = 94.72(4)°; P(2)–Re(1)–Ru(1) = 89.40(4)°; O(1)–C(1)–Ru(1) = 139.8(5)°; O(1)–C(1)–Re(1) = 134.4(5)°; O(2)–C(2)–Ru(1) = 135.5(5)°; O(2)–C(2)–Re(1) = 138.6(5)°.



Scheme 1.

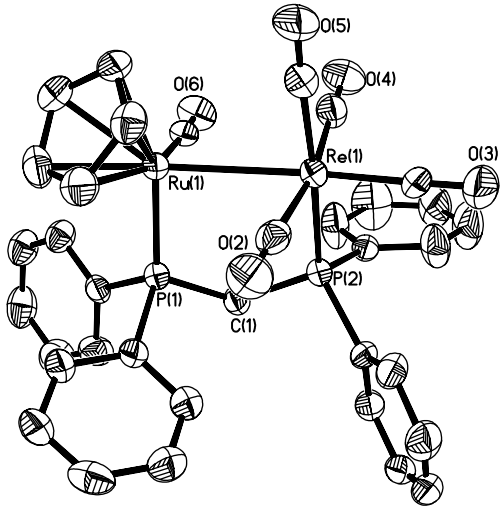


Fig. 2. ORTEP diagram showing the molecular structure (50% probability thermal ellipsoids), and selected bond parameters, of **4b**. Re(1)–Ru(1) = 2.939(10) Å; Ru(1)–P(1) = 2.25(3) Å; Re(1)–P(2) = 2.44(3) Å; Re(1)–C(2) = 1.98(12) Å; Re(1)–C(3) = 1.90(11) Å; Re(1)–C(4) = 1.99(12) Å; Re(1)–C(5) = 1.95(11) Å; Ru(1)–C(6) = 1.83(11) Å; P(2)–Re(1)–Ru(1) = 90.8(6)°; P(1)–Ru(1)–Re(1) = 91.5(7)°.

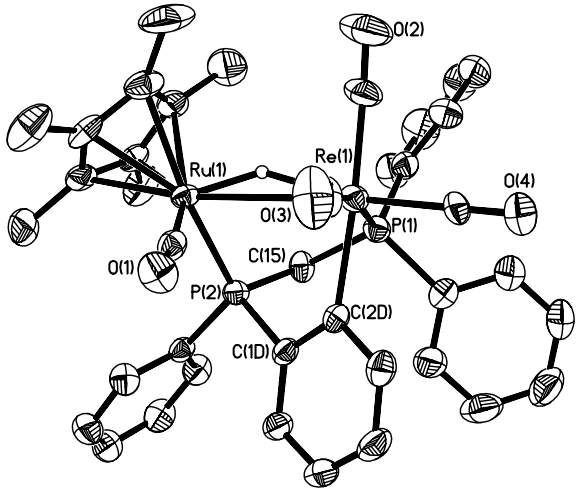


Fig. 4. ORTEP diagram showing the molecular structure (50% probability thermal ellipsoids), and selected bond parameters, of **5**. Re(1)–Ru(1) = 3.2652(5) Å; Re(1)–P(1) = 2.4410(15) Å; Ru(1)–P(2) = 2.2767(14) Å; Re(1)–C(2) = 1.939(6) Å; Re(1)–C(3) = 1.940(6) Å; Re(1)–C(4) = 1.904(5) Å; Re(1)–C(2D) = 2.202(5) Å; Ru(1)–C(1) = 1.868(6) Å; P(1)–Re(1)–Ru(1) = 86.73(3)°; P(2)–Ru(1)–Re(1) = 73.78(3)°.

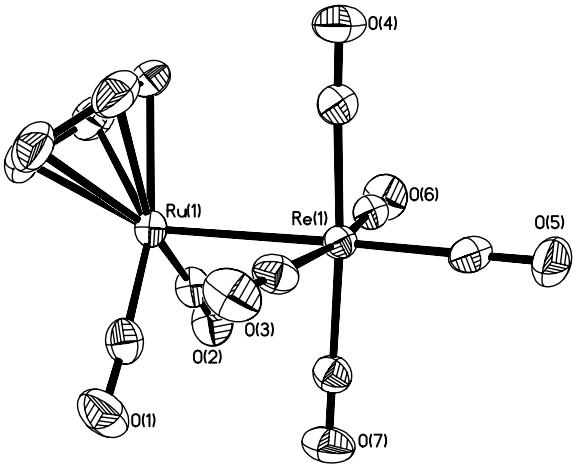


Fig. 3. ORTEP diagram showing the molecular structure (50% probability thermal ellipsoids), and selected bond parameters, of **4c**. Ru(1)–Re(1) = 2.9239(6) Å; Ru(1)–C(1) = 1.861(3) Å; Ru(1)–C(2) = 1.860(3) Å; Re(1)–C(3) = 1.992(3) Å; Re(1)–C(4) = 1.995(3) Å; Re(1)–C(5) = 1.924(3) Å; Re(1)–C(6) = 2.001(3) Å; Re(1)–C(7) = 2.015(3) Å.

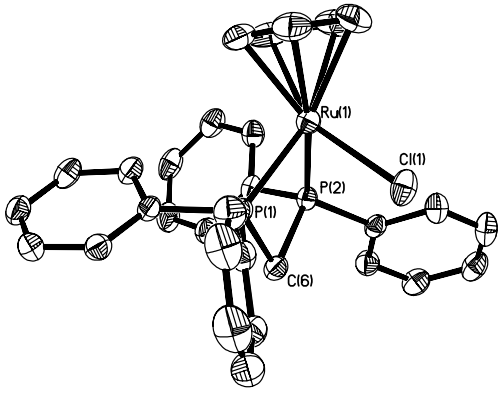
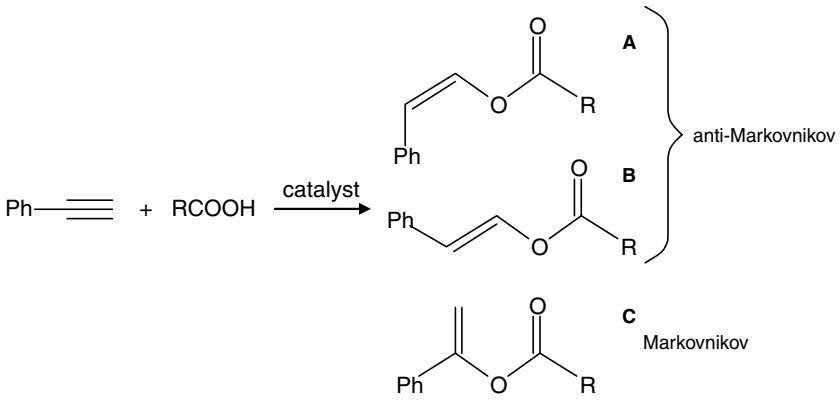


Fig. 5. ORTEP diagram showing the molecular structure (50% probability thermal ellipsoids), and selected bond parameters, of **3b**. Ru(1)–P(1) = 2.2704(5) Å; Ru(1)–P(2) = 2.3048(5) Å; Ru(1)–Cl(1) = 2.4374(6) Å; P(1)–Ru(1)–P(2) = 71.216(19)°.

which range from 2.25(3) to 2.3048(5) Å for the Ru–P bond and from 2.44(3) to 2.4544(15) Å for the Re–P bond in the compounds here. This difference in the covalent radii is also apparent in the metal–carbonyl bond lengths; the sum of the M–C and C–O bond lengths for the terminal carbonyls range from 3.00 to 3.01 Å for ruthenium, and above 3.05 Å for rhenium [8]. In addition, this sum is shorter for carbonyls *trans* to the metal–metal bond (range from 3.05 to 3.07 Å) than for carbonyls *trans* to a phosphorus ligand (~3.1 Å), with that for carbonyls *trans* to another carbonyl being the longest (>3.12 Å). This is a reflection of the increasing π donor ability from a metal fragment to a phosphine ligand then to a carbonyl ligand. The presence of the diphosphine ligands in **4a** and **4b** also imposes a constraint on the relative orientation of the Ru and Re fragments. Thus, the PRuReP torsion angles are 6.8° and 16.6° in **4a** and **4b**, respectively, compared to 43.0° and 46.8° for the C(7)ReRuC(1) and C(7)ReRuC(2) torsion angles, respectively, in **4c**.

We have also carried out preliminary investigations into the possibility of employing these heteronuclear compounds in the catalysed addition of carboxylic acids to 1-alkynes to form enol esters, particularly for various carboxylic acids with phenylacetylene (Scheme 2); the results are summarized in Table 1. This reaction has been reported to be catalysed by ruthenium [9], and more recently rhenium [10], complexes. Some of these led selectively to the



Scheme 2.

Table 1
Enol ester formation catalysed by complexes **4**

Entry	Catalyst	RCOOH	Stereoselectivity	Regioselectivity	Isolated yield (%)
1	**4a**	PhCOOH	2.4	97	95
2	**4b**	PhCOOH	0.8	66	53
3	**4c**	PhCOOH	0.8	90	58
4	**4a**	CH_3COOH	1.2	99	84
5	**4a**	$CH_3(CH_2)_2COOH$	1.8	97	95
6	**4a**	C_6F_5COOH	0.7[a]	72[a]	90
7	**4a**	Crotonic acid	2.1	98	99
8	**4a**	*t*-BuC_6H_4COOH	3.5	67	36
9[b]	**4a**	PhCOOH	1.9	44	21

Stereoselectivity = **A**/**B**; regioselectivity = (**A** + **B**)/(**A** + **B** + **C**).
[a] Based on isolated yields.
[b] Reaction with 1-hexyne.

anti-Markovnikov products, and with some notable exceptions [9j], the *Z*-enol esters were very often the predominant stereoisomers obtained [9,11]. We have also recently found that **3c** and **6** were efficient catalysts for this reaction, offering high regioselectivity for the anti-Markovnikov products, and moderate stereoselectivity for the *E*-enol esters [12].

The yields obtained with the catalysts **4** here are comparable to those obtained with **3c** or **6**, and in a few cases (entries 5–7) are actually higher. The selectivities for the anti-Markovnikov products **A** and **B** are also comparable, although the stereoselectivities are rather poor. However, the results indicate that these heterodinuclear compounds have potential for further development as catalysts for this reaction. The differences in activity and selectivity, although not very great at the moment, suggest that differences in catalytic behaviour from their homometallic analogues and precursors may be anticipated.

3. Concluding remarks

We have thus reported the synthesis of the first heterodinuclear complexes of ruthenium and rhenium containing the Cp or Cp* ligand in moderate yields, and determined their molecular structures. These complexes showed good catalytic potential for the addition of carboxylic acids to terminal alkynes, displaying good regioselectivity for the anti-Markovnikov products. We believe that they represent a new class of catalysts that should be explored further.

4. Experimental

All reactions were carried out using standard Schlenk techniques or in a Vacuum Atmosphere glovebox, under an atmosphere of argon. Solvents used in reactions were of AR grade, and were dried, distilled and kept under argon in flasks fitted with Teflon valves prior to use. The products were generally separated by column chromatography on silica gel. NMR spectra were acquired on a Bruker ACF 300 MHz; ^1H chemical shifts reported were referenced to residual protons of the solvent, and $^{31}P\{^1H\}$ chemical shifts with respect to 85% aq. H_3PO_4. Electrospray mass spectra were carried out on a Finnigan MAT LCQ spectrometer with MeOH as solvent, while FAB-MS were carried out on a Finnigan MAT95XL-T mass spectrometer with a 3-nitrobenzyl alcohol matrix. Microanalyses were carried out by the microanalytical laboratory at the National University of Singapore. The salt $NaRe(CO)_5$ (**2**) was prepared according to the literature method [6], from $Re_2(CO)_{10}$ (**1**) which was from commercial sources and used as supplied, as were all other reagents.

4.1. Reaction of Cp*Ru(dppm)Cl and NaRe(CO)$_5$

A solution of **2** prepared from the reaction of **1** (240 mg, 0.368 mmol) with sodium amalgam, in THF (10 ml) was transferred via cannula onto Cp*Ru(dppm)Cl (**3a**) (241.4 mg, 0.368 mmol) in a Carius tube. The solution turned immediately from an orange red to red. The solution was then heated at 75 °C for 20 h, whereupon a white solid precipitated. The solvent was removed under vacuum and the residue was then purified by column chromatography in a glovebox. Elution with toluene afforded a yellow band of Cp*(CO)Ru(μ-H)[μ-PhP(C_6H_4)CH_2PPh_2]Re(CO)$_3$ (**5**) (yield = 86 mg, 25%). Further elution (toluene:THF, 9:1, v/v) afforded a red band of Cp*Ru(μ-CO)$_2$(μ-dppm)-Re(CO)$_3$ (**4a**) (yield = 206 mg, 59%) followed by unreacted **3a** (yield = 45 mg).

Compound **4a**: IR (KBr): ν_{CO} 2007vs, 1933s, 1914s, 1901s, 1694s. ^{1}H NMR ($CDCl_3$): δ 7.12–7.35 (m, 20H, Ph), 2.35 (t, 2H, CH_2, $^2J_{HP}$ = 10 Hz), 1.53 (s, 15, Cp*). ^{31}P{^{1}H} NMR ($CDCl_3$): δ 51.9 (d, RuP, $^3J_{PP}$ = 235 Hz), −2.6 (d, ReP) ppm. ESI-MS (*m*/*z*): 947.9 (M^+). Calculated for $C_{40}H_{37}O_5P_2ReRu$: C, 50.63; H, 3.93. Found: C, 50.92; H, 3.73%.

Compound **5**: IR (KBr): ν_{CO} 2005vs, 1950vs, 1913s, 1878s cm^{-1}. ^{1}H NMR (C_6D_6): δ 6.7–8.4 (m, 19H, Ph), 3.94 (ddd, 1H, CH_2, $^2J_{HH}$ = 13.3 Hz, $^2J_{HPRe}$ = 11.7 Hz, $^2J_{HPRu}$ = 13.1 Hz), 2.63 (ddd, 1H, CH_2, $^2J_{HPRe}$ = 9.6 Hz, $^2J_{HPRu}$ = 6.9 Hz), 1.32 (s, 15H, Cp*), −17.01 (dd, 1H, $^2J_{HPRe}$ = 9.5, $^2J_{HPRu}$ = 16.5 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ 34.5 (d, RuP, $^3J_{PP}$ = 176 Hz), −3.1 (d, ReP) ppm. ESI-MS (*m*/*z*): 919 (M^+). Calculated for $C_{39}H_{37}O_4P_2ReRu.C_4H_8O$: C, 52.01; H, 4.57. Found: C, 52.36; H, 4.22%.

4.2. Reaction of CpRu(dppm)Cl and NaRe(CO)$_5$

A solution of **2** (0.342 mmol) in THF (8 ml) was transferred onto CpRu(dppm)Cl (**3b**) (200 mg, 0.342 mmol) in a Carius tube and heated at 75 °C for 20 h. The precipitated NaCl was then filtered off via cannula and the solvent removed on the vacuum line. Column chromatographic separation on silica, eluting with a toluene/hexane mixture afforded Cp(CO)Ru(μ-dppm)Re(CO)$_4$ (**4b**) as an orange band (yield = 100 mg, 33.4%). Further elution with THF gave a red band of unreacted **3b** (yield = 113 mg).

Compound **4b**: IR (KBr): ν_{CO} 2036vs, 1954s, 1937s, 1886s. ^{1}H NMR (C_6D_6): δ 6.90–7.44 (m, 20H, Ph), 4.76 (s, 5H, Cp), 3.79 (t, 2H, CH_2, $^2J_{HP}$ = 10 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 60.6 (d, RuP, $^3J_{PP}$ = 204 Hz), −6.5 (d, ReP). ESI-MS (*m*/*z*): 876.8 (M^+). Calculated for $C_{35}H_{27}O_5P_2ReRu$: C, 47.84; H, 3.10. Found: C, 48.16; H, 3.01%.

Table 2
Crystal and structure refinement data for compounds **3b**, **4**, **5a**–**c**

Compound	**3b**	**4a**	**4b**	**4c**	**5**
Empirical formula	$C_{30}H_{27}ClP_2Ru$	$C_{40}H_{37}O_5P_2ReRu \cdot 1.5C_7H_8$	$C_{35}H_{27}O_5P_2ReRu \cdot C_4H_8O \cdot 1/2C_6H_{14}$	$C_{12}H_5O_7ReRu$	$C_{39}H_{37}O_4P_2ReRu \cdot 1/3C_4H_8O$
Formula weight	585.98	1085.11	991.97	548.43	942.93
T (K)	223(2)	223(2)	223(2)	293(2)	223(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Rhombohedral
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$R\bar{3}$
a (Å)	11.2833(5)	11.0725(4)	12.458(2)	6.9480(13)	43.0930(9)
b (Å)	14.1349(6)	19.4030(9)	20.846(4)	9.1523(18)	43.0930(9)
c (Å)	16.2574(7)	21.2766(9)	15.696(3)	12.361(2)	10.5646(4)
α (°)	90	90	90	91.083(4)	90
β (°)	93.8260(10)	99.4500(10)	98.980(4)	104.311(4)	120
γ (°)	90	90	90	111.120(3)	90
V (Å^3)	2587.09(19)	4509.0(3)	4026.4(13)	705.4(2)	16990.1(8)
Z	4	4	4	2	18
D_{calc} (Mg/m^3)	1.504	1.598	1.636	2.582	1.659
Absorption coefficient (mm^{-1})	0.850	3.134	3.503	9.671	3.728
F(000)	1192	2164	1964	504	8376
Crystal size (mm^3)	0.30 × 0.26 × 0.20	0.48 × 0.10 × 0.08	0.24 × 0.20 × 0.16	0.40 × 0.12 × 0.12	0.14 × 0.10 × 0.08
Reflections collected	18247	32058	18292	9208	41079
Independent reflections (R_{int})	5946 (0.0270)	10357 (0.0736)	6786 (0.0352)	3212 (0.0278)	8678 (0.0430)
Maximum and minimum transmission	0.8483 and 0.7845	0.7876 and 0.3146	0.6041 and 0.4869	0.3899 and 0.1129	0.7547 and 0.6234
Data/restraints/parameters	5946/0/307	10357/2/527	6786/14/429	3212/0/190	7717/10/441
Goodness-of-fit on F^2	1.057	1.014	0.846	1.045	1.133
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0304, wR_2 = 0.0736	R_1 = 0.0545, wR_2 = 0.0991	R_1 = 0.0325, wR_2 = 0.0620	R_1 = 0.0182, wR_2 = 0.0422	R_1 = 0.0455, wR_2 = 0.1029
R indices (all data)	R_1 = 0.0368, wR_2 = 0.0763	R_1 = 0.0851, wR_2 = 0.1089	R_1 = 0.0462, wR_2 = 0.0637	R_1 = 0.0190, wR_2 = 0.0426	R_1 = 0.0526, wR_2 = 0.1060
Largest difference in peak and hole (e Å^{-3})	0.655 and −0.263	1.588 and −0.726	1.058 and −0.469	0.728 and −0.772	1.830 and −1.508

4.3. Reaction of $CpRu(CO)_2Cl$ and $NaRe(CO)_5$

A solution of **2** (0.39 mmol) in THF (5 ml) was transferred onto $CpRu(CO)_2Cl$ (**3c**) (100 mg, 0.39 mmol). The mixture was stirred at room temperature with the exclusion of light in a Carius tube for 40 h. The precipitated NaCl was then filtered off via cannula and the solvent removed on the vacuum line. Column chromatographic separation on silica, eluting with toluene/hexane (1:1, v/v) afforded a yellow band of $Cp(CO)_2RuRe(CO)_5$ (**4c**) (yield = 120 mg, 56.4%). Further elution with a toluene/THF mixture afforded brown-red $[CpRu(CO)_2]_2$ (**6**) (yield = 31.6 mg).

Compound **4c**: IR (KBr): ν_{CO} 2103m, 2071w, 1997vs, 1977w, 1963w, 1931w. ^1H NMR (C_6D_6): δ 4.44 (s, 5H, Cp). FAB-MS (*m/z*): 549.8 (M^+). Calculated for $C_{12}H_5O_7ReRu$: C, 26.19; H, 0.92. Found: C, 25.93; H, 1.06%.

4.4. Procedure for the catalytic runs

In a typical run, acetic acid (68 μl, 1.0 mmol), phenylacetylene (0.11 ml, 1.0 mmol) and the catalyst (0.01 mmol) in toluene (1.0 ml) were stirred at 110 °C for 24 h. After cooling, the solution was concentrated by rotary evaporation and then separated by column chromatography on silica gel (eluant: hexane–diethyl ether, 10:1, v/v) to afford a mixture of the *Z*- and *E*-enol esters (0.14 g, colourless oil), followed by the Markovnikov adduct. The ratios of the products obtained were determined by integration of the ^1H NMR spectrum after solvent removal but before chromatographic separation.

4.5. X-ray crystal structure determinations

Diffraction quality crystals were grown by slow diffusion of hexane or toluene onto THF solutions. Crystals were mounted on quartz fibres. X-ray data were collected on a Bruker AXS APEX system, using Mo Kα radiation, at 223 K with the SMART suite of programs [13]. Data were processed and corrected for Lorentz and polarisation effects with SAINT [14], and for absorption effects with SADABS [15]. Structural solution and refinement were carried out with the SHELXTL suite of programs [16]. Crystal and refinement data are summarised in Table 2.

The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. The hydride in **4** was located in a low angle difference map, and refined with a fixed isotropic thermal parameter. All non-hydrogen atoms were generally given anisotropic displacement parameters in the final model. Organic hydrogen atoms were placed in calculated positions and refined with a riding model. Solvent molecules were found in **4a**, **4b** and **5**, and the THF molecule in **5** was disordered; appropriate restraints were placed on the bond parameters of the disordered solvent molecule.

Acknowledgements

This work was supported by an A*STAR grant (Research Grant No. 012 101 0035).

Appendix A. Supplementary material

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 286282–286286. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033 or e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2005.11.061.

References

[1] (a) P. Braunstein, J. Rose, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Elsevier, Oxford, 1995, p. 351;
(b) R.D. Adams, F.A. Cotton (Eds.), Catalysis by Di and Polynuclear Metal Cluster Complexes, Wiley–VCH, New York, 1998;
(c) P. Braunstein, J. Rose, in: I. Bernal (Ed.), Chemical Bonds: Better Ways to Make Them and Break Them, Elsevier, Amsterdam, 1989, p. 89;
(d) G. Süss-Fink, G. Meister, Adv. Organomet. Chem. 35 (1993) 41.
[2] (a) D.W. Stephan, Coord. Chem. Rev. 95 (1989) 41;
(b) N. Wheatley, P. Kalck, Chem. Rev. 99 (1999) 3379;
(c) R.D. Adams, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Elsevier, Oxford, 1995, p. 1;
(d) M.J. Chetcuti, in: E.W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry II, vol. 10, Elsevier, Oxford, 1995, p. 24.
[3] (a) C.D. Nunes, M. Pillinger, A. Hazell, J. Jepsen, T.M. Santos, J. Madureira, A.D. Lopes, I.S. Goncalves, Polyhedron 22 (2003) 2799;
(b) F. Fagalde, M.G. Mellace, d.K. Lis, D. Noemi, N.E. Katz, J. Coord. Chem. 57 (2004) 635.
[4] (a) A. Vogler, J. Kisslinger, Inorg. Chim. Acta 115 (1986) 193;
(b) S. Van Wallendael, D.P. Rillema, J. Chem. Soc., Chem. Commun. (1990) 1081;
(c) S. Van Wallendael, D.P. Rillema, Coord. Chem. Rev. 111 (1991) 297;
(d) M. Furue, M. Naiki, Y. Kanematsu, T. Kushida, M. Kamachi, Coord. Chem. Rev. 111 (1991) 221;
(e) D.W. Thompson, J.R. Schoonover, T.J. Meyer, R. Argazzi, C.A. Bignozzi, J. Chem. Soc., Dalton Trans. (1999) 3729;
(f) G. Albertin, S. Antoniutti, A. Bacchi, G.B. Ballico, E. Bordignon, G. Pelizzi, M. Ranieri, P. Ugo, Inorg. Chem. 39 (2000) 3265;
(g) S. Encinas, F. Barigelletti, A.M. Barthram, M.D. Ward, S. Campagna, J. Chem. Soc., Chem. Commun. (2001) 277;
(h) F. Fagalde, N.E. Katz, J. Coord. Chem. 54 (2001) 367;
(i) J.-L. Zuo, E. Herdtweck, F.E. Kuehn, J. Chem. Soc., Dalton Trans. (2002) 1244;
(j) M.G. Mellace, F. Fagalde, N.E. Katz, Polyhedron 22 (2003) 369.
[5] (a) M. Cazanoue, Z. He, D. Neibecker, R. Mathieu, J. Chem. Soc., Chem. Commun. (1991) 307;
(b) Z. He, D. Neibecker, N. Lugan, R. Mathieu, Organometallics 11 (1992) 817;
(c) Z. He, S. Nefedov, N. Lugan, D. Neibecker, R. Mathieu, Organometallics 12 (1993) 3837.

[6] J.-A.M. Andersent, J.R. Moss, Polyhedron 14 (1995) 1881.
[7] (a) L. Weber, D. Bungardt, J. Organomet. Chem. 311 (1986) 269;
(b) R.D. Fischer, A. Vogler, K. Noack, J. Organomet. Chem. 7 (1967) 135.
[8] For a discussion on the use of the sum of M–C and C–O bond lengths in place of either bond length alone, see: W.K. Leong, F.W.B. Einstein, R.K. Pomeroy, J. Cluster Sci. 7 (1996) 121.
[9] (a) T. Mitsudo, Y. Hori, Y. Watanabe, J. Org. Chem. 50 (1985) 1566;
(b) T. Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, Tetrahedron Lett. 27 (1986) 2125;
(c) C. Ruppin, P.H. Dixneuf, Tetrahedron Lett. 27 (1986) 6323;
(d) Y. Hori, T. Mitsudo, Y. Watanabe, J. Organomet. Chem. 321 (1987) 397;
(e) M. Rotem, Y. Shvo, J. Organomet. Chem. 448 (1993) 189;
(f) H. Doucet, B. Martin-Vaca, C. Bruneau, P.H. Dixneuf, J. Org. Chem. 60 (1995) 7247;
(g) C. Bruneau, P.H. Dixneuf, Chem. Commun. (1997) 507;
(h) H. Kawano, Y. Masaki, T. Matsunaga, K. Hiraki, M. Onishi, T. Tsubomura, J. Organomet. Chem. 601 (2000) 69;
(i) K. Melis, T. Opstal, F. Verpoort, Eur. J. Org. Chem. 22 (2002) 3779;
(j) K. Melis, P. Samulkiewicz, J. Rynkowski, F. Verpoort, Tetrahedron Lett. 43 (2002) 2713;
(k) K. Melis, F. Verpoort, J. Mol. Catal. A 194 (2003) 39;
(l) L. Goossen, J. Paetzold, D. Koley, Chem. Commun. (2003) 706;
(m) K. Melis, D. Vos, P. Jacobs, F. Verpoort, J. Organomet. Chem. 671 (2003) 131.
[10] R. Hua, X. Tian, J. Org. Chem. 69 (2004) 5782.
[11] S. Doherty, J.G. Knight, R.K. Rath, W. Clegg, R.W. Harrington, C.R. Newman, R. Campbell, H. Amin, Organometallics 24 (2005) 2633.
[12] S. Ye, W.K. Leong (submitted).
[13] SMART version 5.628, Bruker AXS Inc., Madison, WI, USA, 2001.
[14] SAINT+ version 6.22a, Bruker AXS Inc., Madison, WI, USA, 2001.
[15] G.M. Sheldrick, SADABS, 1996.
[16] SHELXTL version 5.1, Bruker AXS Inc., Madison, WI, USA, 1997.