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^1H AND ^{13}C NMR STUDIES ON PALLADIUM(II) AND PLATINUM(II) COMPLEXES WITH 4-METHYL- AND 3,5-DIMETHYLPYRIDINIUM 2-PYRIDYLCARBONYLMETHYLIDE LIGANDS

GEN-ETSU MATSUBAYASHI * and YASUO KONDO

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka 565 (Japan)

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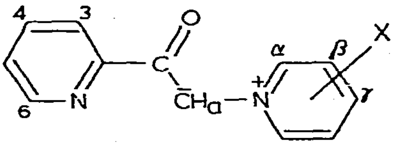
Summary

Chelate ylide ligands, 2-pyridylcarbonylmethylides, $C_5H_4NC(O)\bar{C}H\overset{+}{Z}$ (Z = 4-picoline (Y_{pic}) and 3,5-lutidine (Y_{lut})) and their metal complexes of the MCl_2L and $[PtL_2][ClO_4]_2$ types (M = Pd^{II}, Pt^{II}; L = Y_{pic}, Y_{lut}; L_2 = $(Y_{pic})_2$, $(Y_{lut})_2$, (bpy)(Y_{pic}), (bpy)(Y_{lut}) (bpy = 2,2'-bipyridine)) were prepared. On the basis of IR, ^1H and ^{13}C NMR spectra, it is proposed that the ylide ligands are coordinated to the metal ions via the ylide carbon and pyridine nitrogen atoms. The configurations of the metal complexes as well as the properties of the ylide carbon-to-metal bonds are discussed.

Introduction

Previously we have reported palladium(II) and platinum(II) complexes with several phenacylides, which contain an ylide carbon-to-metal bond [1]. In order to obtain a better understanding of the properties of the ylide—metal bond, we have undertaken an investigation of palladium(II) and platinum(II) complexes with chelate ylides having a carbonyl-stabilized ylide carbon atom and a pyridine ring. Although several chelate ylide complexes with these metal ions have been studied [2—5], no metal complexes with chelate pyridinium ylides are known. This paper reports the preparation of palladium(II) and platinum(II) complexes with chelate pyridinium ylide ligands, 2-pyridylcarbonylmethylides ($C_5H_4NC(O)\bar{C}H\overset{+}{Z}$; Z = 4-picoline ($Y_{pic}$) and 3,5-lutidine ($Y_{lut}$)). Their configurations and the properties of the ylide carbon-to-metal bonds are discussed on the basis of IR, ^1H and ^{13}C NMR spectra.



2 — Pyridylcarbonylmethylides
X = 4 − CH_3 and 3,5 −$(CH_3)_2$

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Results and discussion

$PdCl_2(SMe_2)_2$ and $PtCl_2(SMe_2)_2$ reacted with equimolar amounts of Y_{pic} and Y_{lut} to give the complexes MCl_2L ($M = Pd^{II}, Pt^{II}$; $L = Y_{pic}, Y_{lut}$). Furthermore, $PtCl_2Y_{pic}$ and $PtCl_2Y_{lut}$ reacted with Y_{pic}, Y_{lut}, and bpy (2,2'-bipyridine) to yield $[PtL_2]^{2+}$ complexes ($L_2 = (Y_{pic})_2, (Y_{lut})_2$, (bpy)($Y_{pic}$), and (bpy)($Y_{lut}$)), although the palladium(II) analogs were not obtained under similar reaction conditions.

MCl_2L ($M = Pd^{II}, Pt^{II}$; $L = Y_{pic}, Y_{lut}$)

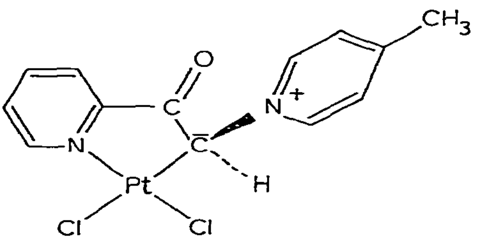
Table 1 summarizes the relevant IR frequencies of the 2-pyridylcarbonylmethylides and their palladium(II) and platinum(II) complexes. Upon complex formation the ν(C=O) bands of the 2-pyridylcarbonylmethylides shift to higher frequencies by 154—182 cm^{-1}, suggesting that coordination to metal ions through the ylide carbon atom has occurred as pointed out previously [1]. The magnitudes of the high frequency shifts of ν(C=O) in these complexes are larger than those observed for the corresponding phenacylide complexes; $\nu_{complexed} - \nu_{free}$ = 144 and 146 cm^{-1} for *trans*-$PtCl_2(PPhMe_2)(PhC(O)\bar{C}H\overset{+}{N}C_5H_4CH_3\text{-}4)$ and *trans*-$PtCl_2(PMe_3)(PhC(O)\bar{C}H\overset{+}{N}C_5H_4CH_3\text{-}4)$, respectively [1]. This may suggest that the metal—carbon bond of the 2-pyridylcarbonylmethylide complexes is more highly stabilized, partly due to the chelate effect, than the M—C bond of the phenacylide complexes. $PdCl_2L$ and $PtCl_2L$ ($L = Y_{pic}, Y_{lut}$) exhibit two ν(Pd—Cl) and ν(Pt—Cl) bands near 290 and 330 cm^{-1}, suggesting the *cis*-configuration of these complexes [6].

In the ^1H NMR spectra of $PtCl_2Y_{pic}$ and $PtCl_2Y_{lut}$, measured in liquid sulfur dioxide, H(6) and H_a signals of the ylides have satellites due to spin-spin coupling with the ^{195}Pt nucleus (see Table 2). This indicates coordination to the metal ion through the pyridine nitrogen atom as well as the ylide carbon. The $^2J(Pt—H_a)$ values of 142 and 143 Hz are comparable with that of *cis*-$PtCl_2(PPhMe_2)(PhC(O)\bar{C}H\overset{+}{S}Me_2)$ (134 Hz) and considerably larger than those of *trans*-$PtCl_2(PPhMe_2)(PhC(O)\bar{C}H\overset{+}{S}Me_2)$ (85 Hz) and *trans*-$PtCl_2(PPhMe_2)(PhC(O)\bar{C}H\overset{+}{N}C_5H_4CH_3\text{-}4)$ (91 Hz) [1]. The magnitude of the ^3J(Pt—H(6)) values (50 and 51 Hz) is somewhat larger than those of $PtCl_2$ (N-substituted 2-pyridylmethanimine) (38—40 Hz) [7], which reflects the stable chelate ring of the 2-pyridyl-

TABLE 1

RELEVANT IR FREQUENCIES OF THE 2-PYRIDYLCARBONYLMETHYLIDES AND THEIR METAL COMPLEXES (in Nujol mulls, cm^{-1})

Compound	ν(C=O)	ν(M—Cl)
Y_{pic}	1529	—
$PdCl_2Y_{pic}$	1687	296, 336
$PtCl_2Y_{pic}$	1694	291, 330
$[Pt(Y_{pic})_2][ClO_4]_2$	1697	—
$[Pt(bpy)(Y_{pic})][ClO_4]_2$	1711	—
Y_{lut}	1530	—
$PdCl_2Y_{lut}$	1684	311, 339
$PtCl_2Y_{lut}$	1696	290, 337
$[Pt(Y_{lut})_2][ClO_4]_2$	1696	—
$[Pt(bpy)(Y_{lut})][ClO_4]_2 \cdot 1/2\ H_2O$	1705	—



(I)

carbonylmethylide complexes. Upon coordination, the H(6) signals of the ylides, as well as the other proton signals of the pyridine ring, shift downfield through inductive effect of the metal ion. On the other hand, the H_a signals occur at higher fields than those of the free ylides. This is also true for the H_α signals. Coordination to the metal ion through the pyridine nitrogen atom leads to a decrease of the original paramagnetic anisotropy effect of the lone-pair electrons of the nitrogen atom on the H_a signal. Also, coordination through the ylide carbon atom would cause a configurational change around the ylide carbon atom from sp^2 to sp^3, as is depicted in I. In this geometry the H_α signal is considered to be not significantly affected by the paramagnetic anisotropy effect of the carbonyl group. These upfield shifts of the H_a and H_α signals are considered to surpass the downfield shifts owing to the inductive effect of the metal ion. Furthermore, it is noteworthy that the sp^3 configuration of the ylide carbon atom results in the sharp H_a signals having no ^{14}N coupling, although in the free ylides the H_a signals were split into three lines owing to ^{14}N coupling [8].

$PdCl_2L$ ($L = Y_{pic}$, Y_{lut}) exhibited similar behavior of the chemical shift to the platinum(II) analogs (see Table 2).

$[PtL_2][ClO_4]_2$ ($L = Y_{pic}$, Y_{lut})

The infrared ν(C=O) bands of these complexes occur at higher frequencies than those of the free ylides, suggesting the ylide carbon—platinum ligation

TABLE 2

RELEVANT ^1H NMR DATA OF THE 2-PYRIDYLCARBONYLMETHYLIDES IN CHLOROFORM-*d* AND OF THEIR METAL COMPLEXES IN LIQUID SULFUR DIOXIDE AT 24°C [a]

Compound	H(6)	H_a	H_α
Y_{pic}	8.52	7.50 [b]	9.61
$PdCl_2Y_{pic}$	9.00	6.91	8.42
$PtCl_2Y_{pic}$	9.34 (50)	6.42 (142)	8.42
$[Pt(Y_{pic})_2][ClO_4]_2$	8.81 (25)	6.47 (138)	8.42
$[Pt(bpy)(Y_{pic})][ClO_4]_2$	[c]	7.15 (126)	8.47
Y_{lut}	8.48	7.46 [b]	9.31
$PdCl_2Y_{lut}$	9.06	6.78	8.25
$PtCl_2Y_{lut}$	9.36 (51)	6.36 (143)	8.26
$[Pt(Y_{lut})_2][ClO_4]_2$	8.71 (26)	6.48 (138)	8.22
$[Pt(bpy)(Y_{lut})][ClO_4]_2$	[c]	7.10 (125)	8.46

[a] Chemical shifts (δ, ppm) and coupling constants between the ^{195}Pt nucleus and protons in parentheses (Hz). [b] $^2J(^{14}N—H_a) = 2.5$ Hz. [c] Not determined because of obscuration by other signals.

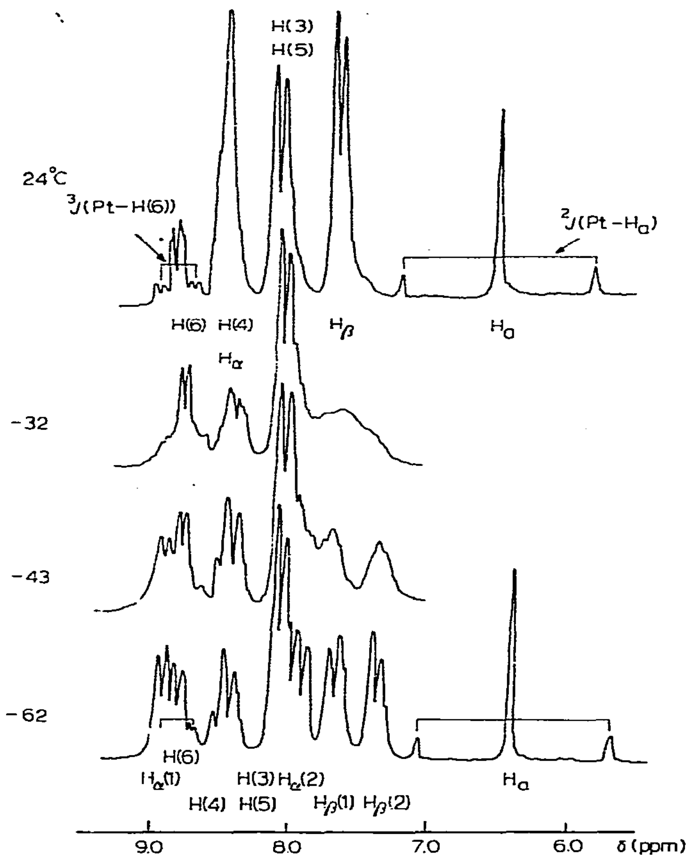
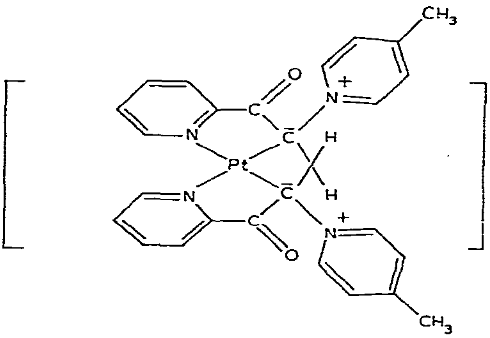


Fig. 1. Temperature-dependent ^{1}H NMR spectra of $[Pt(Y_{pic})_2][ClO_4]_2$ in liquid sulfur dioxide.

(Table 1). Figure 1 shows the ^{1}H NMR spectra of $[Pt(Y_{pic})_2][ClO_4]_2$ in liquid sulfur dioxide at various temperatures. The pyridine ring proton and ylide proton signals, together with the ^3J(Pt—H(6)) and ^2J(Pt—H_a) values, are essentially unchanged in the temperature range measured. However, the proton signals of the 4-methylpyridinium ring vary remarkably. At 24°C both the H_α protons give one signal as do the H_β protons, showing that two H_α and two H_β protons are magnetically equivalent, respectively. At low temperatures these protons become non-equivalent to give four signals ($H_{\alpha 1}$, $H_{\alpha 2}$, $H_{\beta 1}$, and $H_{\beta 2}$), while only one 4-methyl proton signal has been observed, suggesting the equivalence of two 4-methyl groups in the complex.

For the $[Pt(Y_{pic})_2]^{2+}$ cation, where the platinum ion is coordinated by the ylide carbon and pyridine nitrogen atoms, four configurations (II—V) are possible. Non-equivalence of the H_α as well as the H_β signals observed at low temperatures would be due to restricted rotation around the 4-methylpyridinium nitrogen—ylide carbon bond. The configuration of the $[Pt(bpy)(Y_{pic})]^{2+}$ complex is considered to be VI, in which the geometry around the coordinated ylide carbon atom is quite similar to that in IV or V. The spectrum of this bpy



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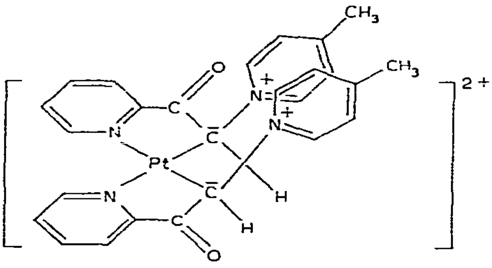

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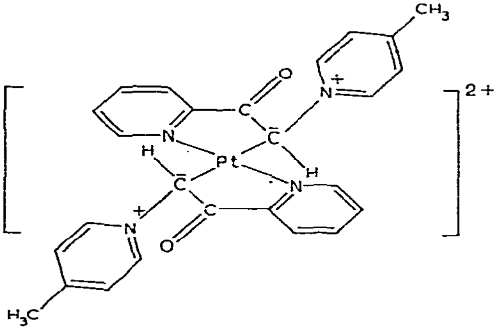

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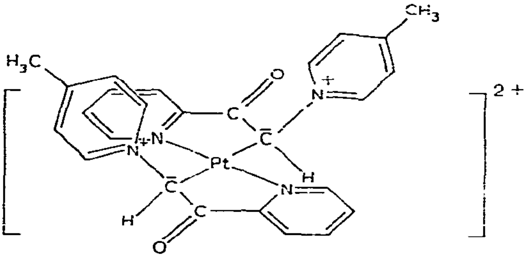

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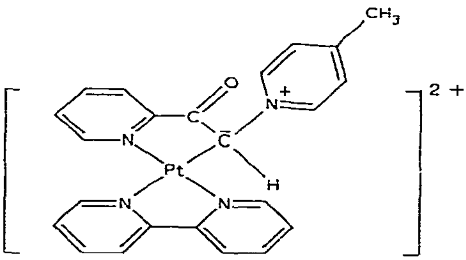

(VI)

complex gave equivalent H_α and H_β signals, respectively, even at —60°C in liquid sulfur dioxide. This finding indicates unhindered rotation around the ylide carbon—4-methylpyridinium nitrogen bond even at this temperature. Accordingly, the restricted rotation around the C—N bond observed in the $[Pt(Y_{pic})_2]^{2+}$ complex may not be attributed to configurations IV or V. Configuration III seems to be unfavorable because the rotation around the C—N bond is impossible owing to large steric hindrance between the 4-methylpyridinium rings. Thus, configuration II is the most plausible one for the $[Pt(Y_{pic})_2]^{2+}$ complex.

Although the ^2J(Pt—H_a) value is similar to that of $PtCl_2Y_{pic}$, the ^3J(Pt—H(6)) value is extremely small compared with that of $PtCl_2Y_{pic}$ (see Table 2). In addition, H(6) resonances occur at a slightly higher field in the $[Pt(Y_{pic})_2]^{2+}$ complex. These findings reflect the weak coordination of the pyridine nitrogen atoms to the platinum ion in the bis-ylide complex, which may be explained in

TABLE 3

^{13}C NMR CHEMICAL SHIFTS (δ, ppm) AND COUPLING CONSTANTS BETWEEN ^{13}C AND DIRECTLY BONDED ^{1}H AND BETWEEN ^{195}Pt AND ^{13}C NUCLEI (Hz) [a] FOR THE YLIDES [b] AND THEIR PLATINUM(II) COMPLEXES [c] AT 34°C

Compound	C(2)	C(3)	C(4)	C(5)	C(6)	C(C=O)	C_a	C_α	C_β	C_γ	CH_3
Y_{pic}	158.5	120.2	136.2	122.9	147.2	165.4	99.1 [d]	133.4 [d]	126.1	143.5	20.5
	(—)	(166)	(163)	(165)	(178)	(—)	(183)	(189)	(166)	(—)	(133)
Y_{lut}	158.9	120.6	136.6	123.4	147.6	166.4	99.2 [e]	131.3 [e]	135.8	133.5	18.5
	(—)	(166)	(162)	(165)	(178)	(—)	(185)	(189)	(—)	(170)	(129)
$[Pt(Y_{pic})_2]^{2+}$	153.3	126.0	142.6	131.8	145.6	200.4	68.0	150.9	129.8	160.7	21.5
	(—)	(173)	(171)	(172)	(189)	(—)	(142)	(189)	(172)	(—)	(131)
	[~0]	[24]	[7]	[25]	[40]	[27]	[891]	[7]	[<3]	[8]	[~0]
$[Pt(Y_{lut})_2]^{2+}$	153.4	126.0	142.6	131.9	143.5	200.3	69.3	146.8	140.9	151.0	20.2
	(—)	(173)	(f)	(174)	(f)	(—)	(143)	(f)	(—)	(184)	(128)
	[~0]	[26]	[7]	[26]	[38]	[29]	[886]	[5]	[<3]	[7]	[~0]

[a] $^{1}J(^{13}C—H)$ in parentheses and $J(^{195}Pt—^{13}C)$ in square brackets. [b] Measured in chloroform-d. [c] Measured in methanol-d_4. [d] $^{1}J(^{14}N—^{13}C)$ = 8.6 Hz. [e] $^{1}J(^{14}N—^{13}C)$ = 8.8 Hz. [f] Not determined precisely owing to complexity of the signals.

terms of mutual steric repulsion between the pyridine rings in configuration II. The $[Pt(Y_{lut})_2]^{2+}$ complex also gave two non-equivalent H_α and β-methyl signals, respectively, at −60°C. The spectral behavior of the H(6) signal was quite similar to that of the Y_{pic} analog.

The ^{13}C NMR parameters for the $[Pt(Y_{pic})_2]^{2+}$ and $[Pt(Y_{lut})_2]^{2+}$ complexes as well as those for the free ylides are summarized in Table 3 *. The ^{13}C signal assignment has been performed by comparing the chemical shifts with those of 2-substituted pyridines [9] and the coupling constants between ^{13}C and directly bonded hydrogen atoms ($^1J(C-H)$) with those of pyridine and pyridinium salts [10]. The C_a signals of the complexes appear at extremely high fields compared with those of free Y_{pic} and Y_{lut}. Furthermore, the $^1J(C_a-H)$ values are smaller than those of free Y_{pic} and Y_{lut} in which the ylide carbon has an sp^2 configuration [8]. These facts reflect the sp^3 configuration of the complexed ylide carbon atom, as has been illustrated in II. The C_a signals occur with satellites due to the ^{195}Pt coupling. Although there have been no data reported on direct ylide carbon—platinum coupling which could be compared with the present values, the $^1J(Pt-C_a)$ values are relatively larger than those of other methylplatinum(II) compounds: *trans*-$PtMeCl(PMe_2Ph)_2$, 673 Hz [11]; *cis*-$PtMe_2(Me_2AsC_6H_4AsMe_2)$, 690 Hz [12]; *cis*-$PtMe_2(AsMe_2Ph)_2$, 685 Hz [13]. This may reflect the stable ylide carbon—platinum(II) bond.

^{195}Pt coupling satellites are also observed at the ^{13}C signals of the pyridine rings of coordinated Y_{pic} and Y_{lut}. The magnitude of the couplings decreases in the order C(6) > C(3) ~ C(5) > C(4). Small values of $^4J(Pt-C(4))$ are comparable with the case of bpy-platinum(II) complexes [14—16]. The $^2J(Pt-C(2))$ values of both the Y_{pic} and Y_{lut} complexes have been measured to be almost zero in spite of large values of $^2J(Pt-C(6))$. This may be explained by assuming that the coupling contributions with opposite sign from the two-bond path (Pt—N—C) and from the three-bond path (Pt—C—C—C) apparently cancel at the C(2) position to produce negligible coupling.

The ^{13}C signals of the 4-methyl- and 3,5-dimethylpyridinium rings also occur with the ^{195}Pt coupling satellites. The relatively large value of the $^5J(Pt-C_\gamma)$ in spite of the long distance between the C_γ and the platinum atoms may reflect an important contribution of the π-mechanism of spin—spin coupling in the pyridinium ring.

Experimental

Preparation of 4-methylpyridinium (Y_{pic}) and 3,5-dimethylpyridinium 2-pyridylcarbonylmethylide (Y_{lut})

4-Picoline (3.3 g, 35 mmol) was added to a methanol (30 cm³) solution of 2-(bromoacetyl)pyridinium bromide [17] (4.0 g, 15 mmol). After it had been stirred for 3 h at room temperature, the solution was evaporated to dryness under reduced pressure. The resulting product was dissolved in water (10 cm³),

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* The ^{13}C NMR spectra were measured for PtL_2Cl_2 (L = Y_{pic}, Y_{lut}) in methanol-d_4, since the solubility of $[PtL_2][ClO_4]_2$ was not enough for the measurement. The ^1H NMR spectra of PtL_2Cl_2 in liquid sulfur dioxide and in methanol-d_4 were essentially identical to those of the perchlorate complexes.

followed by the addition of a 30% K_2CO_3 aqueous solution (80 cm^3). After the solution was extracted with dichloromethane, the extracts were evaporated to dryness to afford a crude solid. This was recrystallized from a mixture of dichloromethane and petroleum ether (30—50°C) to give yellow crystals of Y_{pic} (1.96 g, 65% yield). M.p. 44.5—46°C (decomp.). Found: C, 73.42; H, 5.54; N, 13.04. $C_{13}H_{12}N_2O$ calcd.: C, 73.56; H, 5.70; N, 13.20%.

Y_{lut} was also prepared by the reaction of 3.5-lutidine (3.2 g, 30 mmol) with 2-(bromoacetyl)pyridinium bromide (4.0 g, 15 mmol) in the same way (1.8 g, 58% yield). M.p. 129—131°C. Found: C, 74.26; H, 6.16; N, 12.23. $C_{14}H_{14}N_2O$ calcd.: C, 74.31; H, 6.24; H, 12.38%.

Preparation of dichloro(2-pyridylcarbonylmethylide)platinum(II) and -palladium(II), MCl_2L ($M = Pt^{II}$, Pd^{II}; $L = Y_{pic}$, Y_{lut})

A dichloromethane (2 cm^3) solution of Y_{pic} (0.10 g, 0.47 mmol) was added to $PtCl_2(SMe_2)_2$ [18] (0.22 g, 0.55 mmol) in the same solvent (4 cm^3). The mixture was allowed to stand overnight at room temperature to give a yellow precipitate of crude $PtCl_2Y_{pic}$, which was recrystallized from dimethyl sulfoxide (0.072 g, 32% yield). M.p. 227°C. Found: C, 32.62; H, 2.58; N, 5.69. $C_{13}H_{12}N_2OCl_2Pt$ calcd.: C, 32.63; H, 2.53; N, 5.86%.

$PtCl_2Y_{lut}$ also was prepared by the reaction of Y_{lut} with $PtCl_2(SMe_2)_2$ in the same way (36% yield). M.p. 260°C. Found: C, 33.99; H, 2.76; N, 5.75. $C_{14}H_{14}N_2OCl_2Pt$ calcd.: C, 34.12; H, 2.86; N, 5.69%.

The palladium(II) analogs were prepared by the reaction of $PdCl_2(SMe_2)_2$ [19] with an equimolar Y_{pic} and Y_{lut} in dichloromethane. They were recrystallized from a mixture of dimethyl sulfoxide and acetonitrile (62 and 65% yield). $PdCl_2Y_{pic}$. M.p. 236°C. Found: C, 40.09; H, 3.32; N, 7.37. $C_{13}H_{12}N_2OCl_2Pd$ calcd.: C, 40.08; H, 3.11; N, 7.19%. $PdCl_2Y_{lut}$: M.p. 242°C. Found: C, 41.03; H, 3.46; N, 6.86. $C_{14}H_{14}N_2OCl_2Pd$ calcd.: C, 41.67; H, 3.50; N, 6.86%.

The complexes obtained here were soluble in liquid sulfur dioxide, but poorly soluble in common organic solvents.

Preparation of bis(2-pyridylcarbonylmethylide)platinum(II) perchlorate, $[PtL_2][ClO_4]_2$ ($L = Y_{pic}$, Y_{lut})

A dichloromethane (10 cm^3) solution of Y_{pic} (0.75 g, 3.50 mmol) was added to a stirred solution of $PtCl_2(SMe_2)_2$ (0.50 g, 1.27 mmol) in dichloromethane (10 cm^3). The mixture was stirred overnight at room temperature to give a pale green precipitate of $Pt(Y_{pic})_2Cl_2 \cdot x\,H_2O$ (0.69 g), as confirmed by IR and ^1H NMR spectra. The product was dissolved in methanol (15 cm^3), followed by the addition of magnesium perchlorate (0.35 g) in methanol (10 cm^3) to give a pale yellow precipitate of $[Pt(Y_{pic})_2][ClO_4]_2$, which was recrystallized from acetone (0.42 g, 40% yield). Found: C, 37.85; H, 2.85; N, 6.66. $C_{26}H_{24}N_2O_{10}Cl_2Pt$ calcd.: C, 38.15; H, 2.96; N, 6.84%.

$[Pt(Y_{lut})_2][ClO_4]_2$ was also prepared by the use of Y_{lut} in the same way and recrystallized from acetonitrile to give a white powder (51% yield). Found: C, 40.33; H, 3.48; N, 7.74%. $C_{28}H_{28}N_4O_{10}Cl_2Pt$ calcd.: C, 40.60; H, 3.52; N, 7.89%.

Reactions of $PdCl_2(SMe_2)_2$ with an excess amount of L ($L = Y_{pic}$, Y_{lut}) in dichloromethane did not give PdL_2Cl_2 but yielded only $PdCl_2L$.

Preparation of (2,2'-bipyridine)(2-pyridylcarbonylmethylide)platinum(II) perchlorate, [Pt(bpy)L][ClO$_4$]$_2$ (L = Y_{pic} and Y_{lut})

2,2'-Bipyridine (0.040 g, 0.25 mmol) was added to a suspension of $PtCl_2Y_{pic}$ (0.10 g, 0.21 mmol) in water (7 cm^3). The mixture was stirred for 1.5 h at room temperature, followed by the addition of a 3 cm^3 aqueous solution of sodium perchlorate (0.11 g, 0.78 mmol) to give a pale green powder of $[Pt(bpy)(Y_{pic})][ClO_4]_2$, which was recrystallized from hot water (0.099 g, 62% yield). Found: C, 35.97; H, 2.63; N, 7.41. $C_{23}H_{20}N_4O_9Cl_2Pt$ calcd.: C, 36.23; H, 2.64; N, 7.35%.

A pale green powder of $[Pt(bpy)(Y_{lut})][ClO_4]_2 \cdot \frac{1}{2} H_2O$ was also obtained in the same way (57% yield). Found: C, 36.32; H, 2.69; N, 7.18. $C_{24}H_{23}N_4O_{9.5}Cl_2Pt$ calcd.: C, 36.70; H, 2.95; N, 7.13%.

Spectra

IR and ^{1}H NMR spectra were measured as described previously [1]. ^{13}C NMR spectra were recorded in chloroform-*d* and methanol-d_4 at 15.03 MHz using the pulse Fourier transform technique on a JEOL FX 60 spectrometer at 34°C. ^{13}C chemical shifts were measured relative to TMS as the internal standard.

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