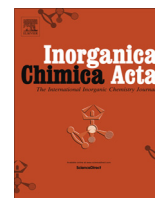




Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica



Research paper

# Half-sandwich hydrazine complexes of iridium: Preparation and reactivity

Gabriele Albertin<sup>a,\*</sup>, Stefano Antoniutti<sup>a</sup>, Marco Bortoluzzi<sup>a</sup>, Jesús Castro<sup>b</sup><sup>a</sup> Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia, Via Torino 155, 30172 Mestre Venezia, Italy<sup>b</sup> Departamento de Química Inorgánica, Universidade de Vigo, Facultade de Química, Edificio de Ciencias Experimentais, 36310 Vigo, Galicia, Spain

## ARTICLE INFO

## Article history:

Received 27 February 2017

Received in revised form 7 April 2017

Accepted 10 April 2017

Available online xxxxx

## Keywords:

Hydrazine

Iridium

Half-sandwich

Pentamethylcyclopentadienyl

Synthesis

Aryldiazene

## ABSTRACT

Chloro complexes  $\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{P}(\text{OR})_3\}$  (**1**) ( $\text{R}=\text{Me}$ ,  $\text{Et}$ ) were prepared by reacting dimer  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]_2$  with phosphites in alcohol. Treatment of **1** with  $\text{R}_1\text{NHNH}_2$  gave monohydrazine complexes  $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{R}_1\text{NHNH}_2)\{\text{P}(\text{OR})_3\}]\text{BPh}_4$  (**2**, **3**, **4**) [ $\text{R}_1=\text{H}$  (**2**),  $\text{Me}$  (**3**),  $\text{Ph}$  (**4**)]. Bis(hydrazine) complexes  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{R}_1\text{NHNH}_2)_2\{\text{P}(\text{OR})_3\}](\text{BPh}_4)_2$  (**5**, **6**) were prepared by reacting chloro complexes first with  $\text{AgOTf}$  and then with an excess of hydrazine. Oxidation with  $\text{Pb}(\text{OAc})_4$  at  $-40^\circ\text{C}$  of both mono- and bis(hydrazine) complexes afforded phenyldiazene derivatives  $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{PhN}=\text{NH})\{\text{P}(\text{OR})_3\}]\text{BPh}_4$  (**7**) and  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{PhN}=\text{NH})_2\{\text{P}(\text{OR})_3\}](\text{BPh}_4)_2$  (**9**). Bis(aryldiazene)  $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{PhN}=\text{NH})_2\{\text{P}(\text{OR})_3\}](\text{BPh}_4)_2$  (**9**, **10**) were also prepared by allowing hydride  $\text{IrH}_2(\eta^5\text{-C}_5\text{Me}_5)\{\text{P}(\text{OR})_3\}$  (**8**) to react with aryldiazonium cations  $[\text{ArN}_2]\text{BF}_4$ . The complexes were characterised spectroscopically and by X-ray crystal structure determination of  $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{NH}_2\text{NH}_2)\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$  (**2b**) and  $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{CH}_3\text{NHNH}_2)\{\text{P}(\text{OEt})_3\}]\text{BPh}_4$  (**3b**).

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

The chemistry of transition metal complexes containing hydrazine and other partially reduced dinitrogen ligands such as diazene  $\text{RN}=\text{NH}$  has attracted interest in recent years [1–5], not only because of their relationship with dinitrogen fixation process intermediates [6–8], but also because their properties led us to consider this class of complexes as having identity and chemistry in itself [1–3,5], with potentially interesting developments.

A large number of hydrazine and substituted hydrazine complexes of several metals have been reported recently [1–5] and several studies on their oxidation [8] and reduction [5–7,9] reactions have revealed their interesting properties, e.g., in conversion of metal-bonded hydrazine to diazene.

However, despite many studies on these issues, the chemistry of hydrazine complexes of iridium has been relatively under-developed when compared with other metals and, except for cluster  $[(\text{Cp}^*\text{Ir})_4(\mu_3\text{-S})_2(\mu_2\text{-H})_2(\text{N}_2\text{H}_4)_2](\text{BF}_4)_2$  [10], only two papers on the preparation of hydrazine complexes of iridium have appeared in the literature [11].

We have a long-standing interest in the “diazo” chemistry of transition metals and have reported the synthesis and reactivity

of hydrazine, diazene and diazoalkane complexes of Ru and Os stabilised by half-sandwich fragments of the type  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{R}_1\text{NHNH}_2)(\text{PPh}_3)_2]\text{BPh}_4$ ,  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{R}_1\text{N}=\text{NH})(\text{PPh}_3)_2]\text{BPh}_4$ ,  $[\text{M}(\eta^5\text{-C}_5\text{H}_5)(\text{Ar}_1\text{Ar}_2\text{CN}_2)(\text{PPh}_3)_2]\text{BPh}_4$ ,  $[\text{M}(\eta^5\text{-C}_9\text{H}_7)(\text{R}_1\text{NHNH}_2)(\text{PPh}_3)_2]\text{BPh}_4$  [ $\text{M}=\text{Ru}$ ,  $\text{Os}$ ;  $\text{R}_1=\text{H}$ ,  $\text{Me}$ ,  $\text{Ph}$ ;  $\text{L}=\text{P}(\text{OR})_3$ ] [12,13].

We have now extended our study to iridium, and report here the synthesis and oxidation reactions of both mono- and bis(hydrazine) iridium(III) complexes stabilised by pentamethylcyclopentadienyl half-sandwich fragments.

## 2. Experimental section

## 2.1. General comments

All synthetic work was carried out under an appropriate atmosphere ( $\text{Ar}$ ,  $\text{N}_2$ ) with standard Schlenk techniques or in an inert atmosphere dry-box. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks.  $\text{IrCl}_3\cdot 3\text{H}_2\text{O}$  (Pressure Chemical Co. (USA) and pentamethylcyclopentadiene  $\text{C}_5\text{Me}_5\text{H}$  (STREM) were used as received. Phosphites  $\text{P}(\text{OMe})_3$  and  $\text{P}(\text{OEt})_3$  were Aldrich products, used as received. Hydrazines  $\text{CH}_3\text{NHNH}_2$  and  $\text{C}_6\text{H}_5\text{NHNH}_2$  were Aldrich products and were used as received. High-purity  $\text{Pb}(\text{OAc})_4$  (99,99%) was an Aldrich product used as received. Hydrazine  $\text{NH}_2\text{NH}_2$  was prepared by decomposition of hydrazine

\* Corresponding author.

E-mail address: albertin@unive.it (G. Albertin).

cyanurate (Fluka) following the reported method [14]. Diazonium salts  $\text{ArN}_2^+\text{BF}_4^-$  were obtained in the usual way [15]. Labelled diazonium tetrafluoroborate  $[\text{C}_6\text{H}_5\text{N}\equiv^{15}\text{N}]\text{BF}_4$  was prepared from  $\text{Na}^{15}\text{NO}_2$  (99% enriched, CIL) and aniline. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on a Perkin-Elmer Spectrum-One FT-IR spectrophotometer. NMR spectra ( $^1\text{H}$ ,  $^{31}\text{P}$ ,  $^{15}\text{N}$ ) were obtained on AVANCE 300 or AVANCE III HD 400 Bruker spectrometers at temperatures between  $-90$  and  $+25$  °C, unless otherwise noted.  $^1\text{H}$  spectra are referred to internal tetramethylsilane.  $^{31}\text{P}\{^1\text{H}\}$  chemical shifts are relative to 85%  $\text{H}_3\text{PO}_4$  and  $^{15}\text{N}$  ones to  $\text{CH}_3^{15}\text{NO}_2$ , in both cases downfield shifts (values in ppm) are considered positive. COSY, HMQC and HMBC NMR experiments were performed with standard programs. The iNMR software package [16] was used to treat NMR data. The conductivity of  $10^{-3}$  mol  $\text{dm}^{-3}$  solutions of the complexes in  $\text{CH}_3\text{NO}_2$  at 25 °C was measured on a Radiometer CDM 83. Elemental analyses were determined in the Microanalytical Laboratory of the Dipartimento di Scienze del Farmaco, University of Padova (Italy).

## 2.2. Synthesis of complexes

The compound  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]_2$  was prepared following the method previously reported [17].

### 2.2.1. $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]_2[\text{P}(\text{OR})_3]$ (**1**) [ $R=\text{Me}$ (**a**), $\text{Et}$ (**b**)]

The appropriate phosphite  $\text{P}(\text{OR})_3$  (2.52 mmol) was added to a solution of the dimeric compound  $[\text{IrCl}_2(\eta^5\text{-C}_5\text{Me}_5)]_2$  (1 g, 1.26 mmol) in the appropriate alcohol ROH (20 mL) and the resulting solution was refluxed for 2 h. The solvent was removed under reduced pressure to give an oil, which was triturated with alcohol (2 mL) until an orange solid separated out, which was filtered and dried under vacuum; yield  $\geq 90\%$ .

**1a:**  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 3.77 (d, 9H,  $\text{CH}_3$  phos), 1.64 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ) ppm.  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 82.54 (s) ppm.  $\text{C}_{13}\text{H}_{24}\text{Cl}_2\text{IrO}_3\text{P}$  (522.42): calcd. C 29.89, H 4.63, Cl 13.57; found C 29.63, H 4.59, Cl 13.72%.

**1b:**  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 4.16 (qnt, 6H,  $\text{CH}_2$ ), 1.63 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ), 1.28 (t, 9H,  $\text{CH}_3$  phos).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 77.65 (s).  $\text{C}_{16}\text{H}_{30}\text{Cl}_2\text{IrO}_3\text{P}$  (564.50): calcd. C 34.04, H 5.36, Cl 12.56; found C 33.85, H 5.43, Cl 12.42%.

### 2.2.2. $[\text{IrCl}(\eta^5\text{-C}_5\text{Me}_5)(\text{R}1\text{NHNH}_2)]_2[\text{P}(\text{OR})_3][\text{BPh}_4]$ (**2–4**) [ $R=\text{H}$ (**2**), $\text{Me}$ (**3**), $\text{Ph}$ (**4**); $R=\text{Me}$ (**a**), $\text{Et}$ (**b**)]

**Method 1:** In a 25-mL, three-necked, round-bottomed flask were placed 0.1 mmol of the appropriate compound **1**, an excess of  $\text{NaBPh}_4$  (0.2 mmol, 68 mg), an excess of the appropriate hydrazine (0.3 mmol), 5 mL of alcohol and 3 mL of dichloromethane. The reaction mixture was stirred at room temperature for 24 h and then the solvent removed under reduced pressure to give an oil, which was triturated with alcohol (2 mL). A yellow solid slowly separated out, which was filtered and crystallised from  $\text{CH}_2\text{Cl}_2$  and ROH; yield  $\geq 80\%$ .

**Method 2:** In a 25-mL, three-necked, round-bottomed flask were placed 0.1 mmol of the appropriate compound **1**, an excess of  $\text{NaBPh}_4$  (0.2 mmol, 68 mg), an excess of the appropriate hydrazine (0.3 mmol), 5 mL of alcohol and 3 mL of 1,2-dichloroethane. The reaction mixture was refluxed for 1 h and then the solvent removed under reduced pressure to give an oil, which was triturated with alcohol (2 mL). The yellow solid which slowly separated out was filtered and crystallised from  $\text{CH}_2\text{Cl}_2$  and ROH; yield  $\geq 85\%$ .

**2a:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3316 (w), 3260 (m), 3221 (w);  $\delta_{\text{NH}_2}$ : 1591 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.40–6.88 (m, 20H, Ph), 4.19, 3.46 (br, 2H, Ir-NH<sub>2</sub>), 3.76 (d, 9H,  $\text{CH}_3$  phos), 2.31 (br, 2H, NH<sub>2</sub>), 1.64 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 77.33 (s).

$\Lambda_{\text{M}} = 52.8 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{37}\text{H}_{48}\text{BClIrN}_2\text{O}_3\text{P}$  (838.24): calcd. C 53.02, H 5.77, Cl 4.23, N 3.34; found C 52.84, H 5.89, Cl 4.11, N 3.20%.

**2b:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3319 (w), 3271 (m), 3221 (w);  $\delta_{\text{NH}_2}$ : 1600 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.36–6.87 (m, 20H, Ph), 4.40, 3.86 (br, 2H, Ir-NH<sub>2</sub>), 4.12 (qnt, 6H,  $\text{CH}_2$ ), 2.70 (br, 2H, NH<sub>2</sub>), 1.62 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ), 1.34 (t, 9H,  $\text{CH}_3$  phos).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 73.24 (s).  $\Lambda_{\text{M}} = 51.5 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{40}\text{H}_{54}\text{BClIrN}_2\text{O}_3\text{P}$  (880.32): calcd. C 54.57, H 6.18, Cl 4.03, N 3.18; found C 54.37, H 6.07, Cl 4.14, N 3.07%.

**3a:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3316 (w), 3215 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.33–6.86 (m, 20H, Ph), 5.05, 4.89 (br, 2H, Ir-NH<sub>2</sub>), 3.83 (d, 9H,  $\text{CH}_3$  phos), 3.53 (m, 1H, NH), 2.48 (d, 3H, NCH<sub>3</sub>), 1.72 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 77.75 (s).  $\Lambda_{\text{M}} = 52.1 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{38}\text{H}_{50}\text{BClIrN}_2\text{O}_3\text{P}$  (852.27): calcd. C 53.55, H 5.91, Cl 4.16, N 3.29; found C 53.41, H 6.00, Cl 4.02, N 3.39%.

**3b:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3301 (w), 3214 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.34–6.88 (m, 20H, Ph), 5.09, 4.92 (br, 2H, Ir-NH<sub>2</sub>), 4.19 (qnt, 6H,  $\text{CH}_2$ ), 3.53 (q, 1H, NH), 2.51 (d, 3H, NCH<sub>3</sub>), 1.37 (t, 9H,  $\text{CH}_3$  phos), 1.71 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 73.91 (s).  $\Lambda_{\text{M}} = 52.4 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{41}\text{H}_{56}\text{BClIrN}_2\text{O}_3\text{P}$  (894.35): calcd. C 55.06, H 6.31, Cl 3.96, N 3.13; found C 54.83, H 6.20, Cl 4.06, N 3.04%.

**4a:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3333 (w), 3221 (w);  $\delta_{\text{NH}_2}$ : 1598 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.35–6.86 (m, 25H, Ph), 5.86, 5.65 (br, 2H, Ir-NH<sub>2</sub>), 3.82 (d, 9H,  $\text{CH}_3$  phos), 5.60 (br, 1H, NH), 1.76 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 77.61 (s).  $\Lambda_{\text{M}} = 52.4 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{43}\text{H}_{52}\text{BClIrN}_2\text{O}_3\text{P}$  (914.34): calcd. C 56.48, H 5.73, Cl 3.88, N 3.06; found C 56.31, H 5.65, Cl 3.99, N 2.97%.

**4b:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3317, 3233 (m);  $\delta_{\text{NH}_2}$ : 1601 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.31–6.77 (m, 25H, Ph), 5.90, 5.82 (br, 2H, NH<sub>2</sub>), 5.54 (br, 1H, NH), 4.17 (qnt, 6H,  $\text{CH}_2$ ), 1.78 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ), 1.29 (t, 9H,  $\text{CH}_3$  phos).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 73.66 (s).  $\Lambda_{\text{M}} = 53.9 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{46}\text{H}_{58}\text{BClIrN}_2\text{O}_3\text{P}$  (956.42): calcd. C 57.77, H 6.11, Cl 3.71, N 2.93; found C 57.54, H 5.99, Cl 3.84, N 3.02%.

### 2.2.3. $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{R}1\text{NHNH}_2)_2]\text{P}(\text{OR})_3][\text{BPh}_4]$ (**5**, **6**) [ $R=\text{Me}$ (**5**), $\text{Ph}$ (**6**); $R=\text{Me}$ (**a**), $\text{Et}$ (**b**)]

In a 25-mL, three-necked, round-bottomed flask were placed 0.1 mmol of the appropriate compound **1**, two equivalents of  $\text{AgOTf}$  (0.2 mmol, 51 mg) and 5 mL of dichloromethane, and the reaction mixture was stirred for 24 h. After filtration to remove the  $\text{AgCl}$  formed, an excess of the appropriate hydrazine (0.3 mmol) was added and the resulting solution was stirred for 15 h. The solvent was removed under reduced pressure to leave an oil, which was treated with alcohol (2 mL) containing an excess of  $\text{NaBPh}_4$  (0.3 mmol, 103 mg). A yellow solid slowly separated out, which was filtered and crystallised from  $\text{CH}_2\text{Cl}_2$  and ROH; yield  $\geq 65\%$ .

**5a:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3326 (m), 3302 (w), 3249 (m);  $\delta_{\text{NH}_2}$ : 1608 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.37–6.87 (m, 40H, Ph), 3.69 (d, 9H,  $\text{CH}_3$  phos), 2.67 (br, 4H, Ir-NH<sub>2</sub>), 2.53 (br, 2H, NH), 2.39 (d, 6H, NCH<sub>3</sub>), 1.69 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 77.68 (s).  $\Lambda_{\text{M}} = 128 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{63}\text{H}_{76}\text{B}_2\text{IrN}_4\text{O}_3\text{P}$  (1182.12): calcd. C 64.01, H 6.48, N 4.74; found C 63.78, H 6.33, N 4.85%.

**6a:** IR (KBr pellet)  $\nu_{\text{NH}}$ : 3316, 3210 (m);  $\delta_{\text{NH}_2}$ : 1597 (m)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 7.37–6.62 (m, 50H, Ph), 5.43 (br, 6H, NH<sub>2</sub>NH), 3.49 (d, 9H,  $\text{CH}_3$  phos), 1.67 (d, 15H,  $\text{CH}_3$   $\text{C}_5\text{Me}_5$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 20 °C)  $\delta$ : 79.36 (s).  $\Lambda_{\text{M}} = 124 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$ .  $\text{C}_{73}\text{H}_{80}\text{B}_2\text{IrN}_4\text{O}_3\text{P}$  (1306.25): calcd. C 67.12, H 6.17, N 4.29; found C 67.34, H 6.08, N 4.20%.

Download English Version:

<https://daneshyari.com/en/article/7750814>

Download Persian Version:

<https://daneshyari.com/article/7750814>

[Daneshyari.com](https://daneshyari.com)