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Solvent-Dependent Formation of Di- and Trinuclear Rhodium and Iridium Complexes Bridged by *N*,*N′*-Donor Ligands

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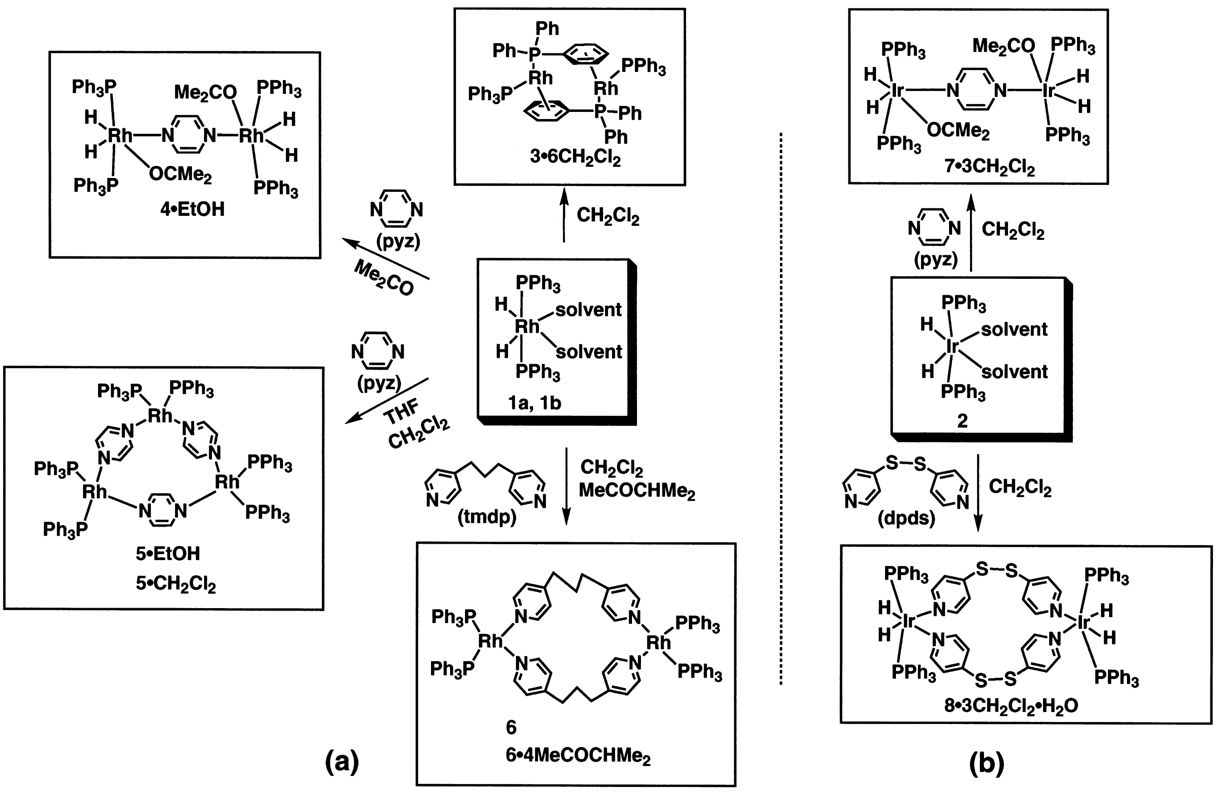
Reactions of Rh and Ir hydrido complexes, $[Rh(H)_2(PPh_3)_2(solv)(EtOH)]ClO_4$ (solv = Me_2CO, **1a**; EtOH, **1b**) and $[Ir(H)_2(PPh_3)_2(Me_2CO)_2]BF_4$ (**2**), with various *N*,*N′*-donor bridging ligands, such as pyrazine (pyz), 4,4′-trimethylenedipyridine (tmdp) and di(4-pyridyl) disulfide (dpds), in some solvents were examined, and their reaction products were characterized by X-ray crystal structure analysis, IR, ^{1}H NMR and UV-vis spectra. Rh hydrido complexes, **1a** or **1b**, formed a dinuclear Rh complex, $[Rh_2(PPh_3)_2\{(\eta^6\text{-}C_6H_5)PPh_2\}_2](ClO_4)_2\cdot6CH_2Cl_2$ ($\mathbf{3}\cdot6CH_2Cl_2$), in dichloromethane with a reductive elimination of hydrogen. The reactions of **1a** or **1b** with the pyz ligand in dichloromethane and tetrahydrofuran gave triangular Rh_3 complexes, $[Rh_3(PPh_3)_6(pyz)_3](ClO_4)_3\cdot CH_2Cl_2$ ($\mathbf{5}\cdot CH_2Cl_2$) and $[Rh_3(PPh_3)_6(pyz)_3](ClO_4)_3\cdot EtOH$ ($\mathbf{5}\cdot$EtOH), respectively, in contrast to the formation of a dinuclear Rh hydrido complex, $[Rh_2(H)_4(PPh_3)_4(Me_2CO)_2(pyz)](ClO_4)_2\cdot EtOH$ ($\mathbf{4}\cdot$EtOH), in acetone. The reactions of **1a** or **1b** with the tmdp ligand in dichloromethane and 3-methyl-2-butanone also afforded dinuclear Rh complexes, $[Rh_2(PPh_3)_4(tmdp)_2](ClO_4)_2$ (**6**) and $[Rh_2(PPh_3)_4(tmdp)_2](ClO_4)_2\cdot4MeCOCHMe_2$ ($\mathbf{6}\cdot4MeCOCHMe_2$), respectively. On the other hand, Ir hydrido complex **2** reacted with pyz and dpds ligands in dichloromethane to afford dinuclear Ir complexes, $[Ir_2(H)_4(PPh_3)_4(Me_2CO)_2(pyz)](BF_4)_2\cdot3CH_2Cl_2$ ($\mathbf{7}\cdot3CH_2Cl_2$) and $[Ir_2(H)_4(PPh_3)_4(dpds)_2](BF_4)_2\cdot3CH_2Cl_2\cdot H_2O$ ($\mathbf{8}\cdot3CH_2Cl_2\cdot H_2O$), respectively, without any reductive elimination of hydrogen. Based on structural studies in solution and in the solid state, it was demonstrated that various Rh and Ir complexes were selectively produced depending on the choice of solvents and *N*,*N′*-donor bridging ligands.

Recently, crystal engineering and the design of solid-state architectures have become interesting and exciting areas of research,[1,2] since they have been implicated in inorganic/organic hybrid materials with such potential utilities as catalysis,[3] nonlinear optics,[4] molecular magnetic materials,[5] electrical conductivity[6] and molecular recognition.[7] Numerous coordination polymers with various dimensionalities, sizes, cavities and shapes have been produced by selecting the chemical structures of organic ligands and the coordination geometry of metals.[8,9] As the simplest linking ligands, *N*,*N′*-donor bridging ligands, such as pyrazine, 4,4′-bipyridine and their related compounds, were chosen in order to generate 1-D, 2-D and 3-D coordination polymers. By the way, the Rh and Ir hydrido complexes of formula $[M(H)_2(L)_2(solv)_2]X$ (M = Rh and Ir; L = phosphine ligand) have been found to be active catalysts.[10–12] Rh and Ir complexes with nitrogen heterocyclic ligands have also been studied in relation to catalytic activities.[13] If the thus-reactive Rh or Ir metal centers could be joined by the *N*,*N′*-donor bridging ligands, it is expected to produce coordination polymers with interesting structures, superior reactivities and properties owing to a cooperative effect of the assembled metal site. However, there have been few investigative reports on Rh or Ir coordination polymers with *N*,*N′*-donor bridging ligands, and their structures and properties are not very obvious.[14a] So far, there have been some reports on mono- and dinuclear complexes by the reaction of Rh and Ir diene, or carbonyl complexes with *N*,*N′*-donor bridging ligands, which were characterized by IR, UV-vis, ^{1}H NMR and elementary analyses.[14,15] Crystallographic studies of di- and trinuclear Rh and Ir complexes with *N*,*N′*-donor bridging ligands are sparse,[14a–c,15a–d,16] although dinuclear Rh and Ir complexes with *cis*-pyrazolate bridging ligands have been widely investigated.[16,17] The aim of this study was to determine the basic preparations of Rh or Ir hydrido complexes with *N*,*N′*-donor bridging ligands toward the construction of Rh or Ir coordination polymers. The reactions of $[Rh(H)_2(PPh_3)_2(solv)_2]^+$ with pyrazine in acetone and tetrahydrofuran were reported in a preliminary communication.[18] In this study, we examined the reactions of Rh and Ir hydrido complexes, $[Rh(H)_2(PPh_3)_2(solv)(EtOH)]ClO_4$ (solv = Me_2CO, **1a**; EtOH, **1b**) and $[Ir(H)_2(PPh_3)_2(Me_2CO)_2]BF_4$ (**2**), with various *N*,*N′*-donor bridging ligands, such as pyrazine (pyz), *4,4′*-trimethylenedipyridine (tmdp) and di(4-pyridyl) disulfide (dpds) in some solvents according to Scheme 1. Their reaction products



Scheme 1.

were characterized by X-ray structure analysis as well as ^{1}H NMR and UV-vis spectra.

Experimental

General Procedures and Reagents. All operations were carried out using standard Schlenk techniques under a nitrogen atmosphere. $RhCl_3 \cdot 3H_2O$, $IrCl_3 \cdot 3H_2O$, pyrazine, 4,4′-trimethylenedipyridine and di(4-pyridyl) disulfide were commercially purchased from Stream and Aldrich, and used without further purifications. All organic solvents were generally distilled before use. Infrared spectra were measured on a Perkin-Elmer System 2000 FT-IR spectrometer as a KBr pellet. ^{1}H NMR spectra were measured at room temperature on a JEOL JNM-A 500 FT NMR spectrometer. Trimethylsilane was used as an internal reference. UV-vis spectra were recorded on a Hitachi U-3500/U-4000 spectrometer.

Safety Note. *Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should be handled with great caution.*

Preparation of Precursor Rh and Ir Complexes. (a) [M(H)$_2$(PPh$_3$)$_2$(solv)$_2$]X (M = Rh and Ir; X = ClO$_4$ and BF$_4$). The precursor Rh and Ir complexes, $[Rh(H)_2(PPh_3)_2(Me_2CO)(EtOH)]ClO_4$[11] (**1a**), $[Rh(H)_2(PPh_3)_2(EtOH)_2]ClO_4$[11] (**1b**) and $[Ir(H)_2(PPh_3)_2(Me_2CO)_2]BF_4$[12a,b] (**2**), were prepared according to the literature.

(b) [Rh$_2$(PPh$_3$)$_2${(η^6-C$_6$H$_5$)PPh$_2$}$_2$](ClO$_4$)$_2$•6CH$_2$Cl$_2$ 3•6CH$_2$Cl$_2$. A 5 mL dichloromethane solution of **1b** (82.1 mg, 0.10 mmol) was layered with hexane as a diffusion solvent in 5 mm diameter glass tubes under N_2. The glass tubes were sealed and the solution was allowed to stand at room temperature for 2 weeks. Red-brown brick crystals of **3**•$6CH_2Cl_2$ were obtained. The complex **3**•$6CH_2Cl_2$ partially lost the solvated dichloromethane molecules by drying to give a compound with the formula **3**•$3CH_2Cl_2$, which was insoluble in common organic solvents. Yield: 44.9 mg (53%). Anal. Calcd. for $C_{75}H_{66}P_4Rh_2O_8Cl_8$ as **3**•$3CH_2Cl_2$: C, 52.72; H, 3.89%. Found: C, 52.80; H, 3.91%. IR (KBr pellet) 3052, 1481, 1435 and 1092 cm^{-1}.

Preparation of Rh Complexes Bridged by *N,N*′-Donor Bridging Ligands. (a) [Rh$_2$(H)$_4$(PPh$_3$)$_4$(Me$_2$CO)$_2$(pyz)](ClO$_4$)$_2$•EtOH 4•EtOH. The preparation of **4**•EtOH was reported in a preliminary communication.[18]

(b) [Rh$_3$(PPh$_3$)$_6$(pyz)$_3$](ClO$_4$)$_3$•EtOH 5•EtOH. The synthesis of **5**•EtOH was reported in a preliminary communication.[18]

(c) [Rh$_3$(PPh$_3$)$_6$(pyz)$_3$](ClO$_4$)$_3$•CH$_2$Cl$_2$ 5•CH$_2$Cl$_2$. After a 5 mL dichloromethane solution of **1b** (41.1 mg, 0.05 mmol) was mixed with a 5 mL dichloromethane solution of pyz (4.0 mg, 0.05 mmol) for 30 min, the reaction solution was filtered. Red-brown filtrates were introduced to 5 mm diameter glass tubes and were layered with hexane. The glass tubes were sealed and the solution was allowed to stand at room temperature for 3 days. Red-brown brick microcrystals of **5**•CH_2Cl_2 were collected. Yield: 32.2 mg (77%). Anal. Calcd for $C_{121}H_{104}P_6N_6Rh_3O_{12}Cl_5$: C, 57.99; H, 4.18; N, 3.35%. Found: C, 57.69; H, 4.37; N, 3.35%. IR (KBr pellet) 1434 and 1094 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 23 °C) δ 7.33, 7.20 and 7.05 (90H, m, PPh$_3$) and 7.74 (12H, s, pyz).

(d) [Rh(PPh$_3$)$_4$(tmdp)$_2$](ClO$_4$)$_2$•4MeCOCHMe$_2$ 6•4MeCOCHMe$_2$. A 5 mL 3-methyl-2-butanone solution of **1b** (41.1 mg, 0.05 mmol) was added to tmdp (9.9 mg, 0.05 mmol) in 3-methyl-2-butanone (5 mL). After stirring for 30 min, the reaction solution was filtered. The filtrates were introduced to 5 mm diameter glass tubes and were layered with hexane. The glass tubes were sealed and the solution was allowed to stand at room temperature for 3 days. Light-yellow crystals were obtained. Yield: 45.5 mg (83%).

Anal. Calcd for $C_{118}H_{128}P_4N_4Rh_2O_{12}Cl_2$: C, 64.57; H, 5.88; N, 2.55%. Found: C, 64.65; H, 5.55; N, 2.56%. IR (KBr pellet) 1618, 1435 and 1094 cm^{-1}. ^1H NMR ($CDCl_3$, 23 °C) δ 7.62, 7.55 and 7.46 (60H, m, PPh_3), 8.46 (8H, d, Ph of tmdp), 7.15 (8H, d, Ph of tmdp), 2.67 (8H, t, CH_2 of tmdp) and 1.98 (4H, p, CH_2 of tmdp).

(e) $[Rh_2(PPh_3)_4(tmdp)_2](ClO_4)_2$ 6. Complex **6** was prepared in the same manner as for **6**·$4MeCOCHMe_2$ using dichloromethane as a solvent. The microcrystalline solids were collected at −10 °C and were dried under a vacuum. Yield: 24.7 mg (53%). Anal. Calcd for $C_{98}H_{88}P_4N_4Rh_2O_8Cl_2$: C, 63.61; H, 4.79; N, 3.03%. Found: C, 63.82; H, 4.74; N, 3.15%. IR (KBr pellet) 1618, 1435 and 1094 cm^{-1}. ^1H NMR ($CDCl_3$, 23 °C) δ 7.62, 7.55 and 7.46 (60H, m, PPh_3), 8.46 (8H, d, Ph of tmdp), 7.15 (8H, d, Ph of tmdp), 2.67 (8H, t, CH_2 of tmdp) and 1.98 (4H, p, CH_2 of tmdp).

Preparation of Ir Complexes Bridged by *N,N′*-Donor Bridging Ligands. (a) $[Ir_2(H)_4(PPh_3)_4(Me_2CO)_2(pyz)](BF_4)_2 \cdot 3CH_2Cl_2$ 7·$3CH_2Cl_2$. A 5 mL dichloromethane solution of **2** (46.1 mg, 0.05 mmol) was added to pyz (4.0 mg, 0.05 mmol) in dichloromethane (5 mL). After stirring for 30 min, the reaction solution was filtered. The light-yellow filtrates were introduced to 5 mm diameter glass tubes and were layered with pentane. The glass tubes were sealed and the solution was allowed to stand at room temperature for 1 day. Colorless brick crystals of **7**·$3CH_2Cl_2$ were obtained, which were insoluble in common organic solvents. Yield: 33.4 mg (65%). Anal. Calcd for $C_{85}H_{86}P_4N_2Ir_2B_2F_8O_2Cl_6$: C, 49.51; H, 4.20; N, 1.36%. Found: C, 49.35; H, 4.02; N, 1.44%. IR (KBr pellet) 2202, 1628, 1435 and 1090 cm^{-1}.

(b) $[Ir_2(H)_4(PPh_3)_4(dpds)_2](BF_4)_2 \cdot 3CH_2Cl_2 \cdot H_2O$ 8·$3CH_2Cl_2 \cdot H_2O$. Complex **8**·$3CH_2Cl_2 \cdot H_2O$ was prepared in the same manner as for **7**·$3CH_2Cl_2$, using the dpds ligand (11.0 mg, 0.05 mmol). Colorless brick crystals were obtained 1 day later at room temperature. Yield: 29.2 mg (50%). Anal. Calcd for $C_{95}H_{88}P_4N_4Ir_2S_4B_2F_8OCl_6$: C, 49.08; H, 3.82; N, 2.41%. Found: C, 49.74; H, 3.80; N, 2.41%. IR (KBr pellet) 2166, 1589, 1435 and 1084 cm^{-1}. ^1H NMR (CD_2Cl_2, 23 °C) δ 7.38, 7.34 and 7.27 (60H, m, PPh_3), 7.51 (8H, d, Ph of dpys), 6.59 (8H, d, Ph of dpys) and −21.74 (4H, t, Ir-H).

X-ray Data Collection and Structure Solution. For each Rh and Ir complex, a suitable crystal was sealed into a glass capillary (0.7 mm, GLAS) and mounted on a crystal goniometer. The intensity data of all the single crystals were collected on a Rigaku Mercury CCD system using graphite-monochromated Mo-$K\alpha$ radiation (λ = 0.710691 Å). The structures of **3**·$6CH_2Cl_2$ and **7**·$3CH_2Cl_2$ were solved by a direct method (SIR92[19a] for **3**·$6CH_2Cl_2$ and SIR97[19b] for **7**·$3CH_2Cl_2$) and the structures of **6**·$4MeCOCHMe_2$ and **8**·$3CH_2Cl_2 \cdot H_2O$ were solved by a Patterson method.[19c] All of the structures were expanded using Fourier techniques.[19d] The hydrogen atoms of hydride were located and refined isotropically in all of the hydrido complexes. All other hydrogen atoms were placed at the calculated positions and were included, but not refined. All non-hydrogen atoms were refined anisotropically, except for two 3-methyl-2-butanone molecules in **6**·$4MeCOCHMe_2$. The positions of C(55), C(56), C(57), C(58), C(59) and O(6) atoms were determined from a Fourier map, but not refined. In **8**·$3CH_2Cl_2 \cdot H_2O$ the O atom of the solvated H_2O molecule are disordered and were refined using 50% O(1) and 50% O(2). All of the calculations were performed using the *TeXsan* crystallographic software package of Molecular Structure Corporation.[20] The atomic-scattering factors and anomalous dispersion terms were taken from Ref. 21. Crystal data and details of the structure determination are summarized in Table 1.

Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; copies can be obtained upon request, free of charge, by quoting the publication citation and deposition numbers 157352, 157356, 157357, 158008, and 158009. The data are also deposited as Document No. 75009 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Crystal Structures. (a) $[Rh_2(PPh_3)_2\{(\eta^6\text{-}C_6H_5)PPh_2\}_2](ClO_4)_2 \cdot 6CH_2Cl_2$ 3·$6CH_2Cl_2$. Single crystals of **3**·$6CH_2Cl_2$ were obtained from a diffusion solution of **1b** in dichloromethane with hexane. The cation moiety of **3**·$6CH_2Cl_2$ is shown in Fig. 1, together with the atomic labeling scheme. Two Rh atoms are bridged by the P atom and one phenyl group

Table 1. Crystallographic Data for **3**·$6CH_2Cl_2$, **6**·$4MeCOCHMe_2$, **7**·$3CH_2Cl_2$ and **8**·$3CH_2Cl_2 \cdot H_2O$

	3·$6CH_2Cl_2$	**6**·$4MeCOCHMe_2$	**7**·$3CH_2Cl_2$	**8**·$3CH_2Cl_2 \cdot H_2O$
Formula	$C_{78}H_{72}P_4Rh_2O_8C_{l14}$	$C_{118}H_{128}P_4N_4Rh_2O_{12}C_{l2}$	$C_{85}H_{86}P_4N_2Ir_2B_2F_8O_2C_{l6}$	$C_{95}H_{88}P_4N_4Ir_2S_4B_2F_8OCl_6$
Formula weight	1963.47	2194.94	2062.29	2324.67
Crystal system	triclinic	triclinic	monoclinic	triclinic
Space Group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a/Å	13.591(3)	11.4277(8)	23.951(1)	14.1461(9)
b/Å	13.648(3)	12.344(1)	24.4059(5)	18.681(1)
c/Å	14.545(3)	23.197(3)	18.5174(3)	20.735(1)
α/°	93.065(9)	83.397(4)	90.00	75.1006(7)
β/°	115.319(9)	74.937(3)	126.970(1)	75.2869(6)
γ/°	116.590(7)	63.331(1)	90.00	70.174(2)
V/Å^3	2078.4(9)	2823.6(5)	8648.2(6)	4897.0(5)
Z	1	1	4	2
μ(Mo-$K\alpha$)/cm^{-1}	9.76	4.55	34.06	31.00
Temperature/K	293.2	213.2	200.2	200.2
Reflections measured	14087	18367	10137	20979
Independent reflections	8385	11412	9903	20896
R	0.052	0.065	0.022	0.031
R_w	0.073	0.080	0.027	0.043

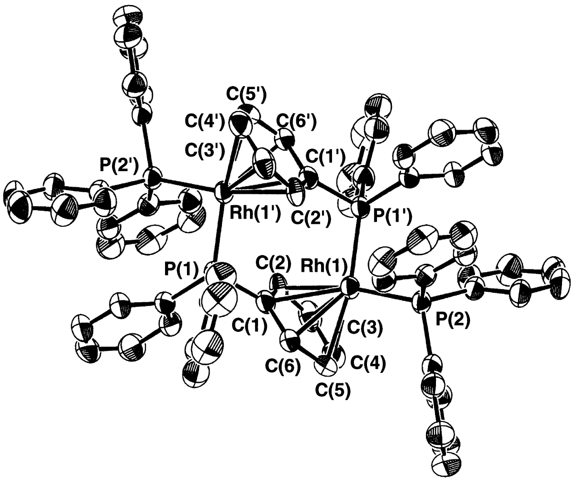


Fig. 1. Molecular structure of the cation moiety of **3**·$6CH_2Cl_2$.

Table 2. Selected Bond Distances (Å) and Bond Angles (°) of **3**·$6CH_2Cl_2$

Rh(1)–P(1)	2.260(1)	Rh(1)–P(2)	2.2532(9)
Rh(1)–C(1)	2.396(4)	Rh(1)–C(2)	2.267(4)
Rh(1)–C(3)	2.328(4)	Rh(1)–C(4)	2.323(4)
Rh(1)–C(5)	2.266(4)	Rh(1)–C(6)	2.375(4)
C(1)=C(2)	1.418(6)	C(1)=C(6)	1.398(6)
C(2)=C(3)	1.409(6)	C(3)=C(4)	1.394(8)
C(4)=C(5)	1.403(7)	C(5)=C(6)	1.417(6)
P(1′)–Rh(1)–P(2)	93.93(4)	Rh(1)–C(1)–P(1)	137.4(2)
Rh(1′)–P(1)–C(1)	110.1(1)	P(1′)–Rh(1)–C(1)	106.91(10)

of PPh_3 ligand in the η^6-coordination mode to afford a dinuclear structure. Each Rh atom is coordinated by the P atom of another non-bridging PPh_3 ligand. The coordination sphere around the Rh atom resembles a piano-stool structure with two legs of P atoms and a fulcrum at the Rh atom. This piano-stool structure has been found in other Rh η^6-arene complexes.[22,23a,b,24] The coordinated arene ring of the PPh_3 ligand is essentially coplanar with a mean plane deviation of 0.0389 Å. The Rh atom is vertically located by 1.849(3) Å to the center of the arene ring. The average C=C bond distance of 1.407 Å and the average Rh–C bond distance of 2.326 Å are similar to those of other Rh arene complexes.[22,23a,b,24] The Rh···Rh separation of 4.52 Å is far from the range of an attractive metal-metal interaction. Selected bond distances and bond angles of **3**·$6CH_2Cl_2$ are listed in Table 2.

So far, several Rh arene complexes including the component of the Rh(η^6-C_6H_5) cation have been characterized crystallographically.[23] It has been known that most of them are mononuclear Rh complexes coordinated by the phenyl group of terminal benzene[23a,c] and the BPh_4^-anion[23d–g], or dinuclear Rh complexes bridged by that of bidentate phosphine ligands.[22,23b,h] The crystal structure of dinuclear Rh arene complex $[Rh_2(H)_2\{Me_2Si(C_6H_5)\}_4]$[24] has only been reported to be structurally relevant to complex **3**·$6CH_2Cl_2$. Complex **3**·$6CH_2Cl_2$ is a significant dinuclear Rh arene complex bridged by the phenyl group of the PPh_3 ligand in the η^6-coordination mode.

Table 3. Selected Bond Distances (Å) and Bond Angles (°) of **5**·EtOH[a)]

Rh(1)–P(1)	2.228(1)	Rh(1)–P(2)	2.248(2)
Rh(2)–P(3)	2.244(1)	Rh(2)–P(4)	2.253(1)
Rh(3)–P(5)	2.260(1)	Rh(3)–P(6)	2.243(2)
Rh(1)–N(1)	2.142(4)	Rh(1)–N(6)	2.161(4)
Rh(2)–N(2)	2.107(4)	Rh(2)–N(3)	2.122(4)
Rh(3)–N(4)	2.132(5)	Rh(3)–N(5)	2.110(4)
P(1)–Rh(1)–P(2)	97.65(5)	P(3)–Rh(2)–P(4)	97.45(5)
Rh(1)···Rh(2)	6.99	Rh(2)···Rh(3)	6.96
Rh(1)···Rh(3)	6.99		
P(5)–Rh(3)–P(6)	95.47(5)	N(1)–Rh(1)–N(6)	80.5(2)
N(2)–Rh(2)–N(3)	81.3(2)	N(4)–Rh(3)–N(5)	81.8(2)
Rh(1)···Rh(2)···Rh(3)	60.14	Rh(2)···Rh(1)···Rh(3)	59.72
Rh(1)···Rh(3)···Rh(2)	60.14		

a) Ref. 18.

(b) $[Rh_3(PPh_3)_6(pyz)_3](ClO_4)_3$·EtOH 5·EtOH. When Rh hydrido complexes **1a** or **1b** reacted with the pyz ligand in tetrahydrofuran and dichloromethane, triangular Rh_3 complexes, **5**·EtOH and **5**·CH_2Cl_2, were produced, respectively, along with a reductive elimination of hydrogen. The crystal structure of **5**·EtOH was here only determined, since the crystals of **5**·CH_2Cl_2 were not suitable for a single-crystal X-ray analysis. The preparation and crystal structure of **5**·EtOH were deposited in a preliminary communication.[18] In a unit cell, there are two molecules of a trinuclear Rh complex, $[Rh_3(PPh_3)_6(pyz)_3](ClO_4)_3$, and two molecules of solvated ethanol, which were dissociated from the precursor Rh complexes, **1a** or **1b**, in tetrahydrofuran. The most interesting feature of **5**·EtOH is that three Rh atoms are bridged by three pyz ligands to form a unique triangular Rh_3 core. Each Rh atom is coordinated by two pyz and two PPh_3 ligands in a slightly distorted square-planar geometry. Each pyz ligand is approximately perpendicular to the Rh_3 plane, forming a regular triangular space. The detailed selected bond distances and bond angles of **5**·EtOH are listed in Table 3.

To the best of our knowledge, the triangular metal complex bridged by pyz and their derivatives has been relatively limited, and triruthenium complexes $[\{Ru_3O(CH_3CO_2)_6(CO)(abco)\}_2(pyz)]\cdot 2CH_2Cl_2$ (abco = 1-azabicyclo[2,2,2]octane)[25a] and $[Ru_3O(CH_3CO_2)_6(mbpy)_2(CO)](ClO_4)_2\cdot 2DMF$ (mbpy = *N*-methyl-4,4′-bipyridine)[25b] and trizinc complex $[Zn_3Cl_6(bppz)_3]\cdot H_2O$ (bppz = 2,5-bis(2-pyridyl)pyrazine)[25c] have been reported. Most of the trinuclear Rh complexes with a triangular Rh_3 core have been formed by bridges of hydride,[26a] CO,[26b,c] and chloride,[26d,e] whereas those bridged by *N*,*N*′-donor bridging ligands are few.[26f,g] Although the triangular Rh_3 core of octahedral Rh units has been only found in $[Rh_3(\mu\text{-tz})_3(\eta^3\text{-}C_3H_5)_6]$ (tz = 1,2,4-triazole),[26f] complex **5**·EtOH is the first trinuclear Rh pyrazine complex with a triangular Rh_3 core of square-planar Rh units.

(c) $[Rh_2(PPh_3)_4(tmdp)_2](ClO_4)_2$·4MeCOCHMe$_2$ 6·4MeCOCHMe$_2$. The reactions of **1a** or **1b** with the tmdp ligand, having a long spacer in dichloromethane and 3-methyl-2-butanone, produced dinuclear Rh complexes **6** and **6**·4MeCOCHMe$_2$, respectively, in contrast to triangular Rh_3 com-

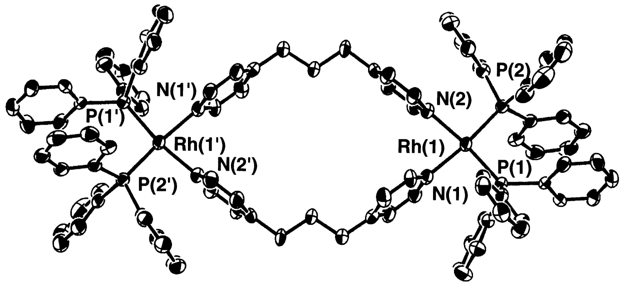


Fig. 2. Molecular structure of the cation moiety of **6**·4MeCOCHMe$_2$.

Table 4. Selected Bond Distances (Å) and Bond Angles (°) of **6**·4MeCOCHMe$_2$

Rh(1)–P(1)	2.248(1)	Rh(1)–P(2)	2.225(1)
Rh(1)–N(1)	2.139(4)	Rh(1)–N(2)	2.113(4)
P(1)–Rh(1)–P(2)	97.30(5)	P(1)–Rh(1)–N(1)	89.6(1)
P(2)–Rh(1)–N(2)	91.0(1)	N(1)–Rh(1)–N(2)	82.2(2)
P(1)–Rh(1)–N(2)	171.7(1)	P(2)–Rh(1)–N(1)	171.0(1)

plexes **5**·EtOH and **5**·CH$_2$Cl$_2$. Here, only the crystal structure of **6**·4MeCOCHMe$_2$ was examined, since the crystals of **6** were not suitable for a single-crystal X-ray analysis. The cation moiety of **6**·4MeCOCHMe$_2$ is presented in Fig. 2. Complex **6**·4MeCOCHMe$_2$ has a center of symmetry at the midpoint of the Rh(1)···Rh(1′) vector. Two Rh atoms are bridged by two tmdp ligands to afford a dinuclear structure. Each Rh atom is coordinated by two N atoms of two tmdp ligands and two P atoms of two PPh$_3$ in a slightly distorted square-planar geometry. The most interesting structural feature is that a large 24-membered Rh–tmdp–Rh–tmdp ring is formed by two Rh atoms and two tmdp ligands. The average Rh–P and Rh–N distances of 2.237 and 2.126 Å are similar to those of the usual Rh complexes.[27] Selected bond distances and bond angles of **6**·4MeCOCHMe$_2$ are listed in Table 4.

Generally, the tmdp ligand is well-known as a useful bridging ligand, and various coordination polymers, such as [Cu$_5$(tmdp)$_8$(SO$_4$)$_4$(EtOH)(H$_2$O)$_5$](SO$_4$)·EtOH·25.5H$_2$O,[28a] [Cu(hfac)$_2$(tmdp)] (hfacac = hexafluoroacetylacetonate),[28b] [Cu(hfacac)$_2$(tmdp)],[28c] [Ag(tmdp)](CF$_3$SO$_3$)·EtOH,[28d] [Ag(tmdp)](CF$_3$SO$_3$),[28d] [Ag$_2$(tmdp)$_4$](CF$_3$SO$_3$)$_2$·tmdp[28d] and [ZnMe$_2$(tmdp)],[28e] have been reported. However, Rh complexes with a tmdp ligand are still sparse and have no X-ray crystal structures.[14d,29] Complex **6**·4MeCOCHMe$_2$ is the first dinuclear Rh tmdp complex characterized crystallographically.

(d) [Ir$_2$(H)$_4$(PPh$_3$)$_4$(Me$_2$CO)$_2$(pyz)](BF$_4$)$_2$·3CH$_2$Cl$_2$ 7·3CH$_2$Cl$_2$. A dinuclear Ir hydrido complex, **7**·3CH$_2$Cl$_2$, was obtained by the reaction of **2** with the pyz ligand in dichloromethane without any reductive elimination of hydrogen. An analogous dinuclear Rh hydrido complex, [Rh$_2$(H)$_4$(PPh$_3$)$_4$(Me$_2$CO)$_2$(pyz)](ClO$_4$)$_2$·EtOH (**4**·EtOH), has been crystallized in acetone, and its crystal structure has already been reported in a preliminary communication.[18] The cation moiety of **7**·3CH$_2$Cl$_2$ is shown in Fig. 3. Two Ir atoms are bridged by two N atoms of one pyz ligand to form a dinuclear complex, in which each Ir atom is coordinated by two P atoms of two PPh$_3$ ligands in a *trans* position; one O atom of acetone and two hydride atoms occupy a *cis* position. Complex **7**·3CH$_2$Cl$_2$ possesses an isomorphous structure to **4**·EtOH.

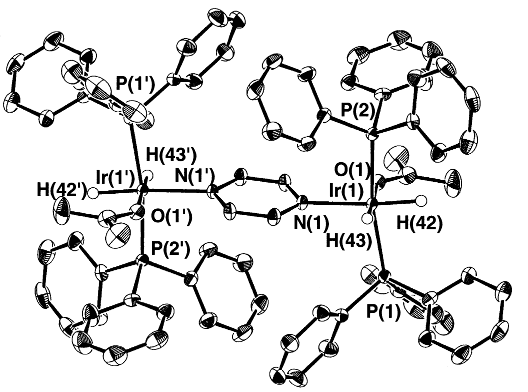


Fig. 3. Molecular structure of the cation moiety of **7**·3CH$_2$Cl$_2$.

The Ir–O and Ir–N distances of 2.202(2) and 2.186(2) Å are close to those (2.216(3) and 2.228(3) Å) in the corresponding Rh complex **4**·EtOH. The average Ir–P distance of 2.301 Å is also similar to that (2.303(1) Å) in **4**·EtOH and analogous Rh and Ir complexes.[15a,30] The Ir–H distances of 1.53(3) and 1.50(3) Å for Ir(1)–H(42) and Ir(1)–H(43), respectively, are within those of other Rh and Ir hydrido complexes.[31,32] The P(1)–Ir(1)–P(2) angle of 165.94(2)° is equal to that (163.20(4)°) of **4**·EtOH, resulting in a decrease of the repulsion between those PPh$_3$ groups on the neighboring Ir atom, as well as **4**·EtOH. The crystal structure of [{Rh(cod)Cl}$_2$(pyz)] has only been reported as a dinuclear Rh complex bridged by the pyz ligand,[14b] in which the pyz plane makes a dihedral angle of 56.9° against the Rh coordination plane. In contrast, it is interesting that the pyz ring in **4**·EtOH and **7**·3CH$_2$Cl$_2$ is nearly coplanar to the square-planer MNOH$_2$ (M = Rh and Ir) coordination plane with a dihedral angle of 6.2 and 12.2°, respectively. The detailed selected bond distances and bond angles of **7**·3CH$_2$Cl$_2$ are listed in Table 5, together with those of the corresponding Rh complex, **4**·EtOH.

Table 5. Selected Bond Distances (Å) and Bond Angles (°) of (a) **4**·EtOH[a)] and (b) **7**·3CH$_2$Cl$_2$

(a) **4**·EtOH[a)]			
Rh(1)–P(1)	2.300(1)	Rh(1)–P(2)	2.306(1)
Rh(1)–O(1)	2.216(3)	Rh(1)–N(1)	2.228(3)
Rh(1)–H(44)	1.45(5)	Rh(1)–H(45)	1.49(4)
P(1)–Rh(1)–P(2)	163.20(4)	P(1)–Rh(1)–O(1)	96.65(8)
P(1)–Rh(1)–N(1)	95.07(9)	P(2)–Rh(1)–O(1)	94.59(8)
P(2)–Rh(1)–N(1)	97.89(9)	O(1)–Rh(1)–N(1)	87.4(1)
H(44)–Rh(1)–H(45)	84(2)		
(b) **7**·3CH$_2$Cl$_2$			
Ir(1)–P(1)	2.3037(6)	Ir(1)–P(2)	2.2974(6)
Ir(1)–O(1)	2.202(2)	Ir(1)–N(1)	2.186(2)
Ir(1)–H(42)	1.53(3)	Ir(1)–H(43)	1.50(3)
P(1)–Ir(1)–P(2)	165.94(2)	P(1)–Ir(1)–O(1)	97.10(5)
P(1)–Ir(1)–N(1)	99.33(6)	P(2)–Ir(1)–O(1)	91.78(5)
P(2)–Ir(1)–N(1)	92.19(6)	O(1)–Ir(1)–N(1)	85.57(7)
H(42)–Ir(1)–H(43)	89(1)		

a) Ref. 18.

Our survey of dinuclear complexes bridged by the pyz

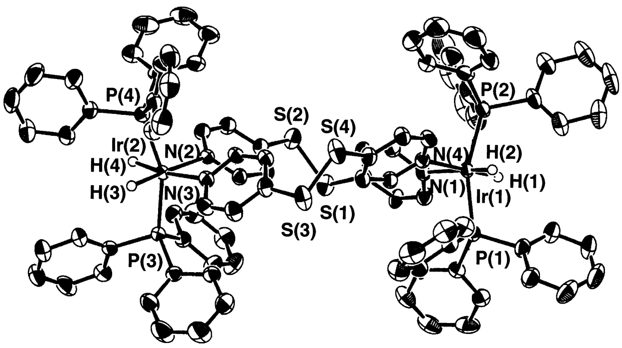


Fig. 4. Molecular structure of the cation moiety of **8**·$3CH_2Cl_2\cdot H_2O$.

ligand describes a copper complex, $[Cu_2(C_9H_7NO_3)_2(pyz)(H_2O)_2]\cdot 2H_2O$;[33a] ruthenium complexes, $Na_2[\{$*trans*-$RuCl_4(Me_2SO$-*S*$)\}_2(pyz)]$,[33b] $[\{Ru(hedta)\}_2(pyz)]_2$ ($hedta^{3-}$ = *N*-(hydroxyethyl)-ethylenediaminetriacetate),[33c] $[\{Ru_2(chp)_4\}_2(pyz)](BF_4)_2\cdot 4CH_2Cl_2$ (chp = 6-chloro-2-hydroxypyridine);[33d] an osmium complex, $[\{Os_2(chp)_4\}_2(pyz)](BF_4)_2\cdot 2CH_2Cl_2\cdot 2pyz$;[33e] a renium complex, $[\{Re(CO)_3(bpy)Br\}\{Re(CO)_3(pyz)Br\}]_2$.[33f] Although $[Ir_2(pyz)_2(CH_3)(CO)_2(P^iPr_3)_2]ClO_4$ has recently been reported,[15b] complex **7**·$3CH_2Cl_2$ is a dinuclear Ir hydrido complex bridged by the pyz ligand.

(e) $[Ir_2(H)_4(PPh_3)_4(dpds)_2](BF_4)_2\cdot 3CH_2Cl_2\cdot H_2O$ 8·$3CH_2Cl_2\cdot H_2O$. A dinuclear Ir hydrido complex, **8**·$3CH_2Cl_2\cdot H_2O$, was isolated using the dpds ligand with a long spacer, in place of the pyz ligand. The cation moiety of **8**·$3CH_2Cl_2\cdot H_2O$ is presented in Fig. 4. Two Ir atoms are bridged by two dpds ligands, providing a large 22-membered Ir–dpds–Ir–dpds ring. Each Ir atom is coordinated by two P atoms of two PPh_3 ligands in the *trans* position, two N atoms of two dpds ligands, and two hydrides in the distorted octahedral geometry. It is interesting that this coordination environment is different from that in a dinuclear Rh complex, **6**·$4MeCOCHMe_2$. The two dpds ligands are unsymmetrical to each other, unlike the tmdp ligands in **6**·$4MeCOCHMe_2$.

The average Ir–N and Ir–P distances of 2.195 and 2.309 Å are within those of general Ir complexes. The Ir–H distances are 1.73(6), 1.41(5), 1.50(5) and 1.41(5) Å for Ir(1)–H(1), Ir(1)–H(2), Ir(2)–H(3) and Ir(2)–H(4), respectively, which are similar to those of other Ir hydrido complexes.[32] The average P–Ir–P angle of 159.28° is slightly smaller than those (163.20(4) and 165.94(2)°) in **4**·EtOH and **7**·$3CH_2Cl_2$. Selected bond distances and bond angles of **8**·$3CH_2Cl_2\cdot H_2O$ are listed in Table 6.

It has been known that most of Ir hydrido complexes are mononuclear complexes, or dinuclear complexes bridged by hydride,[34a–e] CO,[34a,b] diphosphine,[34a,f,g] silylene,[34f] chloride[34h] and sulfide ligands,[34d] the same as Rh hydrido complexes. The Ir hydrido complexes, bridged by the *N*,*N*′-donor bridging ligand,[15c,d] and metal complexes bridged by the dpds ligand,[35] are still limited. Complex **8**·$3CH_2Cl_2\cdot H_2O$ is a dinuclear hydrido complex bridged by the dpds ligand.

Table 6. Selected Bond Distances (Å) and Bond Angles (°) of **8**·$3CH_2Cl_2\cdot H_2O$

Ir(1)–P(1)	2.312(1)	Ir(1)–P(2)	2.301(1)
Ir(2)–P(3)	2.3155(9)	Ir(2)–P(4)	2.308(1)
Ir(1)–N(1)	2.192(3)	Ir(1)–N(4)	2.198(3)
Ir(2)–N(2)	2.193(3)	Ir(2)–N(3)	2.196(3)
Ir(1)–H(1)	1.73(6)	Ir(1)–H(2)	1.41(5)
Ir(2)–H(3)	1.50(5)	Ir(2)–H(4)	1.41(5)
P(1)–Ir(1)–P(2)	160.53(3)	N(1)–Ir(1)–N(4)	89.7(1)
P(3)–Ir(2)–P(4)	158.03(3)	N(2)–Ir(2)–N(3)	88.5(1)
H(1)–Ir(1)–H(2)	95(2)	H(3)–Ir(2)–H(4)	92(2)

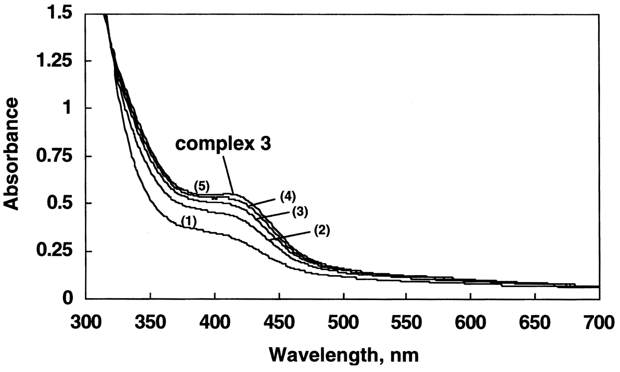


Fig. 5. The time-course of UV-vis spectra of **1b** in dichloromethane (0.18 mol/m^3) at 23 °C. (1) 10, (2) 20, (3) 30, (4) 40 and (5) ≥50 min.

Behaviors of Rh Hydrido Complex 1a or 1b in Dichloromethane. When Rh hydrido complex **1a** or **1b** was dissolved in dichloromethane, the color of the solution gradually changed from yellow to dark brown. This was in sharp contrast to the observation of no color change in the same reaction which occurred in acetone.[18] The time course of the UV-vis spectra of **1b** was measured in dichloromethane at 23 °C. As shown in Fig. 5, the irreversible equilibrium reached a balanced situation after about 50 minutes, providing a new absorption with a MLCT band (λ_{max} = 410 nm (ε = 3.056 × 10^{-2} m^3/mol·m)). The rate constant of this first-order reaction was 1.92 × 10^{-3} s^{-1} based on a kinetics calculation.[36] The ^1H NMR spectrum of **1a** or **1b**, redissolved in CD_2Cl_2, exhibited that there were no hydride species at the up-field region. To identify the final product, we attempted to crystallize it and single crystals of **3**·$6CH_2Cl_2$ were collected. A X-ray crystallographic study demonstrated the formation of a dinuclear Rh η^6-arene complex, **3**·$6CH_2Cl_2$, bridged by two PPh_3 ligands. These facts suggest that Rh hydrido complex, **1a** or **1b**, in dichloromethane induced a reductive elimination of hydrogen, and a dinuclear Rh complex, **3**·$6CH_2Cl_2$, was produced to occupy the resulting vacant coordination site.

Reactions of Rh Hydrido Complex 1a or 1b with *N*,*N*′-donor Bridging Ligands in Dichloromethane. When one equivalent of pyz was added to a dark-brown solution of **1a** or **1b** in dichloromethane, a brown solution with a MLCT band (λ_{max} = 410 nm (ε = 2.291 × 10^{-2} m^3/mol·m)) was obtained. The single crystals of **5**·CH_2Cl_2 were isolated from the dichloromethane solution. The structural study showed that a triangular Rh_3 complex, **5**·CH_2Cl_2, was formed, similar to the **5**·EtOH reported previously.[18] This result is different from the dinuclear Rh complex, **4**·EtOH, produced by the reactions of **1a** or **1b** with the pyz ligand in acetone.[18] At present, the detailed formation mechanism of the triangular Rh_3 complex,

5·CH_2Cl_2, is not obvious. However, as mentioned above, Rh hydrido complex, **1a** or **1b**, could easily release two hydrogens to afford the Rh η^6-arene complex, **3**·6CH_2Cl_2, in dichloromethane, although the Rh hydrido complex, **1a** or **1b**, was stable in acetone. Since the addition of the pyz ligand to the dark-brown solution of **1b** in dichloromethane provided a triangular Rh_3 complex, **5**·CH_2Cl_2, it is considered that the complex, **3**·6CH_2Cl_2, is probably related to the reaction process of the Rh hydrido complex, **1a** or **1b**, with the pyz ligand in dichloromethane. The triangular Rh_3 complex, **5**·CH_2Cl_2, should be produced according to a steric repulsion between bulky PPh_3 and rigid pyz ligands.[18] The suggestion of the formation of a triangular metal complex is supported by the self-assembling reaction of $[Pd(NO_3)_2(2,2'\text{-bpy})]^{2+}$ with the 4,4′-bpy ligand.[37]

On the other hand, the addition of the tmdp ligand with a long spacer to **1a** or **1b** in dichloromethane displayed a color change of dark brown to yellow, and the crystals of complex **6** were collected from the reaction solution. A structural study described that dinuclear Rh complex **6** bridged by two tmdp ligands was formed in dichloromethane, similar to isomorphous **6**·4$MeCOCHMe_2$. These facts were different from those in the case of the pyz ligand in dichloromethane. In comparison with the rigid pyz ligand, the tmdp ligand possesses a long flexible spacer, and provides enough possibility to bridge two Rh centers against the steric hindrance of the bulky PPh_3 ligands. It is reasonable that a structurally stable dinuclear structure should be induced, rather than a triangular Rh_3 structure, such as **5**·EtOH and **5**·CH_2Cl_2. These facts suggest that the nuclearity of Rh complexes is greatly related to the structural feature of the *N*,*N*′-donor bridging ligands, in addition to the effect of the used solvents.

Reactions of Ir Hydrido Complex 2 with pyz and dpds Ligands in Dichloromethane. It was found that Rh hydrido complexes, **1a** or **1b**, gave dinuclear Rh η^6-arene complex **3**·6CH_2Cl_2 in dichloromethane, and triangular Rh_3 complex **5**·CH_2Cl_2 and dinuclear Rh complex **6** were formed by the reaction of **1a** or **1b** with the *N*,*N*′-donor bridging ligands. Similarly, the corresponding Ir hydrido complex **2** is expected to exhibit a similar behavior in dichloromethane. However, Ir hydrido complex **2** was stable in a dichloromethane solution and in the solid state without any reductive elimination of hydrogen, since the characteristic IR and ^1H NMR spectra for hydride species were observed. Reactions of **2** with the pyz and dpds ligands gave dinuclear Ir hydrido complexes **7**·3CH_2Cl_2 and **8**·3CH_2Cl_2·H_2O, respectively, regardless of the solvents. These facts suggest that Ir hydrido complex **2** was less labile than the corresponding Rh complexes, which was supported by a kinetics study.[12] In complex **7**·3CH_2Cl_2, two Ir centers are bridged by one pyz ligand, and one acetone molecule still remains together with two hydrides. The coordinating acetone molecule couldn't be substituted by an excessive amount of the pyz ligands. On the other hand, two metal centers in **8**·3CH_2Cl_2·H_2O are doubly bridged by two dpds ligands, along with the elimination of two acetone molecules. This difference probably concerns the affinity of the *N*,*N*′-donor bridging ligand against the Ir atom and the distance between N···N separation. The dpds ligand possesses a long flexible spacer, just as tmdp ligand. The pyz ligand with a short spacer is difficult to bridge two Ir centers doubly and to provide the dinuclear structure bridged by one pyz ligand,[33a–c] whereas the dpds ligands can feasibly bridge two Ir centers doubly against the bulky PPh_3 ligands, leading to a dinuclear structure doubly bridged by two dpds ligands.

Concluding Remarks

Acetone is the best donor solvent ligand among the acetone, tetrahydrofuran, 3-methyl-2-butanone and dichloromethane used in this study, and can occupy the coordination site of Rh and Ir hydrido complexes, $[M(H)_2(PPh_3)_2(solv)_2]^+$ (**1a**, **1b** and **2**). The high oxidation state of Rh(III) can be stably maintained in acetone, without any reductive elimination of hydrogen. In contrast, other solvents, such as dichloromethane, would tip the Rh(III) species toward the Rh(I) species and induce to the formation of a non-hydrido Rh(I) complex along with the reductive elimination of hydrogen. In fact, the complex **3**·6CH_2Cl_2 could be isolated in dichloromethane and be characterized crystallographically. The Rh hydrido complex, **1a** or **1b**, readily reacted with *N*,*N*′-donor bridging ligands in dichloromethane, and dinuclear and triangular Rh complexes, **6** and **5**·CH_2Cl_2, were formed according to the structural feature of the *N*,*N*′-donor bridging ligands. On the other hand, the Ir hydrido complex **2** was proved to be less labile than the corresponding rhodium complexes, regardless of the solvents. Dinuclear Ir hydrido complexes, **7**·3CH_2Cl_2 and **8**·3CH_2Cl_2·H_2O, were provided according to the structural feature of the *N*,*N*′-donor bridging ligands without any reductive elimination of hydrogen.

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