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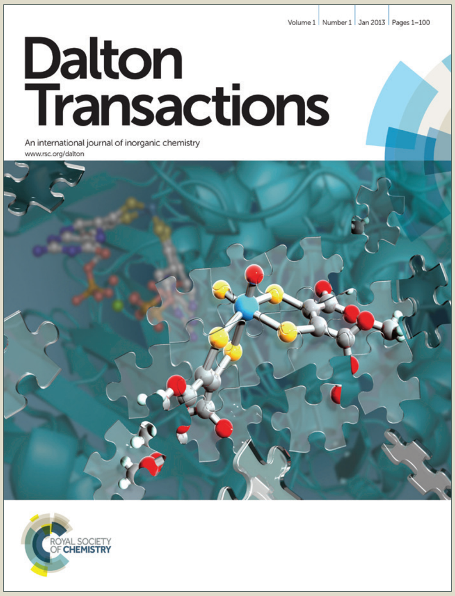

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Palladium(II) mononuclear and palladium(II)/ruthenium(II) heterodinuclear complexes containing 2-quinolyl-substituted (pyridine-2-carbonyl)hydrazone

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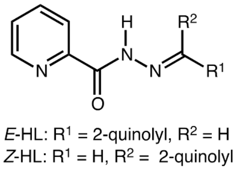
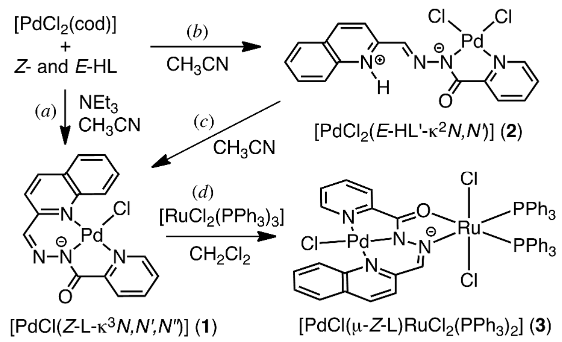
A reaction of [PdCl$_2$(cod)] (cod = 1,5-cyclooctadiene) and an *E/Z* mixture of quinoline-2-carbaldehyde (pyridine-2-carbonyl)-hydrazone (HL) gave two kinds of Pd^{II} mononuclear complexes, [PdCl(*Z*-L-κ^3*N,N′,N″*)] (1) and [PdCl$_2$(*E*-HL′-κ^2*N,N′*)] (2), where L$^-$ is the deprotonated hydrazonate anion and HL′ is the quinolinium–hydrazonate zwitterionic form of HL. Complex 2 is gradually converted to 1 in solution, and complex 1 is a good precursor to prepare a Pd^{II}/Ru^{II} heterodinuclear complex bridged by the hydrazonate, *trans(Cl,Cl)*-[RuCl$_2$(PPh$_3$)$_2$(μ-L)PdCl] (3).



Scheme 1 The substituted 2-picolinoylhydrazones and the ligand HL used in this study.

2-Picolinoylhydrazones[1] having a coordinating substituent at the C(imine) atom (Scheme 1) are promising ligands for stepwise and highly selective construction of heterometallic di- or polynuclear complexes, because they have some different types of donor groups in a molecule. In addition, the hydrazone NH group is capable of deprotonation and reprotonation by the external pH control when the hydrazone coordinates to a metal ion via the imine-N atom,[2] which would be advantageous to the rational and stepwise synthesis of heterometallic complexes. However, synthetic studies for such heterometallic complexes with hydrazones or hydrazonates are still limited. To the best of our knowledge, only a few examples with cyclic tetranuclear structures have been reported, although they were prepared either by a one-pod reaction or by stepwise complexations.[3] Recently, we prepared mononuclear Ru^{II} complexes with quinolyl-2-carbaldehyde (pyridine-2-carbonyl)hydrazone, HL (Scheme 1),[4] and a series of heterodimetallic Ru^{III}–M^{II} (M = Mn, Fe, Co, Ni, Cu and Zn) complexes bridged by the hydrazonate, L$^-$.[5] Upon dinucleation reaction of *trans(P,P)*-[RuCl$_2$(PPh$_3$)$_2${HL-κ*N*(imine),κ*O*(amide)}] with 3d-metal chloride (MCl$_2$), deprotonation from the hydrazone moiety and oxidation of the Ru centre (to Ru^{III}) occurred simultaneously. However, the Ru^{II}–hydrazone complex could not react with typical Pd^{II} chloride precursors, e.g., [PdCl$_2$(cod)] or [PdCl$_2$(PhCN)$_2$]. Therefore, in order to synthesize heterodimetallic Ru–Pd complexes with a bridging L$^-$ by a different strategy, mononuclear Pd^{II} complexes containing HL or its anion are attempted to prepare in advance of the reaction with Ru^{II} precursor complexes.

The ligand, HL, was obtained as a 58:42 mixture of the *E* and *Z* isomers by a reaction of 2-picolylhydrazine and 2-quinolylaldehyde.[4] When an equimolar (0.35 mmol) mixture of [PdCl$_2$(cod)], an *E/Z* mixture of HL and NEt$_3$ in acetonitrile (15 cm^3) was allowed to stand at room temperature for several days, orange crystals of complex **1**•0.5CH$_3$CN were deposited in a nearly quantitative (96%) yield (Scheme 2*a*). The crystal structure of



Scheme 2 Synthetic procedures of the Pd^{II} and Pd^{II}–Ru^{II} complexes described in this communication.

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Electronic Supplementary Information (ESI) available: experimental details, tables of crystal data and selected structural parameters, UV-vis absorption spectra of complexes **1–3**, a cyclic voltammogram and ^{31}P NMR spectra of complex **3**, and crystallographic data in CIF format (CCDC reference Nos. 1406105–1406108). See DOI: 10.1039/x0xx00000x.

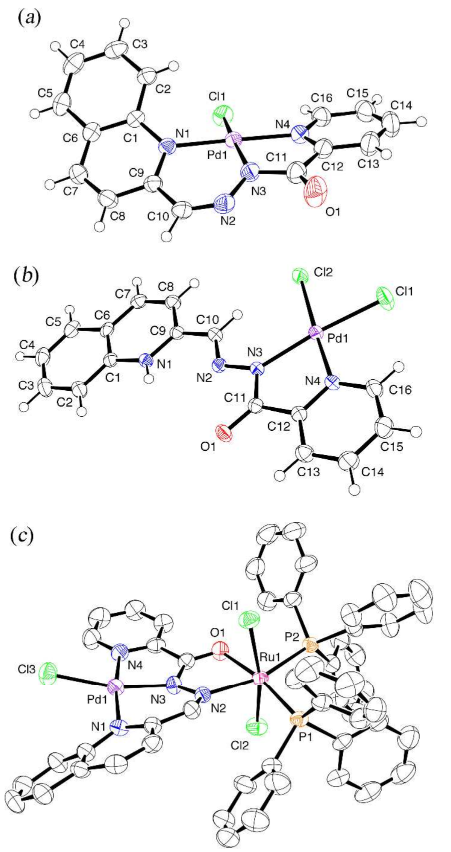

Figure 1 ORTEPs (50% probability level) of (*a*) [PdCl{*Z*-L-κ*N*(pyridine),κ*N*(hydrazonato),κ*N*(quinoline)}] in **1**•0.5CH_3CN, (*b*) [$PdCl_2${*E*-HL′-κ*N*(pyridine), κ*N*(hydrazonato)}] in **2**•0.5CH_3CN•H_2O and (*c*) the heterodinuclear complex in *trans(Cl,Cl)*-[$RuCl_2(PPh_3)_2$(μ-L)PdCl]·2CH_2Cl_2 (**3**·2CH_2Cl_2: H atoms omitted for clarity).

1•0.5CH_3CN was revealed by X-ray analysis,[6] and a perspective drawing of **1** is shown in Figure 1*a*. It is obvious that the hydrazone having a *Z*-form is deprotonated to act as a tridentate ligand to a Pd^{II} center in the κ^3*N*(pyridine),*N*(hydrazonato),*N*(quinoline) mode.

The Pd1–Cl1 bond length in **1**, [PdCl(*Z*-L-κ^3N,N',N'')], is 2.3359(6) Å (Table S2), which is slightly longer than those in $[PdCl(terpy)]^+$ (terpy = 2,2′:6′,6″-terpyridine) complexes (2.29–2.30 Å).[7] Among three Pd–N bonds in **1**, the Pd1–N3(hydrazonato), 1.967(2) Å, is a little shorter than the others, 2.044(2) Å for Pd1–N1(quinoline) and 2.036(2) Å for Pd1–N4(pyridine). However, a similar bond shortening of the central Pd–N bond was also observed in the above terpy complexes.[7] Thus, it is concluded that the anionic hydrazonato-*N* donor gives a stronger *trans* influence on the *trans*-positioned Cl^- ligand than a neutral pyridine-*N* donor. Another remarkable feature in the molecular structure of complex **1** is a large twist of the intrinsically planar hydrazonato ligand, *Z*-L^-.[5] The coordination geometry around the Pd^{II} centre is almost square-planar, as the Cl1–Pd1–N3 and N1–Pd1–N4 bond angles are 168.85(6)° and 171.20(7)°, respectively, and the τ_4 value[8] indicating a tetrahedral distortion is 0.14. In contrast, in the ligand of *Z*-L^- the dihedral angle between the carboxylic acid hydrazine (CAH; –C(O)–N–N=) and the quinoline planes and that between the CAH and the pyridine planes are 27.0(1)° and 15.9(1)°, respectively (Table S2). This distortion could be originated from the steric interaction between the coordinated Cl1 ligand and the H atom bound to C2 in the quinoline group.

The formation of complex **1** in nearly quantitative yield indicated that the *E* to *Z* isomerization, as well as the deprotonation, of HL took place during the reaction with [$PdCl_2$(cod)]. As mentioned in our previous paper,[4] the hydrazone itself did not isomerize to each other under a similar condition in the presence of NEt_3. This result suggests that the Pd^{II} ion assists (or catalyzes) the *E* to *Z* conversion of the ligand. Then, we have examined a reaction of [$PdCl_2$(cod)] and an *E*/*Z* mixture of HL in acetonitrile without addition of NEt_3. After standing the reaction mixture at room temperature overnight, yellow needle or thin platelet crystals of **2**•0.5CH_3CN•H_2O were deposited, together with orange crystals of complex **1**•0.5CH_3CN (Scheme 2*b*).

The X-ray analysis for **2**•0.5CH_3CN•H_2O indicated that it contains the coordinated hydrazone in the *E*-form with a zwitterionic character having the hydrazonate and quinolinium moieties (HL′). The molecular structure of [$PdCl_2$(*E*-HL′)] is depicted in Figure 1*b*, which is a typical square-planar Pd^{II} complex with two Cl^- ligands in the *cis* position. The hydrazone coordinates with a bidentate κ^2*N*(pyridine),*N*(hydrazonato) mode to form a planar five-membered chelate ring. The dihedral angle between the CAH and the quinoline planes and that between the CAH and the pyridine planes are 2.3(1) and 2.4(1)°, respectively. This planarity indicates that the π-electrons of HL′ in complex **2** delocalize over the whole ligand moiety. The Pd1–Cl1 and Pd1–Cl2 bond lengths are 2.296(1) and 2.315(1) Å, respectively, and not so much different from each other. The Pd1–N3 bond, 2.071(3) Å, is longer than the Pd1–N4 bond, 2.020(3) Å, which is a remarkable contrast to the corresponding bond lengths in complex **1**. A similar tendency of the Pd–N bond lengths for the bidentate and tridentate hydrazonato ligands was observed in the related complexes.[9]

An acetonitrile solution of complex **2** exhibited a gradual spectral change as shown in Figure 2*a*, and the converged spectrum (after 2 h at room temperature) was quite similar to the spectrum of **1** (Figure S1). This fact indicates that the *E*-isomer of the zwitterionic hydrazone (HL′) bound to a Pd^{II} ion isomerizes to the *Z*-isomer without addition of any base. In other words, complex **2** is a kinetically preferable product from [$PdCl_2$(cod)] and *E*-L, and is gradually converted to the thermodynamically more stable complex **1** in solution (Scheme 2*c*).

Here, it is noted that the formation of complexes **1** and **2** by a reaction of [$PdCl_2$(cod)] and (a mixture of *Z*- and *E*-isomers of) HL is not straightforward, because in both complexes the ligand coordinates to a Pd^{II} ion via the hydrazonato-*N* atom. It is well-known that the hydrazone N–H itself is not acidic; however, when the hydrazone coordinates to a metal ion through the imine-*N* atom, it becomes highly acidic to induce easy deprotonation.[2] Thus, it is speculated that at the initial stage of reaction a coordinative interaction to a Pd^{II} ion would occur via the imine-*N* donor of HL.[9] The deprotonation from the hydrazone N–H, followed by migration of the $PdCl_2$ fragment, would give a complex of [$PdCl_2${*Z*- or *E*-L-κ^2*N*(pyridine),*N*(hydrazonato)}]$^-$. Then, in order to crystallize the

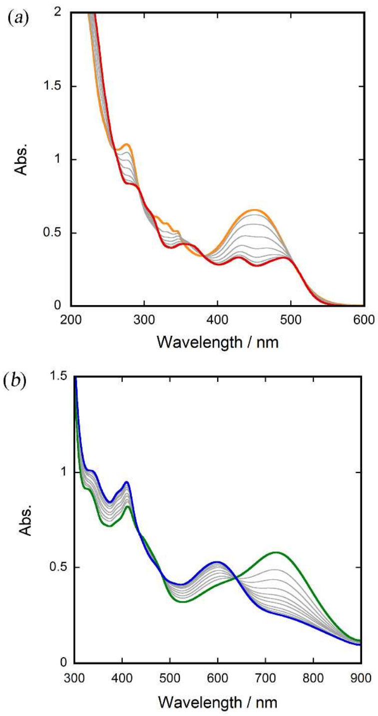

Figure 2 Absorption spectral changes (at room temperature: ~25 °C) of (*a*) **2** in acetonitrile measured at 15 min intervals from 0 (yellow) to 2 h (red) and (*b*) **3** in dichloromethane measured at 6 h intervals from 0 (green) to 60 h (blue).

complex as a neutral species, protonation to the quinoline-*N* atom of *E*-L$^-$ took place to give complex **2**. In the case of the *Z*-L$^-$ complex, a substitution of quinoline donor group for one of the Cl$^-$ ligands occurred to form neutral complex **1**.

In complex **1** the deprotonated hydrazonato ligand, *Z*-L$^-$, coordinates to a Pd^{II} centre in the tridentate κ^3*N*(pyridine),*N*(hydrazonato),*N*(quinoline) mode. Thus, the amide-*O* and imine-*N* donor atoms of the hydrazonate in **1** remain uncoordinated and are capable of binding to another metal ion. In our previous study, a reaction of (an *E*/*Z* mixture of) HL with $[RuCl_2(PPh_3)_3]$ afforded a mononuclear Ru^{II} complex, in which the *Z* form of hydrazone ligand coordinated to a Ru^{II} centre through the amide-*O* and imine-*N* atoms.[4] Moreover, one of the resultant Ru^{II} complexes, *trans(P,P)*-$[RuCl_2(PPh_3)_2(HL)]$, reacted with first-row transition-metal chlorides (MCl_2: M = Mn, Fe, Co, Ni, Cu and Zn) to give the hydrazonato-bridged Ru^{III}–M^{II} complexes, *trans(P,P)*-$[RuCl_2(PPh_3)_2(\mu\text{-L})MCl_2]$.[5] Thus, a reaction of complex **1** with $[RuCl_2(PPh_3)_3]$ was examined to prepare a heterometallic Pd–Ru complex.

Complex **1** was reacted with an equimolar amount of $[RuCl_2(PPh_3)_3]$ in dichloromethane under an argon atmosphere for 3 h at room temperature, and a green precipitate of the product (complex **3**) was obtained in a nearly quantitative (~98%) yield after evaporation of the solvent under reduced pressure, followed by addition of hexane into the concentrate (Scheme 2*d*). Single crystals of **3**•$2CH_2Cl_2$ suitable for X-ray analysis were deposited by slow diffusion of layered hexane into a dichloromethane solution. The analysis revealed that there are one dinuclear complex and two dichloromethane molecules in an asymmetric unit of a triclinic lattice with a space group $P\bar{1}$.

The molecular structure of complex **3** is illustrated in Figure 1*c*, and selected bond lengths and angles are summarized in Table S2. It is obvious that **1** successfully acts as a complex ligand to bind a $RuCl_2(PPh_3)_2$ fragment in a bidentate κ*N*(imine),κ*O*(amide) coordination mode. The structural parameters around the Pd center in **3** are almost unchanged from those in complex **1**, although the ligand twisting is slightly reduced in the dinuclear complex **3**. The coordination geometry around the Ru center is *trans(Cl,Cl)* configuration, which is the same as that of the kinetically formed mononuclear complex, *trans(Cl,Cl)*-$[RuCl_2(PPh_3)_2(HL)]$ (**4**), and the coordination bond lengths around the Ru center in **3** are very similar to those in **4**.[4] Thus, it is concluded that the oxidation states of the metal centers in complex **3** are assigned as Pd^{II}–Ru^{II}.

The ^{31}P NMR spectrum of **3** in $CDCl_3$ showed two doublet signals at δ 47.3 and 37.9 with $J_{P\text{–}P}$ = 35 Hz, which is very similar to the spectrum of complex **4**[4] and coincides with the molecular structure of dinuclear Pd^{II}–Ru^{II} complex determined by the single-crystal X-ray analysis. The redox potential of Ru$^{III/II}$ couples in complex **3** was observed at 142 mV vs. Fc$^+$/Fc (Figure S2), which is almost the same as that in complex **4** (118 mV vs. Fc$^+$/Fc).[4] It was also reported that complex **4** is a kinetically favourable product and exhibited a thermal conversion in solution due to an exchange of the coordinated Cl$^-$ and PPh_3 ligands.[4] The heterometallic Pd^{II}–Ru^{II} complex **3** showed a very similar UV-vis spectral change in dichloromethane (Figure 2*b*), and the converged product (in $CDCl_3$) exhibited two doublet ^{31}P NMR signals at δ 45.3 and 40.7 ($J_{P\text{–}P}$ = 35 Hz) (Figure S3). Although the crystal structure of the product has not been determined yet, the observed spectroscopic features suggested that the geometrical isomerization around the Ru^{II} centre would also take place in this heterometallic complex.

In conclusion, we have prepared two kinds of mononuclear Pd^{II} complexes by a reaction of $[PdCl_2(cod)]$ and an *E*/*Z* mixture of the hydrazone, HL. One is dichlorido complex, $[PdCl_2(E\text{-HL}')]$ (**2**), in which the zwitterionic HL' is coordinated through the pyridine-*N* and hydrazonato-*N* to act as a bidentate ligand. The other is [PdCl(*Z*-L)] (**1**), where an anionic hydrazonate (L$^-$) is ligating through the pyridine-*N*, hydrazonato-*N* and quinoline-*N* to act as a tridentate ligand. It was also found that complex **2** in solution was gradually converted to the thermodynamically more stable complex **1**. In addition, complex **1** reacted with $[RuCl_2(PPh_3)_3]$, affording a heterometallic complex, *trans(Cl,Cl)*-$[ClPd(\mu\text{-L})RuCl_2(PPh_3)_2]$ (**3**) in a high selectivity. In complex **3** the oxidation state of the Ru centre is assigned as Ru^{II}, which is in contrast to the previously reported Ru^{III}–M^{II} (M = Mn, Fe, Co, Ni, Cu and Zn) complexes with the same bridging mode of hydrazonate, L$^-$. Complex **3** showed a similar thermal conversion to the mononuclear Ru^{II} hydrazone complex **4**. The characterization of the converged products, as well as the investigation of the physical and chemical functionalities and catalytic abilities of the reported hydrazonato complexes, are now in progress in our laboratory.

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6 We have also analyzed the crystal structure for a single-crystal of **1**•0.5CH_2Cl_2, which was obtained from a dichloromethane solution by slow evaporation. The details and results of the analysis are reported in Supporting Information.

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A graphical and textual abstract for Table of contents entry

Palladium(II) mononuclear and palladium(II)/ruthenium(II) heterodinuclear complexes containing 2-quinolyl-substituted (pyridine-2-carbonyl)hydrazone

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Two mononuclear Pd^{II} complexes, [PdCl(*Z*-L-κ^3*N*,*N’*,*N’’*)] (**1**) and [PdCl$_2$(*E*-HL’-κ^2*N*,*N’*)] (**2**), where L$^-$ is the deprotonated hydrazonate anion and HL’ is the quinolinium–hydrazonate zwitterionic form of HL, and a heterodinuclear Pd^{II}/Ru^{II} complex bridged by L$^-$, *trans(Cl,Cl)*-[PdCl(μ-L)RuCl$_2$(PPh$_3$)$_2$] (**3**), were prepared stepwise and their structures and properties were characterized.