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Journal of Organometallic Chemistry 640 (2001) 10–20

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Preparation and characterization of ruthenium(II), rhodium(III) and iridium(III) complexes of isocyanide bearing the azo group

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Received 9 April 2001; received in revised form 30 July 2001; accepted 4 August 2001

Abstract

Reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ (**1**) (η^6-arene = *p*-cymene (**1a**), $1,3,5\text{-}Me_3C_6H_3$ (**1b**), $1,2,3\text{-}Me_3C_6H_3$ (**1c**) $1,2,3,4\text{-}Me_4C_6H_2$(**1d**), $1,2,3,5\text{-}Me_4C_6H_2$ (**1e**) and C_6Me_6 (**1f**)) or $[Cp^*MCl_2]_2$ (M = Rh (**2**), Ir (**3**); $Cp^* = C_5Me_5$) with 4-isocyanoazobenzene (RNC) and 4,4′-diisocyanoazobenzene (CN–R–NC) gave mononuclear and dinuclear complexes, $[(\eta^6\text{-arene})Ru(CNC_6H_4N{=}NC_6H_5)Cl_2]$ (**4a**–**f**), $[Cp^*M(CNC_6H_4N{=}NC_6H_5)Cl_2]$ (**5**: M = Rh; **6**: M = Ir), $[\{(\eta^6\text{-arene})RuCl_2\}_2\{\mu\text{-}CNC_6H_4N{=}NC_6H_4NC\}]$ (**8a**–**f**) and $[(Cp^*MCl_2)_2(\mu\text{-}CNC_6H_4N{=}NC_6H_4NC)\}]$ (**9**: M = Rh; **10**: M = Ir), respectively. It was confirmed by X-ray analyses of **4a** and **5** that these complexes have *trans*-forms for the –N=N– moieties. Reaction of $[Cp^*Rh(dppf)(MeCN)](PF_6)_2$ (dppf = 1,1′-bis (diphenylphosphino)ferrocene) with 4-isocyanoazobenzene gave $[Cp^*Rh(dppf)(CNC_6H_4N{=}NC_6H_5)](PF_6)_2$ (**7**), confirmed by X-ray analysis. Complex **8b** reacted with $Ag(CF_3SO_3)$, giving a rectangular tetranuclear complex **11b**, $[\{(\eta^6\text{-}1,3,5\text{-}Me_3C_6H_3)Ru(\mu\text{-}Cl\}_4(\mu\text{-}CNC_6H_4N{=}NC_6H_4NC)_2](CF_3SO_3)_4$ bridged by four Cl atoms and two μ-diisocyanoazobenzene ligands. Photochemical reactions of the ruthenium complexes (**4** and **8**) led to the decomposition of the complexes, whereas those of **5**, **7**, **9** and **10** underwent a *trans*-to-*cis* isomerization. In the electrochemical reactions the reductive waves about − 1.50 V for **4** and − 1.44 V for **8** are due to the reduction of azo group, $[\text{–N=N–}] \rightarrow [\text{–N=N–}]^{2-}$. The irreversible oxidative waves at ca. 0.87 V for the **4** and at ca. 0.85 V for **8** came from the oxidation of $Ru(II) \rightarrow Ru(III)$.

Keywords: Isocyanoazobenzene; Ruthenium; Rhodium; Iridium; Photochemical reaction; Electrochemical reaction

1. Introduction

Azobenzene and its derivatives are a versatile class of colored compounds and are used as dyes and pigments [1]. One of the most important requirements for a variable dye is good light stability. The photochemistry of azobenzene has been the subject of a great deal of research. Azobenzene and its derivatives were found to be characterized by reversible transformations from the generally stable *trans* form to the less stable *cis* form upon irradiation with UV or visible light [2]. Benzyl aryl ether dendrimers with azobenzene central linkers undergo reversible *cis*/*trans* isomerization of azobenzene moiety upon exposure to UV light [3]. They afforded luminescent liquid crystalline materials [4,5].

Isocyanide, compared to isoelectronic carbon monoxide, is able to show diverse electronic and steric properties as a ligand since it can bear a variety of substituents [6]. One of the great properties of isocyanide is a successive insertion different from carbon monooxide [7]. Previously, orthometallated complexes of azobenzene and its derivatives have been used as precursors for the preparation of 3-oxo-2-phenylindazoline [8] in the reaction with carbon monoxide or 3-imino-2-phenylindazolines [9] in the reaction with isocyanide. Recently we reported preparation and characterization of the tetranuclear complexes of pentamethylcyclopentadienyl-rhodium(III) and -iridium(III) bearing 1,4-diisocyano-2,3,5,6-tetramethylbenzene [10].

We were interested in chemical and physical behaviors of the complexes bearing both azo and isocyanide groups in the molecules. 4-Isocyanoazobenzene and 4,4′-diisocyanoazobenzene bearing an azo group were chosen as its candidate. We here report preparation, and photochemical and electrochemical behaviors of

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PII: S0022-328X(01)01189-5

arene ruthenium(II), and pentamethylcyclopentadienylrhodium(III) and -iridium(III) complexes containing 4-isocyanoazobenzene and 4,4′-diisocyanoazobenzene.

2. Experimental

All reactions were carried out under nitrogen atmosphere. Et_2O was distilled from $LiAlH_4$ and CH_2Cl_2 was distilled from CaH_2. Isocyanides [11], $[Cp^*MCl_2]_2$ (M = Rh [12], Ir [13]; Cp* = C_5Me_5), $[(\eta^6\text{-arene})RuCl_2]_2$ (arene = *p*-cymene, 1,3,5-$Me_3C_6H_3$, 1,2,3-$Me_3C_6H_3$, 1,2,3,4-$Me_4C_6H_2$, 1,2,3,5-$Me_4C_6H_3$, and C_6Me_6) [14] and $[Cp^*Rh(dppf)(MeCN)](PF_6)_2$ [15] (dppf = bis(diphenylphosphino)ferrocene) were prepared according to the literature. The infrared and electronic absorption spectra were measured on FTIR-5300 and U-best 30 spectrometers, respectively. NMR spectrometry was carried out on a Bruker AC250. ^1H-NMR spectra were measured at 250 MHz, and $^{31}P\{^1H\}$-NMR spectra were measured at 100 MHz using 85% H_3PO_4 as an external reference. In the photochemical isomerization, the resonances identified as the *cis*-form show the result of the ^1H-NMR spectrum after irradiation.

Spectral data: *trans*-4-isocyanoazobenzene: IR (nujol): 2118 cm^{-1} (2120 cm^{-1} (KBr)) [11]. UV–vis: λ_{max} 327 (log ε 4.36), 445 (2.82) nm (CH_2Cl_2); λ_{max} 326 (4.37), 439 (2.92) nm (DMF). ^1H-NMR (CD_3CN): δ 7.5 and 7.93 (c, ArH). ^1H-NMR spectrum (CD_3CN) after irradiation: *cis*-form: δ 7.3 and 6.9 (m, ArH). *trans*-4,4′-diisocyanoazobenzene: IR (nujol): 2126 cm^{-1} (2120 cm^{-1} (KBr)) [11]. UV–vis: λ_{max} 329 (log ε 4.38), 445 (2.93) nm (CH_2Cl_2); λ_{max} 329 (4.43), 443 (2.88) nm (DMF). ^1H-NMR ($CDCl_3$): δ 7.53 and 7.95 (AB system, J_{HH} = 8.5 Hz, ArH). ^1H-NMR spectrum ($CDCl_3$) after irradiation: *cis*-form: δ 7.52 and 6.83 ((AB system, J_{HH} = 8.5 Hz, ArH).

2.1. Preparation of $[(\eta^6\text{-arene})RuCl_2(CNC_6H_4N{=}NC_6H_5)]$ (4) and $[Cp^*MCl_2(CNC_6H_4N{=}NC_6H_5)]$ (**5**: M = Rh; **6**: M = Ir)

2.1.1. $[(\eta^6\text{-}p\text{-Cymene})RuCl_2(CNC_6H_4N{=}NC_6H_5)]$ (**4a**)

A mixture of $[(\eta^6\text{-}p\text{-cymene})RuCl_2]_2$ (**1a**) (51 mg, 0.083 mmol) and 4-isocyanoazobenzene (40 mg, 0.193 mmol) in CH_2Cl_2 (20 ml) was stirred at room temperature (r.t.) for 3 h. The solvent was removed and the residue was washed with Et_2O in order to remove isocyanide and recrystallized from CH_2Cl_2 and hexane, giving reddish orange crystals of **4a** (43 mg, 50%). IR (nujol): 2135 cm^{-1}. UV–vis: λ_{max} 341 (log ε 4.7) nm (CH_2Cl_2); λ_{max} 326 (log ε 4.09), 407 (3.93) nm (DMF). ^1H-NMR ($CDCl_3$): δ 1.37 (d, J_{HH} = 7.0 Hz, $CHMe_2$, 6H), 2.37 (s, C_6Me, 3H), 2.94 (sep. J_{HH} = 7.0 Hz, $CHMe_2$, 1H), 5.58, 5.76 (AB system, J_{HH} = 6.0 Hz, C_6H_4, 4H), 7.50–7.98 (m, ArH, 9H). Anal. Found: C, 53.03; H, 4.27; N, 8.01. Calc. for $C_{23}H_{23}Cl_2N_3Ru$: C, 53.80; H, 4.52; N, 8.18%.

The reactions were carried out as above, using the corresponsing ruthenium complexes. **4b** (61%). IR (nujol): 2147 cm^{-1}. UV–vis: λ_{max} 341 (log ε 4.53) nm (CH_2Cl_2); λ_{max} 350 (4.33) nm (DMF). ^1H-NMR ($CDCl_3$): δ 2.33 (s, C_6Me_3, 9H), 5.19 (s, C_6H_3, 3H) 7.50–7.96 (m, ArH, 9H). Anal. Found: C, 52.85; H, 4.21; N, 8.53. Calc. for $C_{22}H_{21}Cl_2N_3Ru$: C, 52.91; H, 4.24; N, 8.41%.

4c (46%). IR (nujol): 2136 cm^{-1}. UV–vis: λ_{max} 343 nm (CH_2Cl_2); λ_{max} 350 (4.24) nm (DMF). ^1H-NMR ($CDCl_3$): δ 2.14 (s, C_6Me, 3H), 2.26 (s, C_6Me_2, 6H), 5.39 (d, J_{HH} = 5.5 Hz, C_6H_2, 2H), 5.60 (t, J_{HH} = 5.5 Hz, C_6H, 1H), 7.50–7.96 (m, ArH, 9H). Anal. Found: C, 50.86; H, 4.21; N, 8.19. Calc. for $C_{22}H_{21}Cl_2N_3Ru\cdot 1/4CH_2Cl_2$: C, 51.33; H, 4.16; N, 8.07%. **4d** (61%). IR (nujol): 2143 cm^{-1}. UV–vis: λ_{max} 345 (4.55) nm (CH_2Cl_2); λ_{max} 352 (4.05) nm (DMF). ^1H-NMR ($CDCl_3$): δ 2.08 (s, C_6Me, 3H), 2.26, 2.27 (s, C_6Me_3, 9H), 5.24 (s, C_6H_2, 2H), 7.44–7.95 (m, ArH, 9H). Anal. Found: C, 53.16; H, 4.26; N, 8.21. Calc. for $C_{23}H_{23}Cl_2N_3Ru$: C, 53.80; H, 4.52; N, 8.18%. **4e** (68%). IR (nujol): 2149 cm^{-1}. UV–vis: λ_{max} 346 nm (CH_2Cl_2); λ_{max} 352 (4.35) nm (DMF). ^1H-NMR ($CDCl_3$): δ 2.10 (s, C_6Me_2, 6H), 2.15 (s, C_6Me_2, 6H), 5.37 (s, C_6H_2, 2H), 7.49–7.95 (m, ArH, 9H). Anal. Found: C, 53.06; H, 4.24; N, 8.01. Calc. for $C_{23}H_{23}Cl_2N_3Ru$: C, 53.80; H, 4.52; N, 8.18%. **4f** (68%). IR (nujol): 2132 cm^{-1}. UV–vis: λ_{max} 351 nm (CH_2Cl_2); λ_{max} 354 (4.46) nm (DMF). ^1H-NMR ($CDCl_3$): δ 2.19 (s, C_6Me_6, 18H), 7.44–7.95 (m, ArH, 9H). Anal. Found: C, 56.04; H, 4.90; N, 8.90. Calc. for $C_{25}H_{27}Cl_2N_3Ru$: C, 55.45; H, 5.03; N, 7.76%.

2.1.2. $[(Cp^*RhCl_2(CNC_6H_4N{=}NC_6H_5)]$ (**5**)

A mixture of $[Cp^*RhCl_2]_2$ (**2**) (51 mg, 0.083 mmol) and 4-isocyanoazobenzene (39 mg, 0.19 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 3 h. The solvent was concentrated and Et_2O was added, giving orange powder of *trans*-**5** (67 mg, 79%). IR (nujol): 2170 cm^{-1}. UV–vis: λ_{max} 334 (4.35) nm (CH_2Cl_2); λ_{max} 370 (4.18), 381 (4.18) nm (DMF). ^1H-NMR ($CDCl_3$): *trans*-form: δ 1.84 (s, C_5Me_5, 15H), 7.50–7.63 (m, ArH), 7.90–7.97 (m, ArH). Anal. Found: C, 52.58; H, 4.68; N, 7.91. Calc. for $C_{23}H_{24}Cl_2N_3Rh\cdot 1/4CH_2Cl_2$: C, 51.95; H, 4.59; N, 7.82%. ^1H-NMR spectrum ($CDCl_3$) after the photochemical reaction: *cis*-**5**: δ 1.81(s, C_5Me_5, 15H), 6.77–6.86 (m, ArH), 7.20–7.40 (m, ArH). *cis*/*trans* = 19/81.

Complex *trans*-**6** (58%) is prepared according to the method described above. IR (nujol): 2154 cm^{-1}. UV–vis: λ_{max} 344 (4.43) nm (CH_2Cl_2); λ_{max} 333 (4.28), 352 (4.29) nm (DMF). ^1H-NMR ($CDCl_3$): δ 1.88 (s, C_5Me_5, 15H), 7.50–7.57 (m, ArH), 7.90–7.97 (m, ArH). Anal. Found: C, 45.88; H, 4.06; N, 7.10. Calc. for

$C_{23}H_{24}Cl_2IrN_3$: C, 45.62; H, 3.99; N, 6.84%. ^{1}H-NMR spectrum ($CDCl_3$) after the photochemical reaction: *cis*-**6**: δ 1.84 (s, C_5Me_5, 15H), 6.78–6.86 (m, Ar*H*), 7.20–7.30 (m, Ar*H*). *cis*/*trans* = 17/83.

2.2. Preparation of [Cp*Rh(dppf)(CNC$_6$H$_4$N=NC$_6$H$_5$)](PF$_6$)$_2$ (7)

To a solution of [Cp*Rh(dppf)(MeCN)](PF_6)$_2$ (56 mg, 0.05 mmol) in acetone (10 ml) was added 4-isocyanoazobenzene (11 mg, 0.05 mmol). After stirring for 0.5 h, the solvent was reduced to 2 ml under reduced pressure and Et_2O was added, giving reddish orange crystals of *trans*-**7** (56 mg, 97%). ^{1}H-NMR (CD_3CN): δ 1.32 (t, J_{PH} = 3.9 Hz, C_5Me_5, 30H), 4.42 (s, C_5H, 1H), 4.59 (s, C_5H, 1H), 4.69 (s, C_5H, 1H), 4.73 (s, C_5H, 1H), 7.4–8.3 (m, Ar*H*, 9H). Anal. Found: C, 53.00; H, 4.03; N, 3.19. Calc. for $C_{57}H_{52}F_{12}FeN_3P_4Rh$: C, 53.08; H, 4.06; N, 3.26%. ^{1}H-NMR spectrum (CD_3CN) after the photochemical reaction: *cis*-**7**: δ 1.28 (s, C_5Me_5, 15H). *cis*/*trans* = 12/88.

2.3. Preparation of [{η^6-arene)$_2$Ru$_2$Cl$_4$}-{μ-CNC$_6$H$_4$N=NC$_6$H$_4$NC}] (8) and [{Cp$^*_2$M$_2$Cl$_4$}-{μ-CNC$_6$H$_4$N=NC$_6$H$_4$NC}] (9: M = Rh; 10: M = Ir)

2.3.1. [{η^6-p-Cymene)$_2$Ru$_2$Cl$_4$}-{μ-CNC$_6$H$_4$N=NC$_6$H$_4$NC}] (8a)

To a solution of [(η^6-*p*-cymene)$RuCl_2$]$_2$ (50 mg, 0.082 mmol) in CH_2Cl_2 (30 ml) was added 4,4′-diisocyanoazobenzene (47 mg, 0.202 mmol) at r.t. After several minutes, the brown powder of **8a** (60 mg, 87%) precipitated and was filtered and washed with Et_2O. IR (nujol): 2141 cm^{-1}. UV–vis: λ_{max} 365 nm (CH_2Cl_2); λ_{max} 364 (4.42), 410 (4.36) nm (DMF). Anal. Found: C, 48.63; H, 4.34; N, 6.44. Calc. for $C_{34}H_{36}Cl_4N_4Ru_2$: C, 48.35; H, 4.30; N, 6.63%.

2.3.2. [{η^6-1,3,5-Me$_3$C$_6$H$_3$)$_2$Ru$_2$Cl$_4$}-{μ-CNC$_6$H$_4$N=NC$_6$H$_4$NC}] (8b)

To a solution of [(η^6-1,3,5-$Me_3C_6H_3$)$RuCl_2$]$_2$ (102 mg, 0.175 mmol) in CH_2Cl_2 (40 ml) was added 4,4′-diisocyanoazobenzene (47 mg, 0.202 mmol) at r.t. After 3h, the solvent was removed and the residue was washed with Et_2O. After the powder was dissolved in CH_2Cl_2, Et_2O was added, precipitating brown powder of **8b** (86 mg, 60%). IR (nujol): 2139 cm^{-1}. UV–vis: λ_{max} 364 nm (CH_2Cl_2); λ_{max} 371 (4.49) nm (DMF). ^{1}H-NMR ($CDCl_3$): δ 2.33 (s, C_6Me_3, 18H), 5.20 (s, C_6H_3, 6H), 7.52, 7.94 (AB system, J_{HH} = 8.5 Ar*H*, 8H). Anal. Found: C, 46.83; H, 3.94; N, 7.13. Calc. for $C_{32}H_{32}Cl_4N_4Ru_2$: C, 47.07; H, 3.95; N, 6.86%.

According to the procedure similar to that of **8b**, the following complexes were prepared.

8c (46%). IR (nujol): 2149 cm^{-1}. UV–vis: λ_{max} 366(log ε 4.53) nm (CH_2Cl_2); λ_{max} 372 (4.58) nm (DMF). ^{1}H-NMR (DMSO-d_6): δ 1.99, 2.13, 2.22 (s, C_6Me, 18H), 5.70 (d, J_{HH} = 6.0 Hz, C_6H_2, 4H), 5.92 (t, J_{HH} = 6.0 Hz, C_6H, 2H), 7.81, 8.09 (AB system, J_{HH} = 8.5Hz, Ar*H*, 8H). Anal. Found: C, 47.23; H, 3.97; N, 7.28. Calc. for $C_{32}H_{32}Cl_4N_4Ru_2$: C, 47.07; H, 3.95; N, 6.86%. **8d** (30%). IR (nujol): 2130 cm^{-1}. UV–vis: λ_{max} 379 nm (CH_2Cl_2); λ_{max} 372 (4.38) nm (DMF). ^{1}H-NMR ($CDCl_3$): δ 2.08 (C_6Me, 6H), 2.26, 2.27 (s, C_6Me_3, 18H), 5.24 (s, C_6H_2, 4H), 7.58, 7.94 (AB system, J_{HH} = 8.5Hz, Ar*H*, 8H). Anal. Found: C, 47.58; H, 4.16; N, 7.15. Calc. for $C_{34}H_{36}Cl_4N_4Ru_2$: C, 48.35; H, 4.30; N, 6.63%. **8e** (50%). IR (nujol): 2149 cm^{-1}. UV–vis: λ_{max} 374 nm (CH_2Cl_2); λ_{max} 374 (4.16) nm (DMF). ^{1}H-NMR (DMSO-d_6): δ 2.02, 2.07, 2.12, 2.18 (s, C_6Me, 24H), 5.24 (s, C_6H_2, 4H), 7.80, 8.07 (AB system, J_{HH} = 8.5Hz, Ar*H*, 8H). Anal. Found: C, 48.53; H, 4.36; N, 6.63. Calc. for $C_{34}H_{36}Cl_4N_4Ru_2$: C, 48.35; H, 4.30; N, 6.63%. **8f** (67%). IR (nujol): 2148 cm^{-1}. UV–vis: λ_{max} 374 nm (CH_2Cl_2); λ_{max} 377 (4.38) nm (DMF). ^{1}H-NMR (DMSO-d_6): δ 2.10 (s, C_6Me_6, 36H), 7.77, 8.07 (AB system, J_{HH} = 8.5 Hz, Ar*H*, 8H). Anal. Found: C, 48.10; H, 5.00; N, 6.22. Calc. for $C_{38}H_{44}Cl_4N_4Ru_2\cdot 3/4CH_2Cl_2$: C, 48.26; H, 4.76; N, 5.81%.

2.3.3. [{Cp$^*_2$Rh$_2$Cl$_4$}{μ-CNC$_6$H$_4$N=NC$_6$H$_4$NC}] (9)

To a solution of [Cp*$RuCl_2$]$_2$ (50 mg, 0.081 mmol) in CH_2Cl_2 (20 ml) was added 4,4′-diisocyanoazobenzene (23 mg, 0.10 mmol) at r.t. After 3 h, the solvent was concentrated and Et_2O was added, giving orange powder of *trans*-**9** (62 mg, 90%). IR (nujol): 2172 cm^{-1}. UV–vis: λ_{max} 355 nm (CH_2Cl_2); λ_{max} 413 (4.43) nm (DMF). ^{1}H-NMR ($CDCl_3$): *trans*-**9**: δ 1.84 (s, C_5Me_5, 30H), 7.65, 7.99 (AB system, J_{HH} = 8.5Hz, Ar*H*, 8H). Anal. Found: C, 47.04; H, 4.58; N, 6.35. Calc. for $C_{34}H_{38}Cl_4N_4Rh_2\cdot 1/4CH_2Cl_2$: C, 47.20; H, 4.45; N, 6.43%. ^{1}H-NMR spectrum ($CDCl_3$) after the photochemical reaction: *cis*-**9**: δ 1.83 (s, C_5Me_5, 30H), 7.43, 6.87 (AB system, J_{HH} = 8.5 Hz, Ar*H*, 8H). *cis*/*trans* = 47/53.

A reaction was carried out as above, using **3**. *trans*-**10** (68%): IR (nujol): 2182 cm^{-1}. UV–vis: λ_{max} 369 nm (CH_2Cl_2); λ_{max} 372 (4.43) nm (DMF). ^{1}H-NMR ($CDCl_3$): δ 1.88 (s, C_5Me_5, 30H), 7.59, 7.97 9 (AB system, J_{HH} = 8.5 Hz, Ar*H*, 8H). Anal. Found: C, 39.72; H, 3.86; N, 5.40. Calc. for $C_{34}H_{38}Cl_4Ir_2N_4$: C, 39.69; H, 3.72; N, 5.45%. ^{1}H-NMR spectrum ($CDCl_3$) after the photochemical reaction: *cis*-**10**: δ 1.87 (s, C_5Me_5, 30H), 7.34, 7.84 (AB system, J_{HH} = 8.5 Hz, Ar*H*, 8H). *cis*/*trans* = 6/94.

2.4. Preparation of [{η^6-1,3,5-Me$_3$C$_6$H$_3$)$_4$Ru$_4$(μ-Cl)$_4$}-{μ-CNC$_6$H$_4$N=NC$_6$H$_4$NC}$_2$](CF$_3$SO$_3$)$_4$ (11b)

A solution of **8b** (199 mg, 0.244 mmol) and Ag(CF_3SO_3) (143 mg, 9.557 mmol) in acetone (35 ml) and CH_2Cl_2 (35 ml) was stirred for 10 h at r.t. The solvent was removed under reduced pressure and the residue was extracted with EtOH. EtOH was concentrated and Et_2O was added, giving reddish brown solid of **11b** (75 mg, 29.4%). IR (nujol): 2175 cm^{-1}. UV–vis: λ_{max} 348 nm (CH_2Cl_2); λ_{max} 412 (4.41) nm (DMF). ^1H-NMR (dmso-d_6): δ 2.21 (s, C_6Me_3, 36H), 6.76 (s, C_6H_3, 12H), 7.78, 8.05 (m, ArH, 16H). Anal. Found: C, 39.12; H, 3.30; N, 5.08. Calc. for $C_{68}H_{64}Cl_4F_{12}N_8O_{12}Ru_2S_4$: C, 39.12; H, 3.09; N, 5.37%.

2.5. Data collection

4,4′-Diisocyanoazobenzene and complexes (**4a**, **5** and **7**·$2H_2O$) were recrystallized from CH_2Cl_2–ether. Cell constants were determined from 20 reflections on Rigaku four-circle automated diffractometer AFC5S. Data collection was carried out by a Rigaku AFC5S refractometer at r.t. Intensities were measured by the $2\theta-\omega$ scan method using Mo–K_α radiation ($\lambda = 0.71069$ Å). Throughout the data collection the intensities of the three standard reflections were measured every 200 reflections as a check of the stability of the crystals and no decay was observed. Intensities were corrected for Lorentz and polarization effects. The absorption correction was made with the ψ scan method. Atomic scattering factors were taken from Cromer and Waber with the usual tabulation [16]. Anomalous dispersion effects were included in F_{calc} [17]; the values of $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [18]. All calculations were performed using the teXsan crytallographic software package [19].

2.6. Determination of the structures

Structures of **4a**, **5** and **7** except 4,4′-diisocyanoazobenzene solved by direct methods were solved by Patterson methods. The positions of nonhydrogen atoms of **5**, except two Rh, four Cl and three N atoms refined anisotropically, were refined isotropically by using full-matrix least-squares methods. The positions of all nonhydrogen atoms of the complexes except **5** were refined with anisotropic thermal parameters by using full-matrix least-squares methods. All hydrogen atoms were calculated at the ideal positions with the C–H distance of 0.95 Å, but not refined.

2.7. Photochemical reaction

A $CDCl_3$ or MeCN solution of isocyanide or complex (20 mg) in a NMR tube was set away about 10 cm from a 500 W high pressure mercury lamp and irradiated for 1–5 h. After the reaction was over, ^1H-NMR and electronic spectra were measured.

2.8. Electrochemical reaction

A potential scanning unit model 312 (Fuso) was employed for cyclic voltammetry. The electrolytic cell consisted of a conventional three-electrode system. Working electrode used was a Pt disk electrode (0.02 cm^2). A Pt wire was used as a counter electrode. The reference electrode was Ag | $AgNO_3$ (0.1 mol dm^{-3})–[n-Bu_4N](ClO_4)–MeCN (0.1 mold dm^{-3}) system, whose potential was determined relative to a ferrocene(Fc) | ferrocenium(Fc^+) couple (1×10^{-3} mol dm^{-3}), whose potential was 145 mV versus a reference electrode. The supporting electrolyte was tetra-n-butylammonium perchlorate. Electrochemical measurements were carried out in a 0.1 M solution of [n-Bu_4N](ClO_4)–MeCN under an atmosphere of nitrogen at r.t. after the solution was deaerated by bubbling with nitrogen.

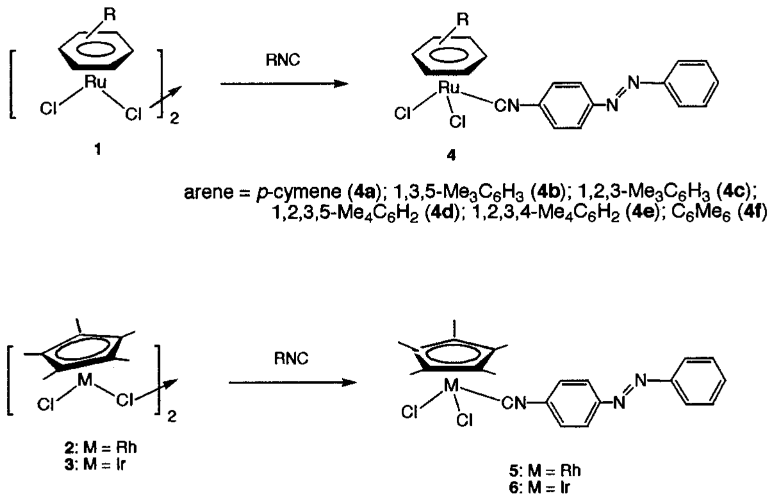
3. Results and discussion

3.1. 4-Isocyanoazobenzene complexes

Bis[dichloro(η^6-arene)ruthenium(II)] (arene = p-cymene (**1a**), 1,3,5-$Me_3C_6H_3$ (**1b**), 1,2,3-$Me_3C_6H_3$ (**1c**), 1,2,3,5-$Me_4C_6H_2$ (**1d**), 1,2,3,4-$Me_4C_6H_2$ (**1e**), 1,2,3,4,5,6-Me_6C_6 (**1f**)), or bis[dichloro(pentamethylcyclopentadienyl)rhodium(III) or -iridium(III)] (**2**: M = Rh; **3**: M = Ir) reacted readily with 4-isocyanoazobenzene, giving the corresponding complexes, (η^6-arene)$RuCl_2$($CNC_6H_4N{=}NC_6H_5$) (**4a**–**f**) and Cp*MCl_2($CNC_6H_4N{=}NC_6H_5$) (**5**: M = Rh; **6**: M = Ir), respectively (Scheme 1). The IR spectra of complexes (**4a**–**f**, **5**, **6**) showed a strong band due to a N–C triplebond around 2140 cm^{-1}. The structures of these complexes were determined by X-ray analyses of **4a** and **5**. The molecules have the piano-stool structures and the azobenzene ligands are *trans*-configuration (Figs. 1 and 2).

The ^1H-NMR spectrum of **4a** showed a doublet at δ 1.37, a singlet at δ 2.37 and a septet at δ 2.94, assigned to isopropyl methyl, methyl and methine protons, respectively, consisting with the structure in the solid state. No isomers were observed in the ^1H-NMR spectra of other ruthenium(II) complexes (**4b**–**f**). The ^1H-NMR spectrum of **5** showed a singlet δ 1.84 due to Cp* protons and two multiplets at δ 7.50–7.63 and δ 7.90–7.97 due to aromatic protons. A similar NMR behavior was observed for **6**. These results suggested that all complexes (**4a**–**f**, **5**, **6**) are assumed to have the *trans*-structure for the –N=N– moieties in the solid state and in solution.

trans-Azobenzene is known to show two absorption bands at λ_{max} 315 and 440 nm assignable to the π–π* and n–π* transitions, respectively [1]. The electronic spectrum of 4-isocyanoazobenzene showed two bands



Scheme 1. Reactions of [(η^6-arene)RuCl$_2$]$_2$ or [Cp*MCl$_2$]$_2$ (M = Rh, Ir) with 4-isocyanoazobenzene.

at λ_{max} 326 (log ε 4.37) and 439 (2.92) nm in CH$_2$Cl$_2$ and λ_{max} 327 (4.36) and 445 (2.82) nm in DMF, respectively. The former is attributable to the π–π* transition, and the latter is due to the n–π* transition in each solution. The MLCT band has been observed around 400 nm with $\varepsilon = 10^3$ dm^3 mol^{-1} cm^{-1} in the UV–vis spectra of the arene ruthenium(II) complexes (η^6-arene)RuCl$_2$L (L = PPh$_3$, XylNC, P(OMe)$_3$, pyridine etc.) [20]. The UV–vis spectra of **4a**–**f** appeared at λ_{max} 341–351 nm in CH$_2$Cl$_2$ and at λ_{max} 350–354 nm in DMF with a molar extinction coefficient (ε) of 10^4 dm^3 mol^{-1} cm^{-1}. From these results and high ε values, the band around λ_{max} 350 nm with $\varepsilon = 10^4$ dm^3 mol^{-1} cm^{-1} for **4a**–**f** may be assigned to a mixture of the π–π* transition and MLCT band, in which the transition energy is ca. 24 kJ mol^{-1} lower than that (λ_{max} 327 nm) of free 4-isocyanoazobenzene ligand.

Reaction of [Cp*Rh(dppf)(MeCN)](PF$_6$)$_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with 4-isocyanoazobenzene gave the reddish orange complex **7** formulated as [Cp*Rh(dppf)(CNC$_6$H$_4$N=NC$_6$H$_5$)](PF$_6$)$_2$ (Scheme 2). It was confirmed by X-ray analysis that the molecule has a chelate dppf ligand, and the –N=N– moiety is a *trans*-form (Fig. 3). The ^{1}H-NMR spectrum showed a triplet at δ 1.32 by coupling with two P atoms due to Cp* protons and four singlets at δ 4.42, 4.59, 4.69 and 4.73 due to cyclopentadienyl protons of ferrocene. The inequivalence of the cyclopentadienyl protons is responsible for the rigid ferrocene moiety arising from the chelation of the dppf ligand. A similar NMR behavior has been observed in [(η^6-arene)RuCl(dppf)](PF$_6$) [15].

3.2. 4,4′-Diisocyanoazobenzene complexes

4,4′-Diisocyanoazobenzene was prepared by a literature method. The *trans*-structure was confirmed by

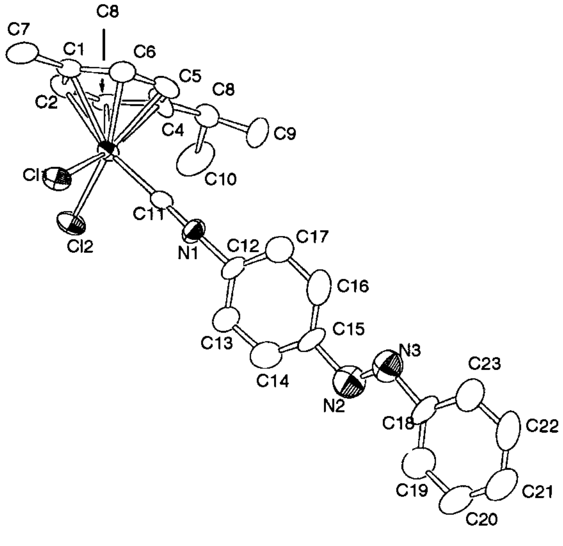


Fig. 1. Molecular structure of **4a**.

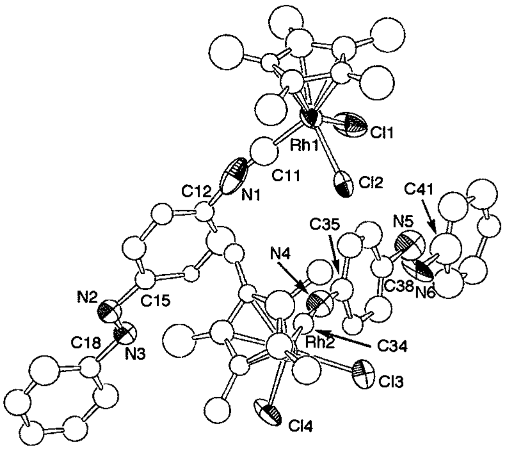
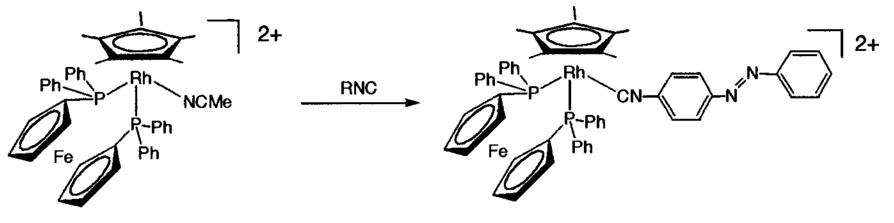


Fig. 2. Molecular structure of **5**.



Scheme 2. Reaction of [Cp*Rh(dppf)(MeCN)]$(PF_6)_2$ with 4-isocyanoazobenzene. The PF_6 atoms were omitted for clarity.

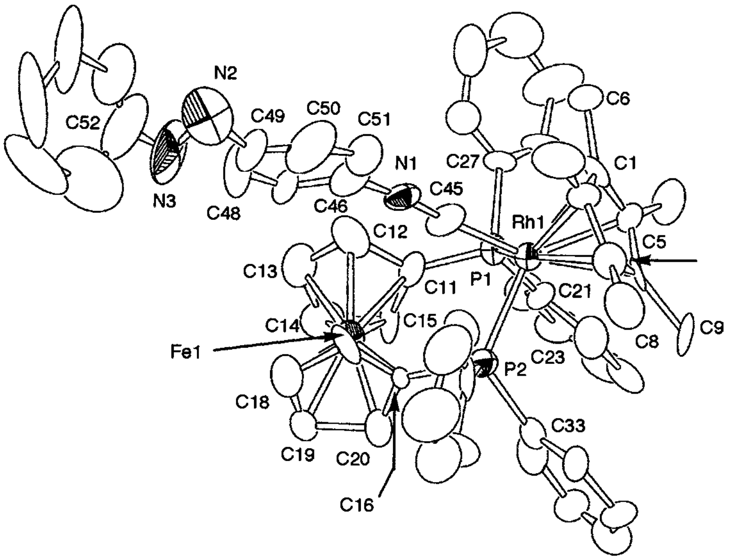


Fig. 3. Molecular structure of **7**. The PF_6 anions and H_2O were omitted for clarity.

X-ray analysis (Fig. 4). The ^{1}H-NMR spectrum showed an AB system consisting of resonances at δ 7.53 and 7.95 ($J_{HH} = 8.5$ Hz), and no isomer was spectroscopically observed.

When complexes (**1a**–**f**, **2**, and **3**) were treated with 4,4′-diisocyanoazobenzene in CH_2Cl_2 at room temperature, brown or orange powders, formulated as [{(η^6-arene)$RuCl_2$}$_2$(μ-$CNC_6H_4N{=}NC_6H_4NC$)] (**8a**–**f**) and [$(Cp^*MCl_2)_2$(μ-$CNC_6H_4N{=}NC_6H_4NC$)] (**9**: M = Rh; **10**: M = Ir), respectively, were obtained in high yields (Scheme 3). The IR spectra of these complexes showed a sharp band due to a N–C triple bond in the region 2125–2150 cm^{-1}. The ^{1}H-NMR spectra showed the absence of isomers. A characteristic feature in the ^{1}H-NMR spectra is an observation of an AB system for *o*- and *m*-protons of 4,4′-diisocyanoazobenzene as well as that for free isocyanide. The structures of these complexes were assumed to have the *trans*-forms for the –N=N– moieties in the solid state and solution, similar to the structure of free 4,4′-diisocyanoazobenzene.

The electronic spectra of **8a**–**f** indicated an absorption band at ca. 370 nm, again assignable to a mixture of the π–π^* transition and MLCT band, which appeared in the lower energy region of ca. 40 kJ mol^{-1} in comparison with the π–π^* transition (λ_{max} 329) of free 4,4′-diisocyanoazobenzene. The π–π^* energy difference between free diisocyanide and the dinuclear complexes **8a**–**f** is about two times larger in comparison with that between free 4-isocyanoazobenzene and the mononuclear complexes **4**. A similar trend was observed for rhodium(III) and iridium(III) complexes of 4-isocyanoazobenzene or 4,4′-diisocyanoazobenzene.

When **8b** in a mixture of CH_2Cl_2 and acetone was treated with $Ag(CF_3SO_3)$ in a 1:2 molar ratio, brown powder **11b** with the empirical formula as [{(η^6-

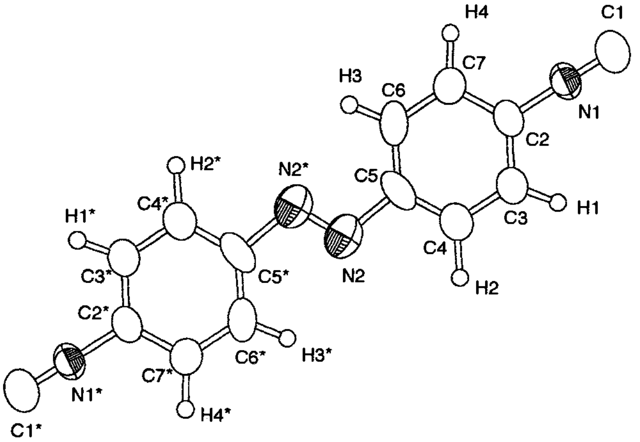
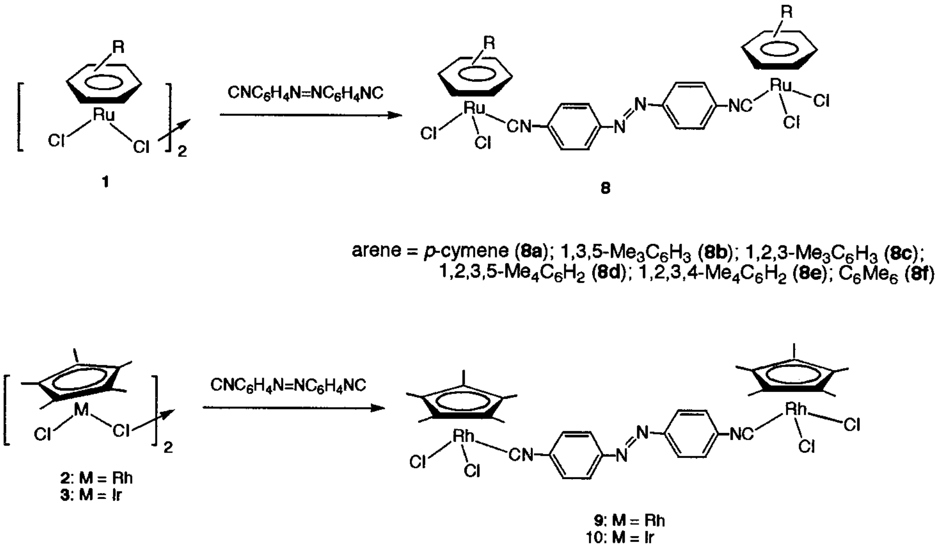
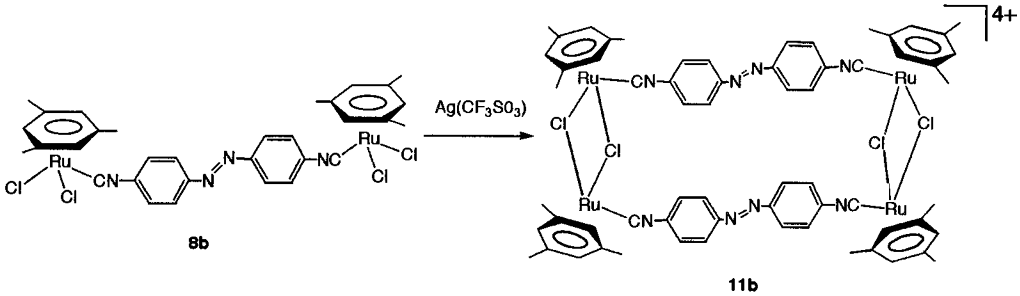


Fig. 4. Molecular structure of 4,4′-diisocyanoazobenzene.



Scheme 3. Reactions of $[(\eta^6\text{-arene})RuCl_2]_2$ or $[Cp^*MCl_2]_2$ (M = Rh, Ir) with 4-isocyanoazobenzene or 4,4′-diisocyanoazobenzene.



Scheme 4. Reaction of **8b** with $Ag(CF_3SO_4)$. The CF_3SO_3 anions were omitted for clarity.

$1,3,5\text{-}Me_3C_6H_3)_2Ru_2Cl_2\}(\mu\text{-}CNC_6H_4N{=}NC_6H_4NC)](CF_3SO_3)_2$ from an elementary analysis was obtained. The IR spectrum showed a sharp N–C triple bond at 2175 cm^{-1}. The ^1H-NMR spectrum in dmso-d_6 showed two singlets at δ 2.21 and 6.76 in a 3:1 intensity ratio, assignable to methyl and aromatic protons of the arene ring, respectively, suggesting a symmetric structure. Based on the 18 electron rule and the formation of the tetranuclear chloro-bridged complex $[\{Cp^*M(\mu\text{-}Cl)\}_4(\mu\text{-}1,4\text{-}(CN)_2\text{-}2,3,5,6\text{-}Me_4C_6)_2](CF_3SO_3)_4$ (M = Rh, Ir) from the reaction of the dimeric complex $[\{Cp^*MCl_2\}_2(\mu\text{-}1,4\text{-}(CN)_2\text{-}2,3,5,6\text{-}Me_4C_6)]$ with $Ag(CF_3SO_3)$ [10], the complex cation **11b** was assumed to have a rectangular structure bridged by four Cl atoms and two diisocyanide ligands with the *trans* –N=N– moieties, in which the rectangular core consists of the Rh···Rh separations of ca. 3.7 and ca. 18 Å on the basis of X-ray analytical data of **4a** and known Cl-bridged complexes [10] (Scheme 4).

3.3. Photochemical reactions

The photochemical isomerization of azobenzene is known. The photochemical isomerizations of free azobenzenes and azobenzene complexes were examined by monitoring the intensity ratio of the aromatic protons or pentamethylcyclopentadienyl protons. In the ^1H-NMR spectra of *trans*-isomers of 4-isocyanoazobenzene and 4,4′-diisocyanoazobenzene, the aromatic protons appeared around δ 7.9 and 7.5; the former showed complicate resonances and the latter showed an AB system. When 4-isocyanoazobenzene in CD_3CN was irradiated with high-pressure mercury lamp for 1–5 h, new resonances due to the aromatic protons in the *cis*-isomer appeared in the higher magnetic field at δ ca. 7.3 and 6.8 (Fig. 5). From the *cis*/*trans* intensity ratio, the *cis*/*trans* ratio is calculated to be ca. 24/76. An up-field shift of an AB system to δ 7.52 and 6.83 was observed for the photolysis of 4,4′-diisocyanoazobenzene and the *cis*/*trans* ratio was ca. 12/88. No attempts to isolate the *cis*-isomer were made. The chemical shifts of *cis*-isomer have been often known to appear at a higher field than those of *trans*-isomer [21]. The photoinduced conversion of *trans*- to *cis*-complex was also observed by ^1H-NMR spectroscopy. For example, the Cp* protons in *trans*-**5** appear at δ 1.84 as a singlet. After irradiation of the NMR sample ($CDCl_3$) of *trans*-**5**, a new singlet for Cp* protons of *cis*-**5** appeared at δ

1.81 in addition to a singlet for *trans*-**5**, and the *cis*/*trans* ratio was 19/81.

In the electronic spectrum, the absorption band at λ_{max} 333 nm due to the *trans*-**5** decreased and a shoulder band at ca. 450 nm increased slightly with irradiation times. This type of behavior is also observed in the *trans* to *cis* isomerization of various azobenzene derivatives [22]. The photochemical reactions of *trans*-**6**, **-9** and **-10** showed the isomerization to the corresponding *cis*-form. From ^{1}H-NMR spectroscopy, the *cis*/*trans* isomer ratios were calculated as 17/83, 47/53 and 6/94 for **6**, **9** and **10**, respectively. The *trans*- to *cis*-isomerization except **9** is very low. The photochemistry of *trans*-**7** isomerized with the *cis*/*trans* ratio of 12/88. Reverse reaction from *cis*- to *trans*-form was very slow even in the dark.

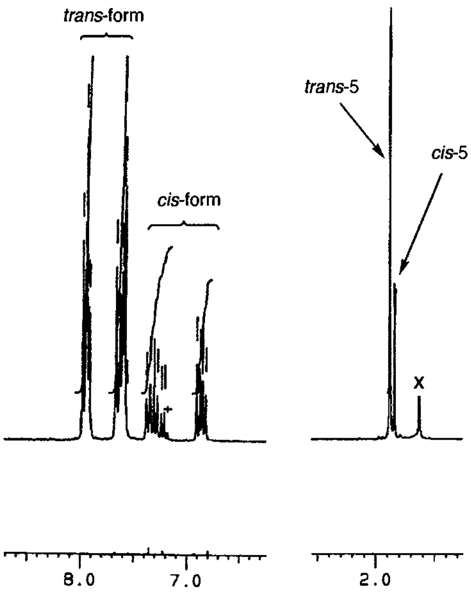


Fig. 5. ^{1}H-NMR spectra: phenyl protons of *cis* and *trans*-4-isocyanobenzene (left) and Cp* protons of *cis* and *trans*-5 (right).

Table 1
CV data of ruthenium(II), rhodium(III) and iridium(III) complexes [a]

Complex	E_{pc} (V)	E_{pa} (V)	Complex	E_{pc} (V)	E_{pa} (V)
4a	−1.54	0.92	**8a**	−1.47	[b]
4b	−1.48	0.90	**8b**	−1.40	0.91
4c	−1.48	0.85	**8c**	−1.45	0.89
4d	−1.48	0.88	**8d**	−1.41	0.90
4e	−1.49	0.83	**8e**	−1.43	0.85
4f	−1.49		**8f**	−1.39	0.80
	0.72	0.81 [c]			
5	−1.43	[b]	**9**	−1.56	[b]
6	−1.51	1.05	**10**	−1.58	[b]

[a] Potentials are against Fc | Fc$^+$, sweep rate 0.1 (V s^{-1}). $\Delta E = |E_{pa} - E_{pc}|$.

[b] No clear peaks were observed.

[c] $E_{1/2} = 0.76$ V, $\Delta E = 0.09$ V.

3.4. Cyclic voltammetry of ruthenium complexes

The cyclic voltammetry (CV) was measured using a platinum electrode in CH_3CN–CH_2Cl_2 (1:1) containing [n-Bu_4N](ClO_4) as a supporting reagent. The potentials were monitored versus a ferrocene | ferrocenium couple (Fc | Fc$^+$). The CV of ruthenium complexes (**4a**–**e**, **8a**–**f**) except **4f** showed irreversible reductive and oxidative waves. The reductive potentials appeared at −1.54 to −1.48 V for the mononuclear complexes (**4a**–**e**) and at −1.47 to −1.39 V for the dinuclear complexes (**8a**–**f**), suggesting that the dinuclear complexes were easily reduced in comparison with the mononuclear complexes (Table 1).

These reductive potentials are assigned to the reduction of the azo group, [–N=N–] → [–N=N–]$^{2-}$, from the facts below. (1) No reductive waves around −1.5 V were observed in the complexes such as [(η^6-arene)$RuCl_2L$] and [Cp*MCl_2L] (L = XylNC, PPh_3; M = Rh, Ir) without containing the azobenzene ligand, and (2) the reductive potentials about −1.5 V are similar to that of 4-isocyanoazobenzene which shows a quasi-reversible wave at $E_{1/2} = -1.65$ V, attributable to a [–N=N–]$^{2-}$ | [–N=N–] couple on the basis of a redox potential of azobenzene [1]. Ease of the reduction of the azo group by the formation of complexes may be related with the π–π* energy gap.

The redox potential of 0.76 V for **4f** is quasi-reversible from $I_{pc}/I_{pa} = 1.2$ and the difference between oxidative and reductive potentials ($\Delta E = 0.09$ V), whereas other complexes showed the irreversible oxidative waves at 0.83–0.92 V for **4** and at 0.80–0.91 V for **8**, suggesting that the HOMO energy level in both complexes are not significantly different. These oxidative waves are attributable to the change from the Ru(II) to Ru(III) state, from comparison with that of [(η^6-arene)$RuCl_2L$] [20]. The reductive and oxidative potentials were independent of the substituent of the arene ring.

3.5. Molecular structures

Crystal data are shown in Table 2.

3.5.1. Crystal structure of 4,4′-diisocyanoazobenzene

Some selected bond lengths and angles are listed in Table 3. The molecule has a crystallographically imposed inversion center in the middle of the N···N* vector. The molecule is a *trans*-form and the two benzene rings are coplanar with the N–N double bond. The N(1)–C(1) bond length of 1.135(4) Å is in agreement with a usual triple bond. The N(1)–C(2) bond length of 1.391(4) Å is shorter than the N(2)–C(5) bond length, due to difference between the sp–sp^2 and sp^2–sp^2 bonds. The N(2)–N(2)* of 1.207(5) Å is in the usual N–N double bond. The C(1)–N(1)–C(2) bond angle is

Table 2
Crystal data of 4,4′-diisocyanoazobenzene, (*p*-cymene)$RuCl_2(CNC_6H_4N{=}NC_6H_5)$ (**4a**), $Cp^*RhCl_2(CNC_6H_4N{=}NC_6H_5)$ (**5**) and $[(\eta^5\text{-pentamethylcyclopentadienyl})Rh(dppf)(CNC_6H_4N{=}NC_6H_5)](PF_6)_2\cdot 2H_2O$(**7**·$2H_2O$)

Compound	Diisocyanide	**4a**	**5**	**7**·$2H_2O$
Empirical formula	$C_{14}H_8N_4$	$C_{23}H_{23}N_3Cl_2Ru$	$C_{46}H_{48}N_6Cl_4Rh_2$	$C_{57}H_{56}N_3F_{12}P_4O_2FeRh$
Molecular weight	232.2	513.4	1032.6	1325.7
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/a$ (No. 14)
Lattice parameters				
a (Å)	4.723(3)	12.10(1)	9.151(7)	13.836(4)
b (Å)	10.469(4)	7.78(2)	18.028(6)	20.644(5)
c (Å)	12.170(2)	23.67(1)	29.10(1)	20.487(5)
α (°)	90.0	90.0	90.0	90.0
β (°)	98.80(4)	91.36(6)	98.13(4)	91.64(2)
γ (°)	90.0	90.0	90.0	90.0
V (Å^3)	594.7(4)	2227(4)	4751(3)	5849(2)
Z	2	4	4	4
D_{calc} (g cm^{-3})	1.297	1.531	1.443	1.505
μ (cm^{-1})	0.82	9.58	9.55	7.212
Scan rate (° min^{-1})	4	4	8	16
Number of reflections ($<2\theta$)	1162 ($<50°$)	4245 ($<50°$)	8663 ($<50°$)	7898 ($<50°$)
Number of data ($I>3.0\sigma(I)$)	2162 ($I>-10.0\sigma(I)$)	2160 ($I>3.0\sigma(I)$)	2168 ($I>3.0\sigma(I)$)	7393 ($I>-10.0\sigma(I)$)
Number of variables	82	262	523	721
R; R_w	0.089; 0.205 [b]	0.052; 0.061 [a]	0.110; 0.132 [a]	0.175; 0.196 [b]
R_1	0.056 (for 613 reflections) [b]			0.071 (for 3487 reflections) [b]
Goodness-of-fit [c]	1.44	1.60	1.93	1.14

[a] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2(F_o)$).

[b] $R = \Sigma(F_o^2 - F_c^2)/\Sigma F_o^2$, $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ and $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$ for $I>2.0\sigma(I)$ data.

[c] Goodness-of-fit $= [\Sigma w(|F_o|-|F_c|)^2/\Sigma(N_o - N_v)]^{1/2}$, where N_o is the number of data, N_v is the number of variables.

linear and the N(2)*–N(2)–C(5) bond angle is 110.8(4)°, narrower than the angle of the ideal sp^2 hybrid.

3.5.2. Crystal structure of (η^6-p-cymene)$RuCl_2(CNC_6H_4N{=}NC_6H_5)$ (4a)

Some selected bond lengths and angles are listed in Table 4. The molecule consists of a piano-stool structure. The ruthenium atom is surrounded by two Cl atoms and a terminal isocyanide carbon atom. The two benzene rings through the N=N bond are coplanar. The average Ru–Cl bond length of 2.413 Å and the Ru–C bond length of 1.92 Å are in the corresponding bonds, respectively. The C(11)–N(1) bond length of 1.17(1) Å is longer than that of free isocyanide. The N(1)–C(12) bond length is shorter than the N(2)–C(15) and N(3)–C(18) bond lengths together with the case of free ligand. The Ru(1)–C(11)–N(1) and C(11)–N(1)–C(12) bond angles are linear, compared well with those for other isocyanide complexes. The three angles around the Ru(1) atom are narrower than 90°.

3.5.3. Crystal structure of (η^5-pentamethylcyclopentadienyl)$RhCl_2(CNC_6H_4N{=}NC_6H_5)$ (5)

Since the data is not good because of poor crystals, the discussion for the data is not made, but some selected bond lengths and angles are listed in Table 5. Complex **5** consists of two independent molecules. The ruthenium atom is surrounded by two chlorine atoms and a carbon atom. The two benzene rings through the N=N bond are coplanar.

Table 3
Selected bond lengths (Å) and angles (°) of 4,4′-diisocyanoazobenzene

Bond lengths			
N(1)–C(1)	1.135(4)	N(1)–C(2)	1.391(4)
N(2)–C(5)	1.490(4)	N(1)–N(2)	1.207(5)
Bond angles			
C(1)–N(1)–C(2)	179.2(4)	N(2)*–N(2)–C(5)	110.8(4)
N(1)–C(2)–C(7)	119.4(3)	N(1)–C(2)–C(3)	119.4(3)

Table 4
Selected bond lengths (Å) and angles (°) of [(*p*–cymene)$RuCl_2(CNC_6H_4N{=}NC_6H_5)$] (**4a**)

Bond lengths			
Ru(1)–Cl(1)	2.049(3)	Ru(1)–Cl(2)	2.416(3)
N(1)–C(12)	1.40(1)	N(2)–N(3)	1.19(1)
N(2)–C(15)	1.46(1)	N(1)–C(11)	1.17(1)
Bond angles			
Cl(1)–Ru(1)–Cl(2)	89.58(10)	C(11)–N(1)–C(12)	176(1)
Ru(1)–C(11)–N(1)	177.4(9)	Cl(2)–Ru(1)–C(11)	84.5(3)
N(2)–N(3)–C(18)	111(1)	N(3)–N(2)–C(15)	112(2)
Cl(1)–Ru(1)–C(11)	87.3(3)		

Table 5
Selected bond lengths (Å) and angles (°) of $(\eta^5\text{-}C_5Me_5)RhCl_2(CNC_6H_4N{=}NC_6H_5)$ (**5**)

Bond lengths					
Rh(1)–Cl(1)	2.42(3)	Rh(1)–Cl(2)	2.42(3)	Rh(2)–Cl(3)	2.41(1)
Rh(2)–Cl(4)	2.39(1)	Rh(1)–C(11)	1.89(5)	Rh(2)–C(34)	1.91(3)
N(1)–C(11)	1.19(5)	N(4)–C(34)	1.24(4)	N(2)–N(3)	1.22(3)
N(5)–N(6)	1.10(4)	N(2)–C(15)	1.47(4)	N(3)–C(18)	1.51(4)
N(5)–C(38)	1.59(5)	N(6)–C(41)	1.55(5)		
Bond angles					
Cl(1)–Rh(1)–Cl(2)	92.3(4)	Cl(1)–Rh(1)–C(11)	88(1)	Cl(2)–Rh(2)–C(11)	88(1)
Cl(3)–Rh(2)–Cl(4)	91.5(4)	Cl(3)–Rh(2)–C(34)	87(1)	Cl(4)–Rh(2)–C(34)	82(1)
Rh(1)–C(11)–N(1)	169(4)	C(11)–N(1)–C(12)	168(4)	N(3)–N(2)–C(15)	105(2)
N(2)–N(3)–C(18)	108(2)	Rh(2)–C(34)–N(4)	168(3)	C(34)–N(4)–C(35)	168(3)
N(6)–N(5)–C(38)	112(3)	N(5)–N(6)–C(41)	112(4)		

Table 6
Selected bond lengths (Å) and angles (°) of $[(\eta^5C_5Me_5)Rh(dppf)(CNC_6H_4N{=}NC_6H_5)]\ (PF_6)_2\cdot 2H_2O$(**7**$\cdot H_2O$)

Bond lengths					
Rh(1)–P(1)	2.376(6)	Rh(1)–P(2)	2.381(6)	Rh(1)–C(45)	1.94(2)
C(45)–N(1)	1.14(2)	N(1)–C(46)	1.45(3)	C(49)–N(2)	1.67(4)
N(2)–N(3)	1.09(3)	N(3)–C(52)	1.54(4)		
Bond angles					
P(1)–Rh(1)–C(45)	91.9(6)	P(1)–Rh(1)–P(2)	96.1(2)	P(2)–Rh(1)–C(45)	87.8(6)
Rh(1)–C(45)–N(1)	169(1)	C(45)–N(1)–C(46)	168(2)	C(49)–N(2)–N(3)	88(2)
N(2)–N(3)–C(52)	93(2)	Rh(1)–P(1)–C(11)	120.0(7)	Rh(1)–P(2)–C(16)	116.6(6)

3.5.4. Crystal structure of $[(\eta^5\text{-}pentamethylcyclopentadienyl)Rh(dppf)(CNC_6H_4N{=}NC_6H_5)](PF_6)_2\cdot 2H_2O\cdot$ **7**$\cdot 2H_2O$

Some selected bond lengths and angles are listed in Table 6. The Rh atom is surrounded by two phosphorus atoms of the dppf ligand and a carbon atom of isocyanide. Two cyclopentadienyl rings are synperiplanar [23]. The dihedral angles between C(49)N(2)N-(3)C(52) and each of two phenyl rings are 33(1) and 29.2(9)°. The dihedral angle between two phenyl rings is 30.0(9)°, different from that of other compounds being coplanar. The Rh(1)–C(45) bond length of 1.94(2) Å and the average Ru–P bond length of 2.379 Å are in the corresponding bond lengths, respectively. The Rh(1)–C(45) bond length of 1.94(2) Å and C(45)–N(1) bond length of 1.14(2) Å is usual Ru–C bond length and C–N triple bond length, respectively. The N(2)–N(3) bond length of 1.09 Å is not significantly different from that of other complexes. The average N–N–C angle of 91° is 20° narrower than that of free isocyanoazobenzene and other complexes (**4a** and **5**), probably coming from difference of the dihedral angle between two phenyl groups. The N(1)–C(46) bond length of 1.45(3) Å is ca. 0.15 Å shorter than the N(2)–C(49) and N(3)–C(52) bond lengths, not different from other compounds.

4. Summary

Mono- and dinuclear complexes of (η^6-arene)ruthenium(II) and pentamethylcyclopentadienyl-rhodium(II) and -iridium(III) complexes bearing 4-isocyanoazobenzene or 4,4′-diisocyanoazobenzene were prepared. These complexes are piano-stool structures and the –N=N– groups have the *trans*-forms in the solid state and in solution. The photochemical reaction of ruthenium complexes led to a decomposition of the complexes, whereas rhodium and iridium complexes underwent *trans*- to *cis*-isomerization. Based on the ^{1}H-NMR spectra, the *cis*/*trans* ratio was found to be small. The electrochemical reactions are irreversible except **4f**. The reductive potentials $[-N{=}N-] \rightarrow [-N{=}N-]^{2-}$ were -1.54 to -1.48 V for mononuclear ruthenium complexes **4** and -1.47 to -1.39 V for monomeric ruthenium complexes **8**. The oxidation potentials from Ru(II) to Ru(III) appeared at 0.80–0.92 V for both complexes **4** and **8**.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic

Data Centre, CCDC nos. 160930 for 4-isocyanoazobenzene, 160931 for **4a**, 106932 for **5**, and 160933 for **7**·$2H_2O$. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan. One of the authors (J.-F. Ma) was supported by a grant-in-aid (the 60th Anniversary Foundation) from Toho University.

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