

A new class of rhodium complexes containing free donor atoms and their intramolecular substitution reaction

JIANG, Hua^a(蒋华) DIAO, Kai-Sheng^b(刁开盛) PAN, Ping-Lai^a(潘平来)
ZHANG, Shu-Feng^a(张抒峰) YUAN, Guo-Qing^{*.a}(袁国卿)

^a Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

^b Guangxi Institute for Nationalities, Nanning, Guangxi 530006, China

A new class of rhodium complexes with high catalytic activity as well as excellent stability, which was used as catalyst for carbonylation of methanol to acetic acid, is reported. It contains free donor (namely un-coordinated donor) atoms which enable to improve its stability by intramolecular substitution reaction. Its synthesis, characteristic and catalytic reaction were discussed here.

Keywords Rhodium complex, substitution reaction, acetic acid, catalytic stability

Used as catalysts for methanol carbonylation to acetic acid and acetic anhydride in homogeneous phase catalytic reaction,¹ square planar Rh(I) complexes are typical metal complexes due to their high catalytic activity. However, they are usually unstable. They were currently anionic complexes which have high catalytic activity but low stability in catalytic reaction.² A new class of *cis*-dicarbonyl Rh(I) cationic complexes exhibiting special properties is reported here. They not only possess high catalytic activity but also outstanding stability attributed to their special structure.

Experimental

The ligands were prepared according to references.³⁻⁷

Preparation of complex PMRh

A tetrahydrofuran solution of $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ was

added dropwise to a tetrahydrofuran solution containing excessive ligand under stirring to give a mixture solution. The rhodium complex was obtained after dropping a tetrahydrofuran solution of excessive NaBPh₄ in the above mixture solution. The product was filtered off, washed with diethyl ether and dried to constant weight under vacuum at normal atmospheric temperature.

Characteristic of the complexes

The XPS measurement of the complexes (solid sample immediately) was carried out on a Krato ES 300 X-ray photoelectron spectroscopy using Mg $K_{\alpha 1,2}$ X-radiation at 1245 eV with the vacuum of 266.67×10^{-7} Pa. Their IR spectra were recorded on a VR-10 IR spectrophotometer.

Results and discussion

Formation of rhodium complex is shown in Scheme 1. The ligand contains two different donors, N and O, which coordinate with rhodium atom to form two coordinate bonds. The strong N→Rh bond makes the complex stable while the weak O→Rh bond makes it active in catalytic reaction. With the formation of the two coordinate bonds, the electronic charge transference happens. As a result the binding energies of N_{1s}, O_{1s}, and Rh_{3d_{5/2}} change following the charge transference. As is shown in Table 1, The binding energy of N_{1s} increases from 398.3 eV of the ligand to 399.8 eV of the complex, which in-

* Received June 29, 1999; accepted March 27, 2000.

Project (No. 29974035) supported by the National Natural Science Foundation of China.

indicates that the nitrogen donor donates electronic charge to rhodium atom. The binding energy of O_{1s} increases from 532.1 eV of the ligand to 533.0 eV of the complex, which indicates that the oxygen donor donates electronic charge to rhodium. However, the binding energy of $Rh_{3d5/2}$ decreases from 310.0 eV of $[Rh-$

$(CO)_2Cl]_2$ to 308.8 eV of the complex, which indicates that the rhodium atom accepts electronic charge from nitrogen and oxygen atoms. The complex's IR spectrum displaying two equal intensity peaks reflected the characteristic absorption of terminal carbonyl in 1,990 cm^{-1} and 2,070 cm^{-1} .

Scheme 1 Formation of the *cis*-dicarbonyl rhodium complex (for convenience, we omit the BPh_4 in the following figure)

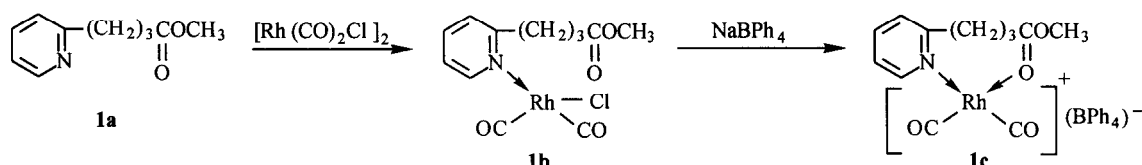


Table 1 Binding energy of samples E_b (eV)

Sample	N_{1s}	O_{1s}	$Rh_{3d5/2}$
1a	398.3	532.1	
1c	399.8	533.0	308.8
$[Rh(CO)_2Cl]_2$			310.0

Compared to the current rhodium complexes reported before,⁸ the above complex has been largely improved on its stability. But it is still easy to decompose at the temperature in reaction condition due to no free donors. On the contrary, the copolymer rhodium complex PVMRh we found has very excellent stability in reaction system while let alone in air.⁹ PVMRh was obtained ac-

cording to above method by using 2-vinyl-pyridine/methyl acrylate copolymer as ligand. After analyzing its structure, it is found that the structure unit of PVMRh is similar to that of common organic rhodium complexes. Both have square planar *cis*-dicarbonyl rhodium structure unit. However, a large amount of free N, O donors in copolymer chain, which are important for the high stability of the complex, differentiate copolymer rhodium complexes from common organic rhodium complexes. In order to study the mechanism of its high stability, we synthesized some small molecular rhodium complexes containing free donors as shown in Scheme 2 and Table 2.⁵⁻⁸

Scheme 2 Formulation of small molecular rhodium complexes containing free donors

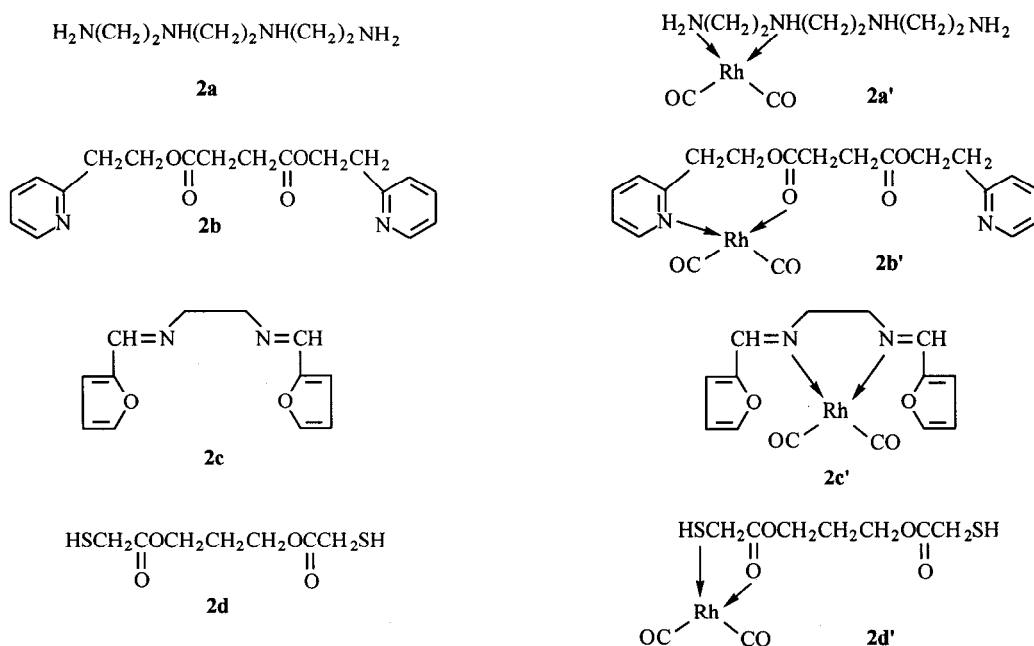


Table 2 Binding energy E_b (eV) and IR bands ν_{CO} (cm^{-1}) of ligands and rhodium complexes

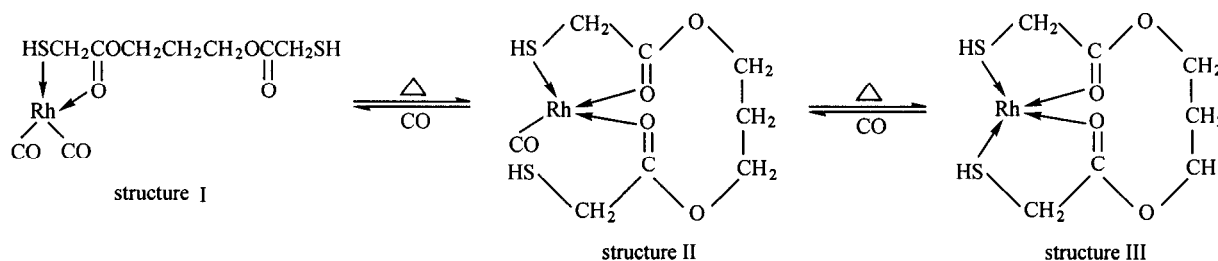
Sample	ν_{CO} (cm^{-1})	Binding energy E_b (eV)			
		N_{1s}	O_{1s}	S_{2p}	$Rh_{3d5/2}$
2a		399.5	532.0 (imp.)		
2a'	2080	400.8 (coord.)	533.8 (coord.)		310.4
	1980	399.5 (free)	532.0 (imp.)		
2b		398.8	532.7		
2b'	2000	399.8 (coord.)	533.4 (coord.)		309.8
	2100	398.8 (free)	532.7		
2c		399.3	532.1		
2c'	2079	399.8 (coord.)	532.1		310.1
	2007				
2d			532.1	162.1	
			534.6 (coord.)	163.3 (coord.)	
2d'			533.0	162.1 (free)	310.1

coord.: coordinated; imp.: impurity.

In rhodium complexes, coordinated donors' binding energy was different from that of free donors. The binding energy of coordinated donor increased because the donor atom transferred electronic charge to rhodium atom, however, the binding energy of free donor was equal to that of ligand. These rhodium complexes are quite stable for possessing special properties. If being placed in air for several days or heated,⁴⁻⁶ their peaks of terminal carbonyl in IR spectrum would gradually change from double peaks to single peak. Furthermore, after being heated at further temperature for a period of time, they lost the single peak remained. Peaks, which reflected the characteristic absorption of terminal carbonyl, were totally lost up to now. However, these complexes do not decompose for the loss of the terminal carbonyl, which is the main reason for the decomposition of the rhodium complexes reported before. Why these complexes were so stable? We consider that it is because of the existing of the free donors. They protect the Rh(I) active unit from decomposing by intramolecular substitution reaction. The substitution process of the coordinated

bond in the square planar metal complex has been studied and confirmed.¹⁰ However, all the intramolecular substitution reactions reported before occurred in solution. Here, we studied the substitution process in solid state.

Here, we take the complex **2d** in Scheme 2, named PMRh, for example. After PMRh being heated in air at 50°C for 30 min, the double peaks reflecting the characteristic absorption of the terminal carbonyl groups changed into single peak, which indicates that one of the two terminal carbonyls had been dropped off.¹¹⁻¹³ As a result the complex changed from structure I to structure II. Even the single peak disappeared when the complex of structure II was heated at 100°C for 1.5 h and structure III was obtained. To our surprise, the double peaks were recovered in its IR spectrum if PMRh with structure III was heated at 100°C for 2 h under an atmosphere of CO. According to the above phenomena, we proposed a reversible intramolecular substitution reaction of such complexes containing two free donor atoms as shown in Scheme 3.

Scheme 3 Intramolecular substitution of complex PMRh

One of the two terminal carbonyls was dropped off if PMRh was heated without efficient protection of the CO, at the same time, neighboring free oxygen donor immediately replaced it to form a O→Rh coordinate bond. After that, the uncoordinated sulfur donor replaced the remaining terminal carbonyl to form quadridentate complex given further heating. And it should be noted that this substitution process is reversible. Under an atmosphere of CO, it will return to its original structure I. That is the reason why the IR spectrum changes.

As is shown in Table 3, further evidence of the change of binding energy conforms that the above intramolecular substitution reaction is reasonable. E_b of sulfur atom which coordinated with rhodium in structure I increased from 162.1 eV of ligand to 163.3 eV, but that of free sulfur atom remained constant. The same was the case with oxygen. In structure II, the free carbonyl oxygen atom of complex replaces the terminal carbonyl to form tridentate complex. But its XPS spectrum does not change because the coordinate status does not change. With the second terminal carbonyl being dropped off, the free sulfur donor immediately coordinates with rhodium atom to form a stable quadridentate complex. As a result the E_b of S_{2p} all increases to 163.4 eV due to no free sulfur donors remained.

Table 3 Binding energies and IR data of the complex PMRh in three different structures

Structure	ν_{CO} (cm^{-1})	Binding energy E_b (eV)		
		S_{2p}	O_{1s}	$Rh_{3d5/2}$
I	2060	163.3 ^a	534.6 ^a	310.1
	1990	162.1 ^b	533.0 ^b	
II	2060	163.3 ^a	534.5 ^a	309.5
		162.1 ^b	533.1 ^b	
III		163.4 ^a	534.5 ^a	308.5
			533.1 ^b	

^a coordinate donor. ^b free donor.

Table 3 shows a downward tendency in the binding energy of $Rh_{3d5/2}$. Compared with 311.2 eV in $[Rh(CO)_2Cl]_2$ (according to the measurement of reference¹⁴), it decreases to 310.1 eV in the structure I. This case is due to the fact that the negative charge transfer is from sulfur and oxygen donors to rhodium in the process of formation of the complex. With the change of the structure I to structure II, the binding energy de-

crease to 309.5 eV can be attributed to more charge accepted by rhodium. For the same reason, it further decreases to 308.5 eV after the structure changes from II to III.

Reversible intramolecular substitution reaction largely improves stability of complex in air. In catalytic reaction system, experiments showed that it was the key factor of high stability for this class of rhodium complexes. Fig. 1 shows the catalyst PMRh for the carbonylation from methanol to acetic acid. After it reacted 150 min, we gave out CO from reactor and aerated air (stirring at normal temperature, 10 kg/cm⁻¹ pressure) into it to test its stability. After 30 min, we let out air and aerated CO to reactor. The reaction went on without any difficulty. This indicates that the catalyst remains its catalytic activity. Compared to the catalyst used before,¹⁵ its stability is greatly improved when lack of protection of CO.

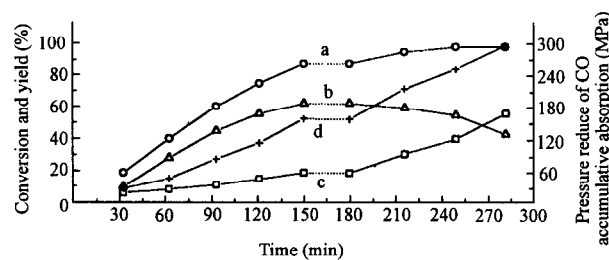


Fig. 1 Carbonylation of methanol. Reaction conditions: 140°C, P_{CO} 4-5 MPa, CH_3OH 120 mL, CH_3I 30 mL, Rh 6×10^{-4} mol, reactor 250 mL. a) conversion of methanol; b) yield of methyl acetate; c) yield of acetic acid; d) pressure reduce of CO accumulative absorption.

The new class of square planar *cis*-dicarbonyl Rh-(I) complexes, on one hand, remains high active in catalytic reaction. On the other hand, its stability is largely improved. So it is a prospective catalyst for methanol carbonylation.

References

1. Fordy, W.A.; Crosby, G.A., *Inorg. Chem.*, **21**, 1023 (1982).
2. Jarrel, M. S.; Gates, B. C., *J. Catal.*, **40**, 225 (1975).
3. Pan, P.L.; Liu, Z.Y.; Yuan, G.Q., *Chin. J. Catal.* (in Chinese), **17**, 45(1996).
4. Peng, W.Q.; Yuan, G.Q., *Chin. Sci. Bull.* (in Chinese), **42**, 935(1996).

5. Peng, W.Q.; Yuan, G.Q., *Chin. Sci. Bull.* (in Chinese), **42**, 1729(1997).
6. Jiang, H.; Yuan, G.Q.; Cheng, X.Z., *Chin. Sci. Bull.* (in Chinese), **44**, 160(1999).
7. Jiang, H.; Pan, P.L.; Yuan, G.Q., *Sci. China*, in press.
8. Pan, P.L.; Liu, Z.Y.; Yuan, G.Q., *Chin. J. Catal.* (in Chinese), **17**, 45(1996).
9. Chen, Y.Y.; Yuan, G.Q.; Chen, R.Y., *J. Mol. Catal.* (in Chinese), **8**, 147(1988).
10. Langford, C.H.; Gray, H.B., *Ligand Substitution Processes*, Ed. Benjamin, W. A., New York Press, New York, 1965.
11. Yuan, G.Q.; Wang, D.H.; Liu, S.H.; Chen, R.Y., *Chin. Sci. Bull.* (in English), **29**, 1053(1984).
12. Liu, Z.Y.; Pan, P.L.; Huang, M.K.; Yuan, G.Q., *J. Functional Poly.*, **7**, 159(1994).
13. Wang, H.H.; Bai, C.L.; Zhu, N. J.; Fu, H.; Tang, Y.Q.; Yuan, G.Q.; Chen, R.Y., *Acta. Phy.-Chem. Sin.* (in Chinese), **2**, 97(1986).
14. Wang, D.H.; Liu, S.H.; Yuan, G.Q.; Chen, R.Y., *Acta Chim. Sin.* (in Chinese), **42**, 747(1984).
15. Vallarino, L.M., *Inorg. Chem.*, **4**, 161(1965).

(E9906078 SONG, J.P.; DONG, L.J.)