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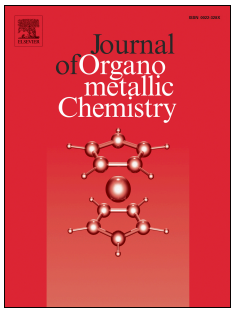

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Synthesis of the cyclopentadienone rhodium complexes and investigation of their catalytic activity in the reductive amination of aldehydes in the presence of carbon monoxide

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Abstract

Reaction of bis(*p*-tolyl-propargyl)-tosylamide with $[(cod)RhCl]_2$ in the presence of CO gives the cyclopentadienone complex $[(Cpd')Rh(CO)Cl]_n$ (Cpd' = $TsN(CH_2)_2C_4(Tol)_2CO$). Its dissolution in DMSO or pyridine leads to decarbonylation and formation of the adducts $(Cpd')Rh(DMSO)_2Cl$ and $(Cpd')Rh(Py)_2Cl$. The reaction of $[(Cpd')Rh(CO)Cl]_n$ with $AgPF_6$ and *p*-xylene produces the sandwich arene complex $[(Cpd')Rh(p\text{-xylene})]PF_6$, in which the arene can be substituted by ^{t}BuNC ligand to give $[(Cpd')Rh(^t BuNC)_3]PF_6$. The arene complex acts as an efficient catalyst for the reductive amination of carbonyl compounds in the presence of CO as deoxygenation agent, producing various amines in 75-85% yields.

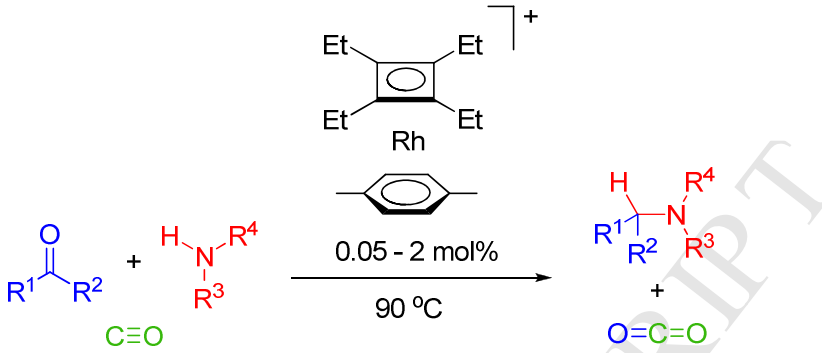
Keywords: Carbon monoxide / Cyclopentadienone / Diyne / Rhodium / Reductive amination

1. Introduction

Diene rhodium complexes, such as $[(cod)RhCl]_2$, are widely used in organometallic synthesis and catalysis [1,2]. On the other hand, the related cyclopentadienone rhodium complexes, such as $[(C_4Ph_4CO)RhCl]_2$, have been much less studied [3,4]. This is, partly, because such compounds are usually prepared from $[(C_2H_4)_2RhCl]_2$ and free cyclopentadienones, which are readily available only with bulky aryl substituents. However, recently Chatani et al. have reported an example of alternative approach, namely the high-yield synthesis of the cyclopentadienone rhodium complex $[\{(CH_2)_3C_4Ph_2CO\}Rh(CO)Cl]_2$ from 1,7-diphenyl-1,6-heptadiyne, $[(cod)RhCl]_2$ and CO [5,6]. This route potentially allows one to prepare a number of cyclopentadienone complexes with various substituents.

Recently, we have developed a novel approach for the reductive amination of aldehydes and ketones, which employs carbon monoxide as the only reducing agent [7,8,9] (Scheme 1). The most active catalysts for this reaction discovered so far are the diene and cyclobutadiene rhodium complexes [10]. On the other hand the classical reductive amination is known to

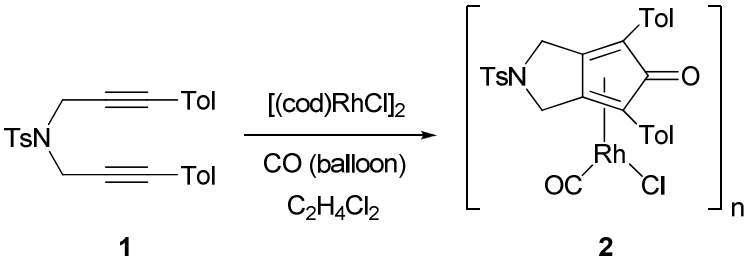
proceed in the presence of ruthenium cyclopentadienone complexes (e.g. Shvo catalyst $[(C_4Ph_4CO)Rh(CO)_2]_2H_2$) [11]. Therefore we have become interested in the synthesis of the cyclopentadienone rhodium complexes and their application in reductive amination. Herein we report the results of this investigation.



Scheme 1. Previously reported reductive amination in the presence of CO.

2. Results and Discussion

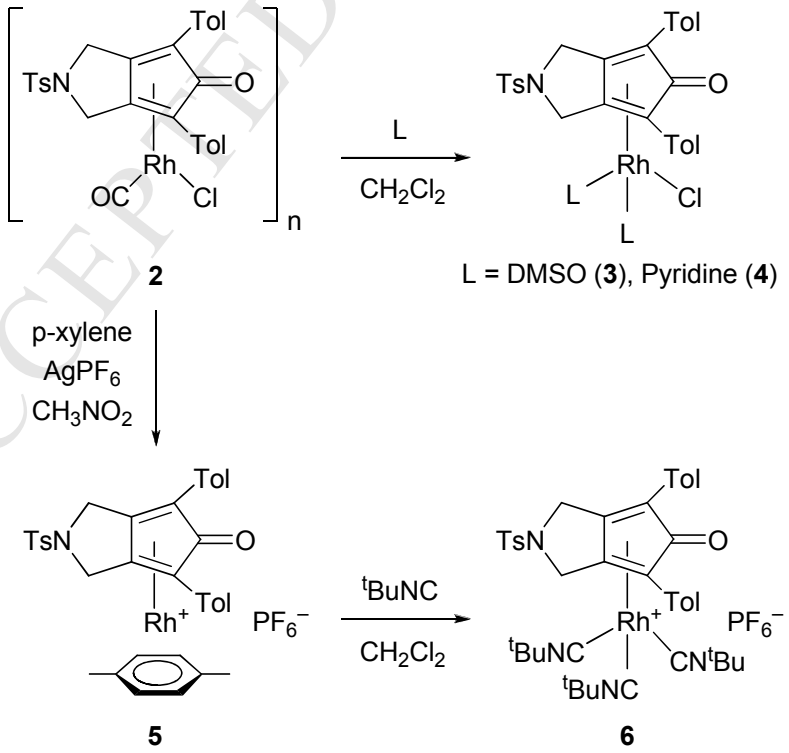
As a ligand source we chose N,N-bis(*p*-tolyl-propargyl)-tosylamide (**1**), which was synthesized following the published procedure in two steps from tosylamide, propargyl bromide and *p*-iodotoluene [12]. Tolyl substituents (designated as Tol) were purposely used instead of more common phenyl groups in order to obtain more informative ^{1}H NMR spectra of the compounds. Following the approach of Chatani et al. [5], we reacted the diyne **1** with $[(cod)RhCl]_2$ under CO atmosphere (1 bar from balloon) to obtain the cyclopentadienone complex $[(Cpd')Rh(CO)Cl]_n$ (**2**) in 70−80% yield (Cpd' = substituted cyclopentadienone = $TsN(CH_2)_2C_4(Tol)_2CO$, see Scheme 2). It is interesting to note, that analogous reactions with the terminal diyne N,N-bis(propargyl)tosylamide or with the internal mono-alkyne 3-hexyne did not give cyclopentadienone complexes. The product **2** precipitated from the reaction mixture capturing some amount of the starting diyne **1**, which decreased the yield of **2**. Compound **2** was insoluble in common organic solvents so the admixture of **1** was removed simply by washing the product with hot nitromethane. Low solubility of **2** apparently is caused by the formation of oligomers with Rh−Cl and Rh−OC bridges [3a]. The degree of oligomerization of **2** remains unknown and, in fact, may be variable.



Scheme 2. Synthesis of the cyclopentadienone rhodium complex.

Dissolution of complex **2** in dimethyl sulfoxide or pyridine led to decarbonylation (clearly visible in IR spectra) and formation of bis-adducts (Cpd')Rh(DMSO)$_2$Cl (**3**) and (Cpd')Rh(Py)$_2$Cl (**4**) in ca. 90% yield (Scheme 3). These compounds were much more soluble than **2** and therefore were expected to have more reproducible catalytic behavior. Noteworthy, the cyclopentadienone rhodium chloride **2** readily forms the 18 valence-electron bis-ligand adducts **3** and **4**, while the related diene complex [(cod)RhCl]$_2$ produces only the 16 valence-electron mono-adduct (cod)Rh(py)Cl with pyridine [13] (the reaction of [(cod)RhCl]$_2$ with DMSO does not give a stable adduct even with one DMSO molecule [14]). This tendency was noted previously for [(C$_4$Ph$_4$CO)RhCl]$_n$ complexes [3a]. The reluctance of cyclopentadienone rhodium complexes to form 16 valence-electron species may affect their catalytic activity.

Reaction of the chloride complex **2** with AgPF$_6$ and *p*-xylene gave the arene complex [(Cpd')Rh(*p*-xylene)]PF$_6$ (**5**) in 60% yield. As a close analogue of the cyclobutadiene complex [(C$_4$Et$_4$)Rh(*p*-xylene)]PF$_6$ this compound was expected to undergo facile replacement of *p*-xylene to give the catalytically active half-sandwich complexes [15]. Indeed, addition of *p*-anisidine to the solution of **5** in acetone-d$_6$ led to displacement of *p*-xylene and formation of the tentative solvate species [(Cpd')Rh(NH$_2$C$_6$H$_4$OMe)$_x$]PF$_6$ (according to ^{1}H NMR), which, however, could not be isolated. On the other hand, the reaction of **5** with a stronger ligand ^{t}BuNC gave the stable half-sandwich complex [(Cpd')Rh(^{t}BuNC)$_3$]PF$_6$ (**6**), which was isolated in 72% yield.



Scheme 3. Ligand substitution in the cyclopentadienone rhodium complexes.

All the compounds obtained were stable in air, both in solution and the solid state. They were characterized by IR spectra, ^{1}H and ^{13}C NMR spectra (except the insoluble **2**), as well as elemental analysis. The structures of **3**, **4** and **5** were established by X-ray diffraction (Figures 1, 2 and 3). The geometry of Cpd' ligand is similar for the complexes **3**−**5** and is notably different from the free cyclopentadienone C_4Ph_4CO [16]. In particular, C=C double bonds are elongated upon coordination with rhodium (average length 1.431 Å in **3**−**5** vs. 1.348 Å in C_4Ph_4CO). At the same time C=O bond length in **3**−**5** (average 1.225 Å) is similar to that in C_4Ph_4CO (1.211 Å) suggesting only minor participation of the ketone group of Cpd' in bonding with metal [17]. It may be also noted, that DMSO ligand in the complex **3** shows strong trans-influence, which leads to elongation of Rh1−C7 bond (2.224(5) Å) compared to the formally equivalent Rh−C2 bond (2.181(4) Å).

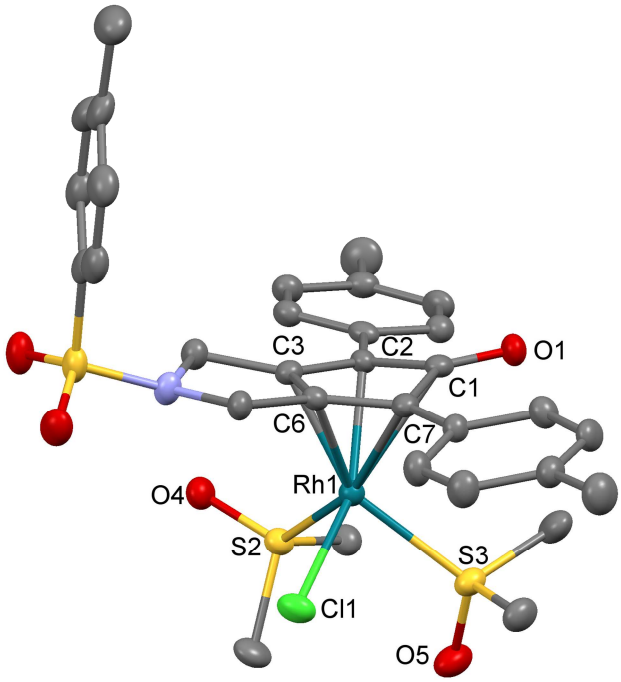


Fig. 1. The structure of complex **3** in 50% thermal ellipsoids. Only one of two independent molecules is shown. The solvate molecules and the hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1−C1 2.436(4), Rh1−C2 2.181(4), Rh1−C3 2.145(4), Rh1−C6 2.173(4), Rh1−C7 2.224(5), Rh1−S2 2.3200(12), Rh1−S3 2.3613(12), Rh1−Cl1 2.4222(12).

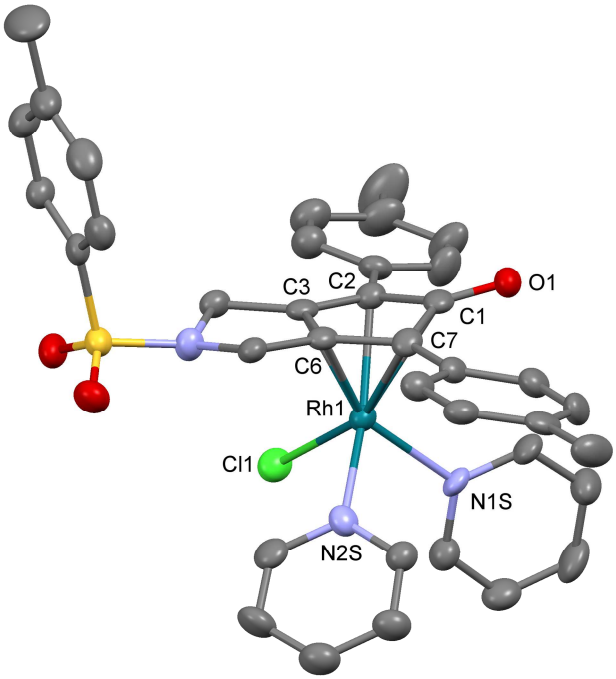


Fig. 2. The structure of complex **4** in 50% thermal ellipsoids. The solvate molecules and the hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1−C1 2.382(7), Rh1−C2 2.150(7), Rh1−C3 2.106(7), Rh1−C6 2.090(7), Rh1−C7 2.140(7), Rh1−N1S 2.144(5), Rh1−N2S 2.112(6), Rh1−Cl1 2.3981(19).

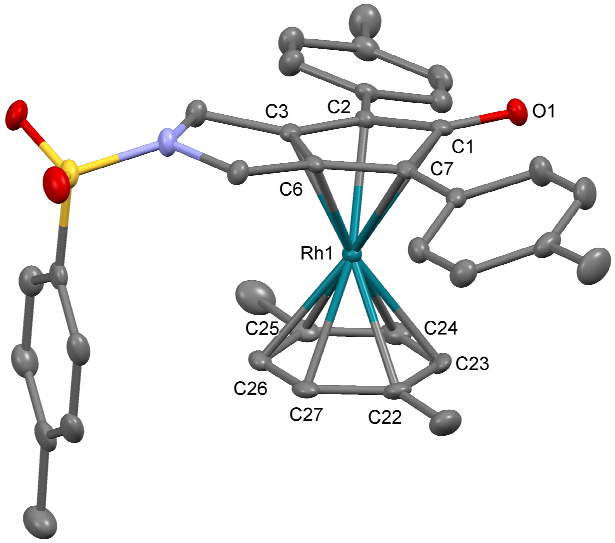
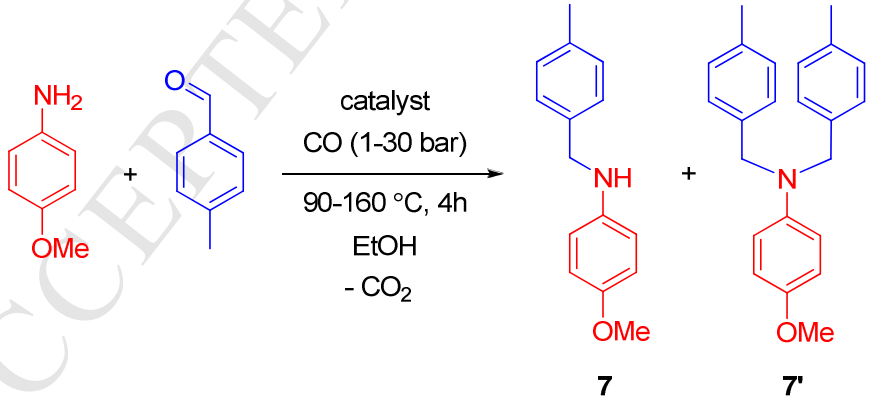


Fig. 3. The structure of complex **5** in 50% thermal ellipsoids. The counter-ion and the hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Rh1−C1 2.433(3), Rh1−C2 2.188(3), Rh1−C3 2.131(3), Rh1−C6 2.127(3), Rh1−C7 2.209(3), Rh1−C22 2.290(3), Rh1−C23 2.288(3), Rh1−C24 2.276(3), Rh1−C25 2.279(3), Rh1−C26 2.282(3), Rh1−C27 2.274(3), Rh···C_6(plane) 1.793.

We investigated the catalytic activity of the complexes **2**−**6** for the model reaction of *p*-tolylaldehyde with *p*-anisidine in the presence of carbon monoxide as a reducing agent (Scheme 4; Table 1). At 90 °C and 30 bar pressure of CO the *p*-xylene complex **5** (1 mol% loading) produced the target amine **7** in only 32% yield. However, at 120 °C the yield reached reasonable 80%. Further increase of the temperature did not increase the yield of the product **7** but resulted in additional formation of the double alkylated amine **7'** (entries 3−4). The amount of **7'** can be reduced by using the excess of *p*-anisidine; however, we preferred to run the process with a near stoichiometric ratio of the reactants and therefore fixed the temperature at 120 °C. Additional tests shown that CO pressure can be decreased from 30 bar to 5 bar without compromising the yield, while further decrease to 3 and 1 bar significantly slowed down the reaction (entries 5−7). The catalyst loading can be decreased to 0.5 mol% but not to 0.1 mol% (entries 8−9). In overall, the catalytic activity of the complex **5** was close to that of the state-of-the-art catalyst $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$ (entries 8 vs. 10), although the latter can operate at more mild conditions (3 bar of CO, 90 °C) [10a]. Other cyclopentadienone rhodium complexes **2**−**4** and **6** shown very low activity (entries 11-14) presumably because CO was not able to displace the strong ligands like Cl or ^{t}BuCN. This correlates with the previously observed low catalytic activity of some other chloride complexes, such as $[(cod)RhCl]_2$ and $[Cp^*RhCl_2]_2$ [10a].

The detailed mechanism of the reductive amination is so far unclear. However, we found that the reaction proceeds in ^{t}BuOH solution, which ruled out the transfer hydrogenation mechanism involving oxidation of an alcohol solvent to an aldehyde.



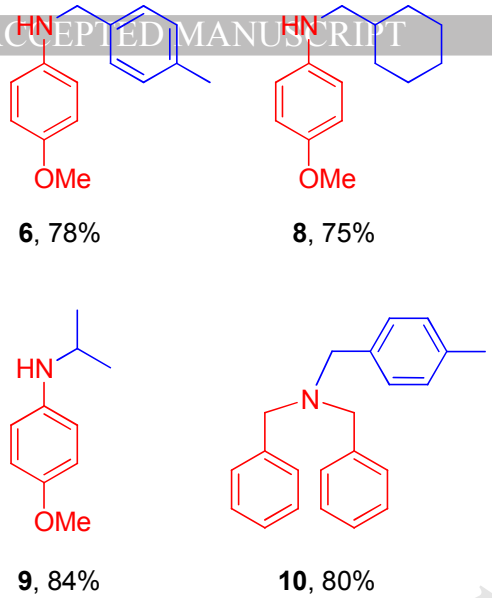
Scheme 4. Catalytic reductive amination.

Table 1. Optimization of reaction conditions for the reductive amination of *p*-tolualdehyde with *p*-anisidine in the presence of carbon monoxide as the reducing agent.[a]

Entry	Catalyst (loading)	CO pressure, bar	Temperature, °C	Yield of the product **7**
1	**5** (1 mol%)	30	90	32%
2	**5** (1 mol%)	30	120	80%
3	**5** (1 mol%)	30	140	75% (**7'**, 12%)
4	**5** (1 mol%)	30	160	66% (**7'**, 18%)
5	**5** (1 mol%)	5	120	81%
6	**5** (1 mol%)	3	120	44%
7	**5** (1 mol%)	1	120	9%
8	**5** (0.5 mol%)	30	120	83%
9[b]	**5** (0.1 mol%)	30	120	51%
10	$[(C_4Et_4)Rh(p\text{-xylene})]PF_6$ (0.5 mol%)	30	120	85%
11	**2** (1 mol%)	5	120	4%
12	**3** (1 mol%)	5	120	3%
13	**4** (1 mol%)	5	120	2%
14	**6** (1 mol%)	5	120	2%

[a] Reaction conditions: *p*-anisidine (15 mg, 0.12 mmol), *p*-tolylaldehyde (14 µL, 0.12 mmol), 100 µL of ethanol, 4 hours. Yields were determined by gas chromatography. [b] in 24 hours.

We briefly investigated the reaction scope using several challenging substrates and 1 mol% loading of the catalyst **5**. It was found that the reductive amination of cyclohexanecarboxaldehyde, which is prone to aldol condensation, smoothly gives the amine **8** in 75% isolated yield (Scheme 4). Acetone, which is much less reactive than aldehydes, also produced the amine **9** in a good yield 84%. Finally, the reaction of tolylaldehyde with a secondary aliphatic dibenzylamine gave the target product **10** in 80% yield.



6, 78% **8**, 75%

9, 84% **10**, 80%

Scheme 4. Various amines synthesized by the catalytic reductive amination (isolated yields are given).

3. Conclusion

In overall, it can be concluded that the cyclopentadienone rhodium complexes can be conveniently synthesized from $[(cod)RhCl]_2$, CO and the readily available 1,6-diynes. Unlike the diene congeners, these cyclopentadienone complexes prefer 18 valence-electron configuration instead of 16 valence-electron. Nevertheless, such complexes can be active and thermally stable catalysts for the reductive amination of aldehydes in the presence of CO.

4. Experimental section

4.1. General

Unless otherwise noted all reactions were carried out under ambient atmosphere in anhydrous solvents, which were purified and dried using standard procedures. ^{1}H and ^{13}C NMR spectra were measured with a Bruker Avance 400 spectrometer at 20°C. The chemical shifts are reported relative to redisual signals of the solvent (for $CHCl_3$: 7.26 ^{1}H, 77.16 ^{13}C; for CHD_2NO_2: 4.33 ^{1}H, 62.80 ^{13}C) Infrared spectra (IR) were measured with Shimadzu IRPrestige-21 spectrometer. Gas chromatography analysis was carried out using Chromatec Crystal 5000.2 apparatus (helium as career gas, flow rate 1.6 ml/min; yields were calculated using calibration curve). Complex $[(cod)RhCl]_2$ [18] and diyne **1** [12] were synthesized according to the published procedure. NMR spectra of the compounds are given in the supplementary data.

*4.2. Synthesis of [(Cpd')Rh(CO)Cl]$_n$ (**2**)*

CO was bubbled through a stirred solution of [(cod)RhCl]$_2$ (50 mg, 0.1 mmol) and diyne **1** (86 mg, 0.2 mmol) in 1,2-dichloroethane (4 ml) for 1 hour at 50 °C (the reaction at room temperature gave lower yield 68%). Then the flow of CO was stopped and the dark red mixture was stirred for additional 3 days at room temperature under CO atmosphere (balloon attached) to ensure complete precipitation of the product. The orange precipitate of **2** was collected by centrifugation and washed with CH_2Cl_2 (3×5 ml). The solid was heated in nitromethane (15 ml) for 30 minutes to dissolve admixture of **1**, then nitromethane was decanted, the residue was washed again with CH_2Cl_2 (3×5 ml) and dried in vacuum to give complex **2** as orange solid (103 mg, 83% yield).

Due to extremely low solubility of **2** the NMR spectra were measured in DMSO-d_6 solution, which led to formation of complex **3** (vide infra). FT-IR (vaseline oil, cm^{-1}): 2059 (metal bonded CO), 1666 cm^{-1} (carbonyl group of Cpd' ligand). Anal. Calc. for $C_{29}H_{25}O_4SNRhCl$: C 56.00, H 4.05, N 2.25; found: C 55.94, H 3.91, N 2.29. Does not melt or decompose up to 230 °C.

*4.3. Synthesis of (Cpd')Rh(DMSO)$_2$Cl (**3**)*

DMSO (100 µl, excess) was added to a suspension of complex **2** (31 mg, 0.05 mmol) in CH_2Cl_2 (2 ml) and the mixture was stirred for 2 hours at 30 °C in order to dissolve all the precipitate. The resulting solution was evaporated to dryness in vacuum, the residue was washed with Et_2O (2×3 ml), dissolved in chloroform (2 ml) and precipitated by a mixture of Et_2O/petroleum ether (1:1, 10 ml) to give **3** as red powder, which was dried in vacuum (35 mg, 93% yield). Crystals for X-ray diffraction analysis were grown by slow diffusion of Et_2O vapors into solution of **3** in $CHCl_3$. ^{1}H NMR (400 MHz, $CDCl_3$ + 5% DMSO-d_6): δ = 7.88 (d, J = 8.2 Hz, 4H, Tol), 7.83 (d, J = 8.3 Hz, 2H, Ts), 7.25 (d, J = 8.3 Hz, 2H, Ts), 7.08 (d, J = 8.2 Hz, 4H, Tol), 4.96 (d, J = 13.4 Hz, 2H, CH_2), 4.13 (d, J = 13.4 Hz, 2H, CH_2), 2.53 (s, 12H, DMSO), 2.31 (s, 3H, Ts), 2.18 (s, 6H, Tol). The spectra in $CDCl_3$ without DMSO-d_6 additive shown a second set of signals, presumably, due to partial dissociation of DMSO ligands. This second set disappeared upon addition of DMSO-d_6. ^{13}C NMR (101 MHz, $CDCl_3$ + 5% DMSO-d_6): δ = 166.7 (CO of Cpd'), 143.1, 138.2, 133.5, 129.4, 129.2, 127.5, 127.2, 127.0, 47.0 (CH_2), 21.0 (Tol), 20.9 (Ts). The signals of the coordinated carbon atoms were not observed. FT-IR (vaseline oil, cm^{-1}): 1626 (carbonyl group of Cpd' ligand). Anal. Calc. for $C_{32}H_{37}ClNO_5S_3Rh$: C 51.23, H 4.97, N 1.87; found: C 50.60, H 4.84, N 1.67. Decomposes without melting at about 200 °C.

*4.4. Synthesis of (Cpd')Rh(Py)$_2$Cl (**4**)*

Pyridine (1 ml) was added to a suspension of complex **2** (62 mg, 0.1 mmol) in CH_2Cl_2 (2 ml) and the mixture was stirred for 2 hours at 30 °C in order to dissolve all the precipitate. The solution was then placed into 10 ml vial and the product was crystallized by diffusion of Et_2O vapors into

solution. The red rhombic crystals were collected, washed with petroleum ether (3×5 ml) and dried to give **4** (69 mg, 92% yield). Crystals for X-ray diffraction analysis were grown by slow diffusion of Et_2O vapors into solution of **4** in CH_2Cl_2 with a small additive of pyridine (to prevent possible dissociation).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (br.s, 4H, Py), 7.92 (d, J = 7.9 Hz, 2H, Ts), 7.71 (d, J = 7.8 Hz, 4H, Tol), 7.63 (br.s, 2H, Py), 7.41 (d, J = 7.9 Hz, 2H, Ts), 7.09 (br.s, 4H, Py), 6.99 (d, J = 7.8 Hz, 4H, Tol), 4.53 (d, J = 12.5 Hz, 2H, CH_2), 3.95 (d, J = 12.5 Hz, 2H, CH_2), 2.47 (s, 3H, Ts), 2.18 (s, 6H, Tol). The signals of pyridine ligands are broad, which may indicate their hindered rotation or partial dissociation. ^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.3 (CO of Cpd'), 151.7 (Py), 144.0, 137.5 (Py), 137.0, 134.4, 130.1, 129.7, 129.6, 127.9, 127.1, 125.1 (Py), 94.0 (coordinated C), 63.5 (coordinated C), 48.2 (CH_2), 21.7 (Ts), 21.5 (Tol). FT-IR (vaseline oil, cm^{-1}): 1602 (carbonyl group of Cpd' ligand), 1570, 1520. Anal. Calc. for $C_{38}H_{35}ClN_3O_3SRh\times CH_2Cl_2$: C 55.96, H 4.46, N 5.02; found: C 55.43, H 4.82, N 4.30. Decomposes without melting at about 180 °C.

*4.5. Synthesis of [(Cpd')Rh(p-xylene)]PF_6 (**5**)*

Under argon atmosphere a mixture of complex **2** (100 mg, 0.16 mmol), $AgPF_6$ (41 mg, 0.16 mmol), *p*-xylene (400 μl, 3.2 mmol) and nitromethane (1 ml) was vigorously stirred for 12 hours at 50 °C. The mixture was then opened to air, the precipitate was removed by centrifugation and the red solution was evaporated. The residue was dissolved in CH_2Cl_2 (2 ml) and yellow product was precipitated by Et_2O (15 ml). The precipitate was washed Et_2O (2×5 ml), dissolved again in CH_2Cl_2 (2 ml) and crystallized by diffusion of Et_2O vapor to give **5** as orange crystals, which were dried in vacuum (78 mg, 60% yield). Crystals for X-ray diffraction analysis were grown by slow diffusion of Et_2O vapors into solution of **5** in acetone with a small additive of *p*-xylene (to prevent possible dissociation).

^{1}H NMR (400 MHz, CD_3NO_2): δ = 7.94 (d, J = 8.1 Hz, 4H, Tol), 7.88 (d, J = 8.0 Hz, 2H, Ts), 7.56 (d, J = 8.0 Hz, 2H, Ts), 7.36 (d, J = 8.1 Hz, 4H, Tol), 6.49 (s, 4H, *p*-xylene), 4.89 (d, J = 14.2 Hz, 2H, CH_2), 4.47 (d, J = 14.2 Hz, 2H, CH_2), 2.48 (s, 3H, Ts), 2.39 (s, 6H, Tol), 1.80 (s, 6H, *p*-xylene). ^{13}C NMR (101 MHz, CD_3NO_2): δ = 166.0 (CO of Cpd'), 147.0, 143.6, 134.0, 131.7, 131.5, 130.3, 129.3, 126.0, 117.8, 107.5 (coordinated C of *p*-xylene), 103.3 (coordinated C of Cpd'), 85.2 (coordinated C of Cpd'), 55.3, 50.0, 21.8, 21.7, 17.50. The coordinated substituted carbon atom of *p*-xylene was not observed. FT-IR (vaseline oil, cm^{-1}): 1648 (carbonyl group of Cpd' ligand). Anal. Calc. for $C_{36}H_{35}F_6NO_3PSRh$: C 53.41, H 4.36, N 1.73; found: C 53.48; H 4.74; N 1.67. Decomposes without melting at about 200 °C.

*4.6. Synthesis of [(Cpd')Rh(^{t}BuNC)$_3$]PF$_6$ (**6**)*

Under argon atmosphere a solution of complex **5** (24 mg, 0.03 mmol) and ^{t}BuNC (12 µL, 0.1 mmol) in CH_2Cl_2 (1 ml) was for 12 hours. The mixture was then opened to air, and the product was crystallized by diffusion of Et_2O vapor into the solution to give **6** as yellow needle crystals, which were dried in vacuum (22 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.2 Hz, 4H, Tol), 7.63 (d, J = 8.3 Hz, 2H, Ts), 7.44 (d, J = 8.3 Hz, 2H, Ts), 7.18 (d, J = 8.2 Hz, 4H, Tol), 4.77 (d, J = 16.2 Hz, 2H, CH_2), 4.33 (d, J = 16.2 Hz, 2H, CH_2), 2.46 (s, 3H, Ts), 2.33 (s, 6H, Tol), 1.45 (s, 27H, (Me)$_3$C). ^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2 (CO of Cpd'), 146.1, 139.1, 134.1, 130.5, 129.8, 127.7, 127.5, 127.3, 104.6, 59.7, 49.1 (CH_2), 30.0 (t-Bu), 21.7 (Tol), 21.6 (Ts). FT-IR (vaseline oil, cm^{-1}): 1641, 1654 (carbonyl group of Cpd' ligand), 2199, 2221 (isonitrile). Anal. Calc. for $C_{43}H_{52}F_6N_4O_3PRhS$: C 54.20, H 5.50, N 5.88; found: C 53.80, H 5.36, N 5.78.

4.7. General procedure for catalytic experiments

A glass vial in a 10 mL stainless steel autoclave was charged with prescribed amount of the catalyst, the solvent, the amine and the carbonyl compound. The use of a glass vial is crucial: interaction of the catalyst with the metal surface of the autoclave can leads to decreased catalytic activity. The autoclave was sealed, flushed three times with 10 bar of CO, and then charged with the indicated pressure of CO. The reactor was placed into a preheated oil bath. After the indicated time, the reactor was cooled to room temperature and depressurized. The residue was dissolved in dichloromethane, passed through a short layer of silica gel and analyzed by GC and ^{1}H NMR. Further purification was achieved by column chromatography using hexane/ethyl acetate mixtures as eluent. Experimental details for each particular amine are given in the supplementary data.

4.8. X-ray crystallography

Data for single crystals of **3**×4$CHCl_3$ and **5** were collected at 120 K with a Bruker APEX2 diffractometer, while those for **4**×0.5C_5H_5N×0.5CH_2Cl_2 with a Bruker APEX2 DUO diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å, ω-scans). They were integrated with the program SAINT and then scaled, merged and corrected for Lorentz-polarization effects. Note that the best available crystal for **3**×4$CHCl_3$ was twinned, so indexing with the Cell_Now software [19] was needed to describe this twinning as a superposition of two components. The structure of **3**×4$CHCl_3$ structure was then refined using HKLF5 instruction and additional scale factor (BASF instruction). Semi-empirical absorption correction from equivalents was applied using the package SADABS [20] (for **4**×0.5C_5H_5N×0.5CH_2Cl_2 and **5**) or TWINABS [21] (for **3**×4$CHCl_3$). The structures were solved by the direct method and refined by

the full-matrix least-squares against F^2 in anisotropic approximation for non-hydrogen atoms. The positions of hydrogen atoms were calculated, and they were refined in isotropic approximation in riding model. All calculations were performed using the SHELXTL PLUS 5.0 software [22].

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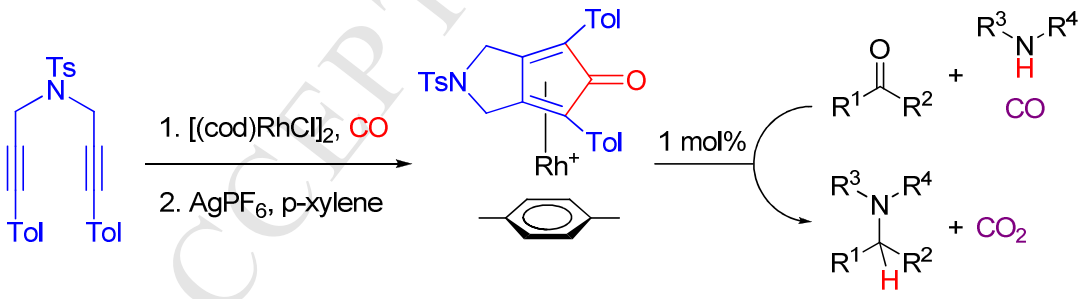
Appendix A. Supplementary data

CCDC 1505673 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data associated with this article can be found online.

Graphical abstract



Graphical abstract synopsis

Cyclopentadienone rhodium complex was prepared from $[(cod)RhCl]_2$, 1,6-diyne and CO. This complex catalyzed the reductive amination of aldehydes in the presence of carbon monoxide, as the only reducing agent.

Highlights

A series of cyclopentadienone rhodium complexes were synthesized from a 1,6-dyine.

Unlike diene congeners, cyclopentadienone complexes prefer 18-VE configuration.

These complexes show good catalytic activity in hydrogen-free reductive amination.

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