Research paper

Dihydrogen and dinitrogen rhodium complexes bearing metalloocene-based pincer ligands

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\textbf{A R T I C L E   I N F O}

\textbf{Keywords:}
Pincer complex
Metallocene
Small molecules activation
Rhodium
H-D coupling constant

\textbf{A B S T R A C T}

Pincer complexes are widely used in catalysis and activation of small molecules. We present here the synthesis and spectroscopic study of rhodium dihydrogen and dinitrogen complexes with metalloocene-based P,C,P pincer ligands. Relative electron donor ability of ferrocene-, ruthenocene- and benzene-derived pincer ligands, as well as H–H distance were elucidated based on J_{\text{HD}} coupling constants and T$_1$ relaxation time for dihydrogen complexes.

\section{1. Introduction}

Pincer complexes are able to catalyze a large variety of important reaction as well activate the majority of small molecules [1–6]. Pincer complexes possess unprecedented activity, for example, in alkane dehydrogenation, and some pincer ligands shows cooperativity that opens great perspectives in catalysis [7–9]. The most impressive example of processes driven by pincer complexes is alkane dehydrogenation with iridium-based complexes [10–21], water splitting with ruthenium complex [18], CO$_2$ conversion to methanol with nickel [22], iridium [23], ruthenium [24] complexes, nitrogen activation with molybdenum one [25], metal-ligand cooperativity with 3d metals [26–29]. Small molecules, such as H$_2$, N$_2$, CO, CO$_2$ and NH$_3$, are not only substrates or intermediates in multiple catalytic processes [30–32], they also can poisoned catalysis as H$_2$ or N$_2$ in alkane dehydrogenation process [33]. That is a reason why adducts of small molecules with pincer complexes are of special interest. We also could learn from this adduct about electronic and steric properties of pincer scaffold as we showed H$_2$, N$_2$, O$_2$ and CO adducts of rhodium benzene-based bis(phosphinite) pincers [34].

Previously, iridium ferrocene and ruthenocene-based P,C,P-pincer hydrides showed much higher activity in alkane dehydrogenation reaction compared to their benzene and resorcinol-based counterparts. The P-M-P angle was claimed to be responsible for this effect [17]. Van Coten and Brown reported the synthesis of ferrocene-based rhodium analogs but newer pursue a goal of small molecule activation with this scaffold [35]. Here we report the synthesis and spectroscopic properties of H$_2$, N$_2$ and CO adducts of metalloocene-based bis(phosphinite) rhodium pincer complexes. We discuss binding modes of those adducts and compare them with benzene-based systems. We calculate donor power of different pincer scaffolds and compare those results with iridium [17] and palladium pincers [36].

\section{2. Results and discussion}

The rhodium chlorohydride pincer complexes 3 [35] and 4 were obtained as a mixture of diastereoisomers from [RhCl(coe$_2$)]$_2$ and diphenylphosphines 1 and 2 after reflux in toluene (Scheme 1).

Hydride signals appeared in $^1$H NMR spectrum as dt at $\delta$ = −26.8; −27.5 ppm ($J_{\text{Rh-H}}$ = 47, $J_{\text{P-H}}$ = 13) Hz for 4a and 4b, respectively [35]. $^{31}$P($^1$H) NMR showed two doublets with $J_{\text{P-Rh}}$ 115–117 Hz that is typical for 5-coordinated rhodium pincers. We used NOESY experiment to assign configuration of complexes 3 and 4. The endo-isomers 3b and 4b had NOE contact with protons of unsubstituted Cp ring and endo-oriented (pseudoequatorial) t-Bu groups on phosphorus atoms. Fig. 1 shows all NOE contacts found for both isomers. The $^{13}$C NMR spectra agreed with proposed structures. The C(1) carbon atom signal appeared in the spectrum of 3a and 4a as dt at 122.2 and 122.4 ppm ($J_{\text{Buc}}$ = 30 Hz), respectively, that confirmed cyclometallation. Full assignment of signals was completed with HMQC and HMBC.

Complexes 3 and 4 reacts completely with CO at room temperature with elimination of HCl and formation of 16-e CO adducts 5 and 6, respectively, no formation of 18-e adduct was detected nor with IR neither with NMR (Scheme 2). It is common for rhodium P,C,P pincer
complexes with bulky 'Bu groups on P atoms to from 16ē-adducts with CO and eliminate HCl[4] even in the absence of a base[34]. At the same time, benzene based Ir P,C,P pincer complex formed 18ē product of CO addition [4] but in the case of the metallocene-based Ir ones formation of both 16ē and 18ē adducts were detected[17]. When 'Pr or even less bulkier groups were installed on P-atoms of pincer ligand, formation of 18ē adducts were observed for all metals and ligand types. We conclude that formation of 16ē adducts was directed with steric bulk resulted from substituents on P-atoms and shorter M-P contacts[6].

The phosphorous atoms signal in 31P{1H} NMR spectrum of the complex 5 appeared at 108.6 ppm (J_{P-Rh} = 155.3 Hz); CO carbon atom signal shows up in 13C{1H} NMR at 201.7 ppm (J_{C-Rh} = 57.7 Hz). The IR spectra showed the presence of an intense band at 1925 cm\(^{-1}\) assigned as CO stretch for both 5 and 6.

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Treatment of complexes 3 or 4 with NaOtBu in C\(_6\)D\(_6\) in H\(_2\) atmosphere (low-pressure J-Young NMR tube) resulted in color change from raspberry (3) or greenish (4) to yellow (7, 8). The hydride resonances in 1H NMR at \(-26\) to \(-27\) ppm disappeared and broad doublets at \(-3.57\) ppm (J_{Rh-H} = 17.1 Hz) and \(-3.84\) ppm (J_{Rh-H} = 17.4 Hz) appeared for 7 and 8, respectively. Small negative chemical shifts and broad character of the signals indicated that 7 and 8 are the complexes with molecular hydrogen (Scheme 3). We should mention that for Ir complexes with all P,C,P-pincer scaffolds formation of 18ē tetrahydrides were detected under H\(_2\) pressure and removal of H\(_2\) atmosphere led to 16ē true dihydride formation[4]. In case of Rh complexes explored we have no evidence of tetrahydride formation, they persisted as 16ē adducts with molecular dihydrogen.

Complexes 7 and 8 could exchange H\(_2\) with N\(_2\). When evacuation of H\(_2\) and refill with N\(_2\) the reaction mixture changed color from yellow to reddish-brown. Signals of coordinated H\(_2\) in high field disappeared in 1H NMR and 31P{1H} NMR showed that signals from phosphorous atoms of 7 or 8 were completely gone and instead two new set of signals corresponding to mononuclear (9b, 10b) and binuclear (9a, 10a) complexes appeared (Scheme 4). Phosphorus atoms in mononuclear complexes 9b and 10b are equivalent and appeared in 31P{1H} NMR as doublets at \(\delta = 96.8\) ppm (J\(_{P-H}\) = 165.6 Hz) and 96.6 ppm (J\(_{P-H}\) = 165.1 Hz), respectively. Phosphorous atoms of each pincer in dinuclear complexes 9a or 10a are not equivalent because of the symmetry broken with metallocene backbone and showed up in 31P{1H} NMR as ABX system in the range 93–98 ppm. This broken symmetry

![Scheme 1. Synthesis of ferrocene-based (3a, b) and ruthenocene-based (4a, b) rhodium chloro-hydride complexes.](image1)

![Scheme 2. Formation of CO adducts 5 and 6.](image2)

![Scheme 3. Formation of dihydrogen complexes 7 and 8.](image3)

![Scheme 4. Formation of NOE contacts for two diastereoisomers of complexes 3 and 4.](image4)
advantage of ferrocene-based pincers compared to benzene-based ones allowed us undoubtfully assign signals of mono and dinuclear dinitrogen complexes.

Phosphorous atoms are equivalent in all binuclear pincer complexes with bridged nitrogen ligands and appeared as single signal in $^{31}$P{1H} NMR spectra due to deposition of pincer’s aromatic backbones in two orthogonal planes [15,25,33,37,38]. Metallocene backbone in complexes 9a, 10a breaks symmetry and four P-atoms appeared as ABX system in the spectra (Fig. 2). As in the case of benzene-based rhodium pincers, mono 9a/9b and dinuclear 10a/10b complexes with molecular nitrogen are in equilibrium in solution. Higher N$_2$ pressure favors formation of mononuclear ones. Complexes 9 and 10 are stable only under N$_2$ atmosphere and slowly degraded under argon. Dinitrogen ligand can be completely substituted with molecular hydrogen after 3 freeze-pumpthaw cycles quenched with H$_2$ gas.

Understanding of dihydrogen activation is crucial for development of a new hydrogenation/dehydrogenation catalysts [12,39,40]. The H–H distance is one of the key parameters important for understanding of H$_2$ coordination. Dihydrogen molecule has high pKa value (pKa = 35 in THF [41]) but became much more acidic after coordination with metal center [42,43]. For HD gas the spin–spin coupling $J_{D-H}$ 43.2 Hz decreases when HD is coordinated with metal center with the rate proportional to H-D distance. Two semiempirical linear correlations were proposed for calculation of H–H distance (Eqs. (1) and (2)) [44,45]:

$$d_{HH} = 1.42 - 0.0167J_{HH} \AA$$  \hspace{1cm} (1) \\
$$d_{HH} = 1.44 - 0.0168J_{HH} \AA$$  \hspace{1cm} (2)

Another useful parameter for establishing of H–H distance is spin-lattice relaxation time of coordinated H$_2$, it was proposed that $T_1$ of true dihydrogen complexes should not exceed 150 ms at 400 MHz [46,47]. When 1 atm of D$_2$ gas was added to the complexes 7 or 8 a mixture of H$_2$, D$_2$ and H/D coordinated compounds was obtained with predominantly HD coordinated ones (Scheme 5).

The signals of coordinated HD in $^1$H NMR spectra of complexes 7-d$_1$ and 8-d$_1$, appeared at $\delta \sim 3 \div -4$ ppm as dt due to the coupling with $^{103}$Rh and $^2$H (Fig. 3a). We also measured $T_1$, for all complexes synthesized (Table 1).

As mentioned above, $J_{H-D}$ is proportional to H–H distance and the last one is proportional to a back donation from metal to $\sigma^*$ of H$_2$ molecule. That mean we can use H-D coupling constant to compare donor power of pincer ligands in a series of complexes with H$_2$. Based on the data presented in Table 1 electron donor ability of pincer ligands decreases in the following order $d_{out}(P,C,P)^{Fe}$, $d_{out}(P,C,P)^{Ru}$, $d_{out}(P,C,P)^{Fe}$, $d_{out}(P,C,P)^{Ru}$, $d_{out}(PO,C,OP)$. This order is in agreement with previously obtained in our group based on IR stretches of carbonyl adducts of iridium pincer complexes and on $^{1}P$ and $^{13}$C chemical shifts of palladium p-fluorophenyl complexes with the same set of pincer ligands [36].
Table 1
HD-ligand parameters in complexes 7, 8, 11 [34] and 12 [48].

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ (H) (ppm)</th>
<th>J_{H-H} (Hz)</th>
<th>T1 (µs)</th>
<th>r(H-H) Å</th>
<th>r(H-H) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-d1 [13]</td>
<td>3.01</td>
<td>38.8</td>
<td>53.0</td>
<td>0.77</td>
<td>0.79</td>
</tr>
<tr>
<td>7-d1</td>
<td>3.57</td>
<td>31.3</td>
<td>65.2</td>
<td>0.90</td>
<td>0.91</td>
</tr>
<tr>
<td>8-d1</td>
<td>3.43</td>
<td>32.7</td>
<td>61.0</td>
<td>0.87</td>
<td>0.89</td>
</tr>
<tr>
<td>12-d1 [26]</td>
<td>33</td>
<td>46 (500 MHz)</td>
<td>0.87</td>
<td>0.89</td>
<td></td>
</tr>
</tbody>
</table>

3. Conclusion
Rhodium dihydrogen and dinitrogen complexes with P,C,P metallocene-based pincer ligands were synthesized and characterized. Relative electron donor ability of metallocene- and benzene-based pincer ligands, as well as H-H distance in complexes with H2 were calculated based on H-D coupling constants J_{H-D} in complexes with HD and T1 relaxation time.

4. Experimental
4.1. General consideration
All reactions were carried out under an atmosphere of purified argon. All solvents were refluxed and distilled over appropriate reagents under argon atmosphere. The NMR spectra were recorded on a Bruker Avance 300, 400 and 600 MHz spectrometers. 1H and 13C(1H) NMR chemical shifts are reported in parts per million from tetramethylsilane; for 1H NMR spectra residual signals of deuterated solvents were used as references (7.26 ppm for CDCl3, 7.16 ppm for CD2D2O, 5.32 ppm for CD3Cl, 3.7 ppm for t-butyl alcohol). 31P NMR chemical shifts are reported in parts per million from H3PO4 referred to an external 85% solution of phosphoric acid in D2O. IR spectra were recorded on Nicolet Magna-IR 750. Elemental analyses were performed at the A.N. Nesmeyanov Institute of Organoelement Compounds of RAS. Compounds 1 and 2 were synthesized according to published procedure [49,50].

4.1.1. RhH(Cl)(2.5-(tBu2PCH2)2C5H2)Fe(C5H5) (3)
In 25 ml Schlenk flask [Rh(COE)2Cl]2 (50 mg, 0.08 mmol) and pincer ligand precursor 1 (100 mg, 0.19 mmol) were mixed in 15 ml of toluene. The reaction mixture was refluxed for 3 h and volatiles were removed under reduced pressure. A brown residue was dissolved in 10 ml of CH2Cl2 and 5 ml of hexane was added. The solution was concentrated up to 5 ml and placed in a fridge for 12 h at −18 °C. Violet crystalline precipitate was separated from solvent and washed with hexane and dried in vacuum. Yield: 80% (102 mg). Mixture of exo/endo isomers 3a/4b in 3:1 ratio. 3a: 1H NMR (400 MHz, CD2Cl2): δ 4.32 (2H, 4.5-C5H2), 3.91 (c, 5H, C5H5), 2.64 (dt, 2H, J_{H-P} = 2.9 Hz, J_{H-H} = 16.6 Hz, 2*endo-CH2), 2.20 (dt, 2H, J_{H-P} = 3.9 Hz, J_{H-H} = 17.0 Hz, 2*exo-CH2), 1.53 (vt, J_{H-P} = 6.8 Hz, 18H, endo-C(CH3)3), 1.10 (vt, J_{H-P} = 6.5 Hz, 18H, exo-C(CH3)3), −27.23 (dt, J_{H-P} = 12.7 Hz, J_{H-Rh} = 47.4 Hz, 1H, Rh-H), 31P(1H) NMR (243 MHz, CD2Cl2): δ 92.8 (d, J_{IP} = 116.1 Hz). 13C NMR (100 MHz, CD2Cl2): δ 122.0 (m), 91.8 (dt, J_{C-H} = 12 Hz, J_{C-Rh} = 3 Hz), 70.7 (C), 64.5 (broad, dt, J_{H-C} = 7 Hz), 36.0 (t, J_{C-H} = 6 Hz), 35.1 (d, dt, J_{C-P} = 8 Hz, J_{H-C} = 7 Hz), 29.4 (t, J_{C-P} = 3 Hz), 28.9 (t, J_{C-P} = 3 Hz), 25.8 (dt, J_{C-P} = 11 Hz, J_{C-Rh} = 2 Hz). 3b: 1H NMR (400 MHz, CD2Cl2): δ 4.28 (2H, 4.5-C5H2), 3.88 (c, 5H, C5H5), 2.70 (dt, 2H, J_{H-P} = 2.9 Hz, J_{H-H} = 17.1 Hz, 2*endo-CH2), 2.36 (dt, 2H, J_{H-P} = 12.2 Hz, J_{H-H} = 17.1 Hz, 2*exo-CH2), 1.42 (dt, J_{H-P} = 7.0 Hz, 18H, endo-C(CH3)3), 1.17 (vt, J_{H-P} = 6.3 Hz, 18H, exo-C(CH3)3), −27.02 (dt, J_{H-P} = 12.2 Hz, J_{H-Rh} = 45.6 Hz, 1H, Rh-H), 31P(1H) NMR (243 MHz, CD2Cl2): δ 86.7 (d, J_{IP} = 116.8 Hz). 13C NMR (100 MHz, CD2Cl2): δ 93.1 (dt, J_{C-P} = 12 Hz, J_{C-Rh} = 3 Hz), 70.6 (C), 70.2 (m), 36.1 (t, J_{C-P} = 6 Hz), 34.7 (d, dt, J_{C-P} = 8 Hz, J_{H-C} = 7 Hz), 29.9 (t, J_{C-P} = 3 Hz), 29.7 (t, J_{C-P} = 3 Hz), 25.2 (dt, J_{C-P} = 11 Hz, J_{C-Rh} = 2 Hz). Calculated for C30H28Fe3P2Rh (%) C, 52.48; H, 7.55. Found: C 52.33, H 7.80

Fig. 3. A) The signals of coordinated HD for complexes 11-d1 (1), 7-d1 (2) and 8-d1 (3). B) T1(t) diagram for complex 8.
4.1.3. Rh(CHO)\{(2,5-(tBu2PCH2)2C6H4)Fe(C6H5)\} (6)

The solution of 20 mg (0.031 mmol) of the compound 3 in C6D6 was treated with gentle stream of CO for 10 min and reaction mixture color changed from violet to yellow. Volatiles were removed and yellow crystals were formed. Yielded 19.5 mg (100%). 1H NMR (400 MHz, C6D6): δ 4.44 (c, 2H, C2H2), 3.97 (s, 5H, C6H5), 2.99 (dt, 2H, JH-H = 16.6 Hz, 2°endo-CH2), 2.52 (dt, 2H, JH-H = 16.6 Hz, 2°endo-CH2), 1.38 (vt, 18H, JH-H = 6.5 Hz, C(CH3)3), 1.14 (vt, 18H, JH-H = 6.6 Hz, C(CH3)3), 31p \(1\)H NMR (162 MHz, C6D6): δ 108.6 (d, Jp-D = 155.3). 13C NMR (100.5 MHz, C6D6): δ 201.2 (dt, Jp-C = 57.7 Hz, 195.9 (dt, Jp-C = 28.7 Hz, 28.7 (t), Jp-C = 18.2 Hz, 28.7 (t), Jp-C = 18.2 Hz, 28.7 (t); IR (C6D6) νCO 1928 Cm\(^{-1}\); Calculated (%): C, 55.08; H, 7.49. C28FeH47OP2Rh; Found (%): C, 54.99, H, 6.91.

4.1.4. Rh(CHO)\{(2,5-(tBu2PCH2)2C6H4)Ru(C6H5)\} (7)

Compound 6 was obtained using the procedure for compound 5 as yellow crystals. Yielded 19.5 mg (100%). 1H NMR (400 MHz, CDCl3): δ 4.94 (c, 2H, C2H2), 4.52 (s, 5H, C6H5), 2.90 (dt, 2H, JH-H = 16.3 Hz, JH-H = 2.7 Hz, 2°endo-CH2), 2.75 (dt, 2H, JH-H = 16.3 Hz, JH-H = 3.8 Hz, 2°endo-CH2), 1.39 (vt, 18H, JH-H = 6.4 Hz, C(CH3)3), 1.31 (vt, 18H, JH-H = 6.4 Hz, C(CH3)3), 31p \(1\)H NMR (162 MHz, C6D6): δ 107.9 (d, Jp-D = 154.4); IR (C6D6) νCO 1928 Cm\(^{-1}\). Calculated for C28FeH47OPRh: C, 51.40; H, 6.99; Found: C, 51.12; H, 6.77.

4.1.5. Rh(HH)\{(2,5-(tBu2PCH2)2C6H4)Fe(C6H5)\} (7)

In Young NMR tube 20 mg (0.031 mmol) of the compound 3 was dissolved in 0.6 ml of C6D6 and freeze-pump-thaw for 3 times. Then the tube was frozen in liquid nitrogen, the valve was opened and 5 mg (0.052 mmol) of NaOtBu was placed over a frozen solution, a tube was closed with the valve, the atmosphere was removed under vacuum, and 1 atm of H2 gas introduced into the cold tube. The frozen solution was warmed to r.t. and vigorously shaken for 10 min. 1H NMR (400 MHz, C6D6): δ 4.42 (c, 2H, C2H2), 4.04 (s, 5H, C6H5), 2.94 (dt, 2H, JH-H = 16.4 Hz, JH-H = 2.0 Hz, 2°endo-CH2), 2.50 (dt, 2H, JH-H = 16.4 Hz, JH-H = 2.9 Hz, 2°endo-CH2), 1.33 (vt, 18H, JH-H = 6.3 Hz, C(CH3)3), 1.11 (vt, 18H, JH-H = 6.3 Hz, C(CH3)3), -3.57 (broad,d, 2H, JH-H = 17.1 Hz, Rh-H). 31p \(1\)H NMR (162 MHz, C6D6): δ 108.5 (d, Jp-D = 161.9). 13C NMR (100.5 MHz, C6D6): δ 125.8 (d, Jp-C = 36.9 Hz, 94.7 (d, Jp-C = 5.4 Hz, 70.0 (C), 64.2 (t), 35.1 (t), 33.4 (t), 30.0 (C), 29.8 (C), 27.6 (d, Jp-C = 3.1 Hz).

4.1.6. Rh(HH)\{(2,5-(tBu2PCH2)2C6H4)Ru(C6H5)\} (8)

The compound 8 was obtained from the complex 4 using the procedure for compound 7. 1H NMR (400 MHz, C6D6): δ 4.92 (c, 2H, C2H2), 4.47 (s, 5H, C6H5), 2.75 (dt, 2H, JH-H = 16.4 Hz, JH-H = 2.6 Hz, 2°endo-CH2), 2.60 (dt, 2H, JH-H = 16.4 Hz, JH-H = 4.7 Hz, 2°endo-CH2), 1.24 (vt, 18H, JH-H = 6.4 Hz, C(CH3)3), 1.17 (vt, 18H, JH-H = 6.0 Hz, C(CH3)3), -3.84 (broad,d, 2H, JH-H = 17.4 Hz, Rh-H). 31p \(1\)H NMR (162 MHz, C6D6): δ 108.5 (d, Jp-D = 161.9). 13C NMR \(1\) (100.5 MHz, C6D6): δ 125.8 (d, Jp-C = 36.9 Hz, 94.7 (d, Jp-C = 5.4 Hz, 70.0 (C), 64.2 (t), 35.1 (t), 33.4 (t), 30.0 (C), 29.8 (C), 27.6 (d, Jp-C = 3.1 Hz).

4.1.7. Rh(HH)\{(2,5-(tBu2PCH2)2C6H4)Fe(C6H5)\} (7-dl)

The solution of compound 7 in C6D6 was freeze-pump-thaw for 3 times and quenched with D2 gas. The tube was vigorously shaken for 5 min. 1H NMR (400 MHz, C6D6): δ 4.82 (c, 2H, C2H2), 4.04 (s, 5H, C6H5), 2.94 (dt, 2H, JH-H = 16.4 Hz, JH-H = 2.0 Hz, 2°endo-CH2), 2.50 (dt, 2H, JH-H = 16.4 Hz, JH-H = 2.9 Hz, 2°endo-CH2), 1.33 (vt, 18H, JH-H = 6.3 Hz, C(CH3)3), 1.11 (vt, 18H, JH-H = 6.3 Hz, C(CH3)3), -3.57 (broad,d, 2H, JH-H = 17.1 Hz, Rh-H) -3.01 (t,d, 1H, Rh-Hd, JH-H = 17.6, Jd-H = 31.3).