1538 *Organometallics* **1986**, *5*, 1538–1544

# Binuclear and Tetranuclear Mixed Oxidation State Platinum Complexes Containing Both $\mu$-2,2′-Bipyrimidine and $\mu$-Hydrocarbyl Ligands

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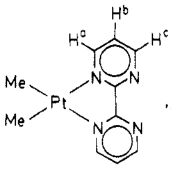
*Received February 20, 1986*

A method is described for the synthesis of organoplatinum complexes containing up to four metal atoms, including tetranuclear $Pt^{IV}_2$–$Pt^{II}_2$ derivatives with $\mu$-hydrocarbyl groups bridging the platinum(IV) centers. Reaction of [$PtMe_2$(bipym)] (**2**, bipym = 2,2′-bipyrimidine) with alkyl halides gave [$PtXMe_2R$(bipym)] (**4**, X = I, R = Me, Et, Pr, *i*-Pr; **5**, X = I, R = I($CH_2$)$_n$ where $n$ = 3–6; **6**, X = Br, R = 2-$BrCH_2C_6H_4CH_2$; **7**, X = Br, R = 4-$BrCH_2C_6H_4CH_2$). Further reaction of **4** and **5** with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] gave the corresponding complexes [$PtIMe_2R$($\mu$-bipym)$PtMe_2$], containing both Pt(IV) and Pt(II) centers. Reaction of **5** or **6** with **2** gave [{$PtIMe_2$(bipym)}$_2$($\mu$-$CH_2$)$_n$] (**15**) or [{$PtBrMe_2$(bipym)}$_2$($\mu$-*o*-$CH_2C_6H_4CH_2$)] (**16**) which are binuclear platinum(IV) complexes with $\mu$-hydrocarbyl ligands. Further reaction of **15** or **16** with [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] gave [{$PtIMe_2$($\mu$-bipym)$PtMe_2$}$_2$($\mu$-$CH_2$)$_n$] (**17**) or [{$PtBrMe_2$($\mu$-bipym)$PtMe_2$}$_2$($\mu$-*o*-$CH_2C_6H_4CH_2$)] (**18**) which contain $\mu$-hydrocarbyl bridges between the two platinum(IV) centers and $\mu$-bipym bridges between each pair of platinum(IV) and platinum(II) centers. The characterization of these and related complexes by IR, UV–visible, and $^1$H NMR spectroscopies is described.

## Introduction

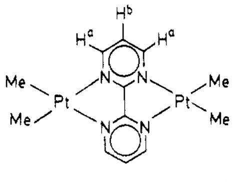
We wish to report details of a strategy which has allowed the synthesis of many novel multinuclear organoplatinum complexes containing one or two $\mu$-hydrocarbyl[1] ligands. Such complexes are of current interest, and several binuclear 1,10-phenanthroline platinum(IV) complexes containing Pt($CH_2$)$_n$Pt units have been characterized.[2] The present system was developed on the basis of trans oxidative addition of alkyl halides and $\alpha,\omega$-dihalogenoalkanes to dimethylplatinum(II) centers[2,3] with additional coordination of dimethylplatinum(II) units by the bis(chelate) ligand 2,2′-bipyrimidine (bipym)[4-7] to yield numerous examples of rare mixed oxidation state Pt(IV)–Pt(II) complexes.[8]

[$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**1**) with weakly bound $Me_2S$ ligands[9] was used as a convenient source of $Me_2Pt^{II}$ units and gave high yields of the complexes *cis*-[$PtMe_2$(bipym)] (**2**) and [$Pt_2Me_4$($\mu$-bipym)] (**3**) on reaction with bipym in dichloromethane solution. These complexes have been prepared independently by Sutcliffe and Young during the course of our work.[4]



**2**

**3**



Complex **3** was insoluble in common organic solvents, and hence the more soluble **2** was used in most subsequent syntheses. The presence of the extra two nitrogen donors in **2** compared to [$PtMe_2$(1,10-phenanthroline)][2] has allowed the construction of higher nuclearity complexes, including binuclear and tetranuclear complexes containing equal numbers of platinum(IV) and platinum(II) centers. A preliminary account of parts of this work has been published.[10]

## Results and Discussion

**Characterization of Complexes 2 and 3.** Complex **2** is a deep red crystalline solid; the color is due to the presence of a platinum(II) to bipym charge-transfer (MLTC) band in the visible region of the spectrum (Figure 1).[4,11] The complex was characterized by a variety of techniques. Complex **2** gave a molecular ion in the mass spectrum with an isotope pattern characteristic of a mononuclear platinum complex. The bonding mode of the bipym ligand can be deduced from the presence of two distinct imine C=N stretches in the IR spectrum due to both coordinated and uncoordinated nitrogen atoms. In contrast, complex **3**, with all nitrogen atoms coordinated, gave only one C=N stretching vibration in the IR spectrum. This is found to be a very useful method of distinguishing between symmetrical and unsymmetrical bipym complexes (see later).

The $^1$H NMR spectrum of **2** contained a singlet due to the $Me_2Pt$ groups, with $^2J$(PtH) = 88 Hz, and three separate signals for the bipym protons H$^a$, H$^b$, and H$^c$. As well as the expected HH couplings, the signals due to H$^a$ and H$^b$ showed satellites due to coupling to $^{195}$Pt, thus aiding assignment of the resonances. Details are given in the Experimental Section and the spectrum is shown in Figure 2.

**Synthesis of Mononuclear Platinum(IV) Complexes.** Complex **2**, which gives an intense red solution in acetone, reacted rapidly with primary alkyl iodides to give the products of trans oxidative addition **4a–c**, which give pale yellow solutions in acetone. With the less reactive isopropyl iodide, photochemical initiation of the reaction in the absence of air gave the analogous product **4d**.

The stereochemistry of complexes **4** was established by the observation of a single MePt resonance in the $^1$H NMR spectrum. As expected the coupling constant $^2J$($PtCH_3$)

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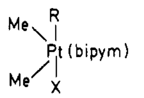
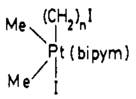


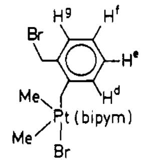
4a, X = I, R = Me
4b, X = I, R = Et
4c, X = I, R = Pr
4d, X = I, R = i-Pr
4e, X = Cl, R = Me
4f, X = Br, R = Me



5a, n = 3
5b, n = 4
5c, n = 5
5d, n = 6

decreased from 88 Hz in **2** to ca. 74 Hz in **4**, as platinum is oxidized from Pt(II) to Pt(IV), respectively. Similarly the coupling to the ortho proton $H^a$ of the bipym ligand, $^3J(PtH^a)$, decreased from 20.5 Hz in **2** to ca. 17 Hz in **4**. Similar observations have been made for the corresponding products from $[PtMe_2(NN)]$, where NN = 2,2′-bipyridine or 1,12-phenanthroline.[2,12-17]

In a similar way, reaction of **2** with excess $\alpha,\omega$-diiodoalkanes gave the adducts **5a–d**, and reaction with $\alpha,\alpha'$-dibromo-*o*-xylene or $\alpha,\alpha'$-dibromo-*p*-xylene gave **6** or **7**, respectively. The $^1H$ NMR spectrum of **6** is shown in Figure 3a. The signal at $\delta$ 6.1 is assigned as the aryl proton, $H^d$, of the xylyl group ortho to the $CH_2Pt$ group and is strongly shielded by the ring current of the bipym ligand. The remaining aryl protons of the xylyl group are less strongly shielded and resonate in the region $\delta$ 6.6–6.9. The broad resonances of the bipym protons are thought to be due to restricted rotation about the Pt–$CH_2$–Ar bonds; much sharper bipym resonances were observed for **2**, **4**, and **5** (Figure 2).



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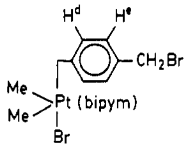

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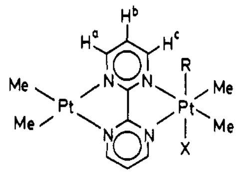
Finally, the chloro and bromo derivatives **4e** and **4f** were prepared by reaction of **4a** with silver nitrate, to remove the iodide as AgI, followed by addition of lithium chloride or bromide, respectively.

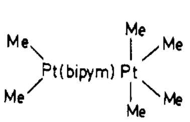
All of these complexes were prepared in high yields and were then used to prepare complexes with higher nuclearity.

**Synthesis of Binuclear Pt(IV)–Pt(II) Mixed Oxidation State Complexes.** The mixed oxidation state complexes **8a–f** were prepared by displacement of dimethyl sulfide from complex **1** by the free nitrogen donor atoms of complexes **4a–f**, respectively. In addition, complex **9** was prepared by displacement of dimethyl sulfide from $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ by the free nitrogen donor atoms of complex **2**.

These complexes were readily characterized by $^1H$ NMR. For example, complex **9** gave three methylplatinum resonances of equal intensity due to methylplatinum(IV) groups trans to nitrogen [$\delta$ 1.01 ($^2J(PtH)$ = 77 Hz)] or methyl [$\delta$ −0.52 ($^2J(PtH)$ = 44 Hz)] and methylplatinum(II) [$\delta$ 1.20 ($^2J(PtH)$ = 90 Hz)] groups, with $^2J(PtCH_3)$ coupling constants in the expected ranges for these groups. Three resonances due to the bipym protons were observed as expected (see Experimental Section for details).



8a, X = I, R = Me
8b, X = I, R = Et
8c, X = I, R = Pr
8d, X = I, R = i-Pr
8e, X = Cl, R = Me
8f, X = Br, R = Me



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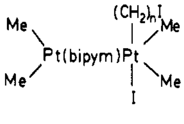
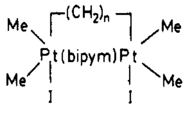
The complexes were isolated as air-stable green solids. There was a very significant shift in the absorption maximum in the UV–visible spectra from 480 nm for the monomer **2** to 556–570 nm for the new complexes **8a–f** and **9** (see Figure 1). For the complexes of general formula $[PtMe_3X(\mu\text{-bipym})PtMe_2]$ the values (nm) in acetone solution were as follows: 558, X = Cl; 564, X = Br; 570, X = I; 556, X = Me. These values do not suggest that there is much Pt(II) → Pt(IV) charge transfer character in these bands but rather that coordination of the two free nitrogen atoms of **2** to give the binuclear complexes leads to a higher level $d_\pi$ level on platinum(II) and so results in a lower energy Pt(II) → bipym MLCT transition for **8** or **9** compared to **2**.[18] A similar effect has been observed for ruthenium(II) bipym complexes.[19]

Similar mixed oxidation state complexes **10a–d** were formed by reaction between complexes **1** and **5a–d**, respectively. We had expected that a subsequent intramolecular oxidative addition of the C–I bond of **10** to the platinum(II) center would occur to give the derivatives **11**, but no such reaction occurred. Since the platinum(II) center is reactive in oxidative addition to other alkyl halides (see later), this lack of reactivity to intramolecular oxidative addition must be due to unfavorable steric and/or ring strain effects in the transition state. When $n = 6$, the $(CH_2)_n$ chain is certainly long enough to span the two platinum centers, but it seems that the coplanarity of the two platinum centers in **10** is unfavorable for intramolecular oxidative addition. Similar oxidative additions have been shown to occur by the $S_N2$ mechanism[3] for which there are stringent conformational requirements.



10a, n = 3
10b, n = 4
10c, n = 5
10d, n = 6



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**Synthesis of Binuclear Platinum(IV) Complexes.** Oxidative addition of methyl iodide to the platinum(II) center of **9** gave complex **12**. The analogous oxidative additions to complexes **8** could give **13** or **14**, and, in general a mixture of these isomers was obtained as shown by the $^1H$ NMR spectra. The ratios of **13**:**14** formed were as follows: 2.8, X = I, R = Me; 2.0, X = Br, R = Me; 1.2, X = Cl, R = Me; 0, X = I, R = *i*-Pr. The most dramatic effect is observed for the isopropyl derivative **8d**, when the bulky isopropyl group must block access of MeI and so only one isomer, presumed to be **14d**, was formed. The remaining data are also consistent with steric effects having

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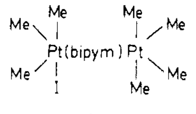

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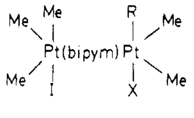
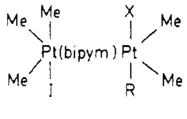




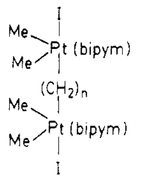
13a, X = I, R = Me
13b, X = Br, R = Me
13c, X = Cl, R = Me
13d, X = I, R = i-Pr

14a, X = I, R = Me
14b, X = Br, R = Me
14c, X = Cl, R = Me
14d, X = I, R = i-Pr

a dominant role in determining the isomer ratio of **13**:**14**. The ratios were determined by integration of the methylplatinum signals due to each isomer, and assignments were based on the assumption that **8d** gave only **14d**, as expected for oxidative addition by the $S_N2$ mechanism.

The symmetrical octamethyldiplatinum complex $[Me_4Pt(\mu\text{-bipym})PtMe_4]$ was prepared by reaction of $[Pt_2Me_8(\mu\text{-SMe}_2)_2]$ with an equimolar amount of the ligand bipym, the dimethyl sulfide ligands being displaced easily, and a mixture of **13a** and **14a** could also be prepared by oxidative addition of excess methyl iodide to a suspension of **3** in acetone.

**Synthesis of ($\mu$-Hydrocarbyl)diplatinum(IV) Complexes.** Intermolecular oxidative addition between **5** or **6** and complex **2** gave the ($\mu$-hydrocarbyl)diplatinum(IV) complex **15** or **16**, respectively.



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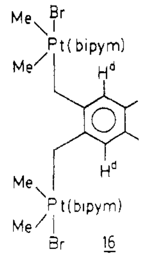

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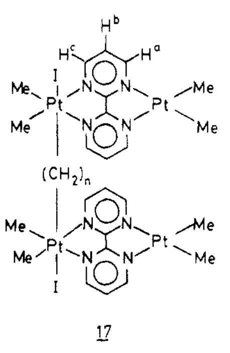
Complexes **15** with $n = 3$ or 4 were insufficiently soluble to give NMR spectra, but **15** with $n = 5$ or 6 and **16** were structurally characterized by their $^1H$ NMR spectra. The protons $H^d$ and $H^e$ of the o-xylyl group appeared at $\delta$ 5.71 and 6.11, respectively, even more strongly shielded than in **6**. These complexes are analogous to known 1,10-phenanthroline derivatives, but they contain four free nitrogen donors which can be used to build complexes with higher nuclearity.

**Synthesis of Tetranuclear Complexes.** Complexes **17** and **18** were prepared by reaction of **15** and **16**, respectively, with complex **1**, with displacement of dimethyl sulfide ligands from **1**. They appear to be among the first tetranuclear complexes to contain $\mu$-hydrocarbyl groups.[1]



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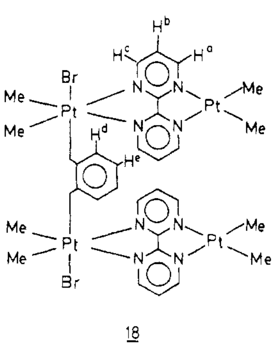

18

Complexes **17** and **18** are green solids, and their UV-visible spectra contained maxima at ca. 570 nm. These spectra were very similar to those of the binuclear complexes **8** and **10**, and it seems that the two chromophores in **17** and **18** [the Pt(II)-bipym centers] are insulated from one another by the $\mu$-hydrocarbyl group and do not interact significantly.

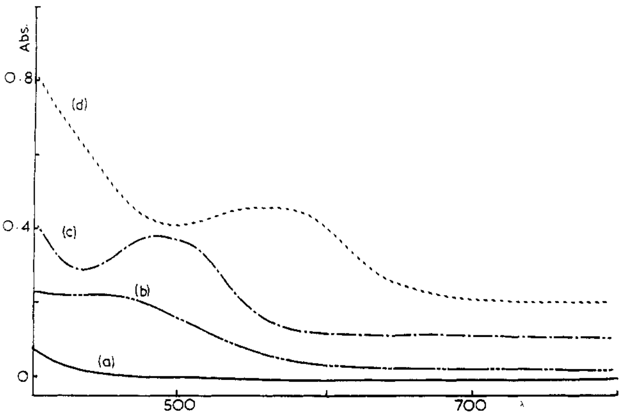

**Figure 1.** UV-visible spectra of complexes (a) **4a** ($\lambda_{max}$ = 375 nm), (b) **14d** ($\lambda_{max}$ = 450 nm), (c) **2** ($\lambda_{max}$ = 485 nm), and (d) **8d** ($\lambda_{max}$ = 566 nm). The base lines are displaced for clarity.

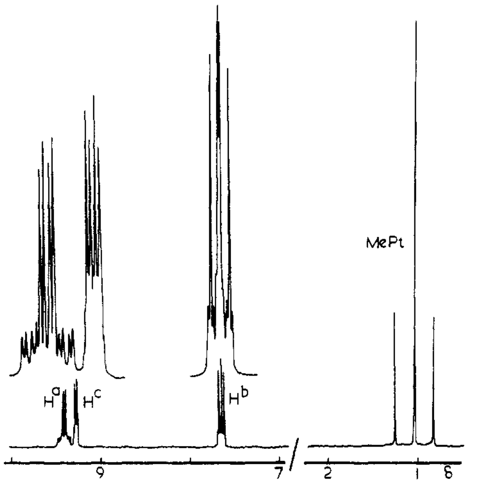

**Figure 2.** $^1H$ NMR spectrum (200 MHz) of complex **2**. The peaks due to bipym protons are expanded above to show the HH and PtH couplings.

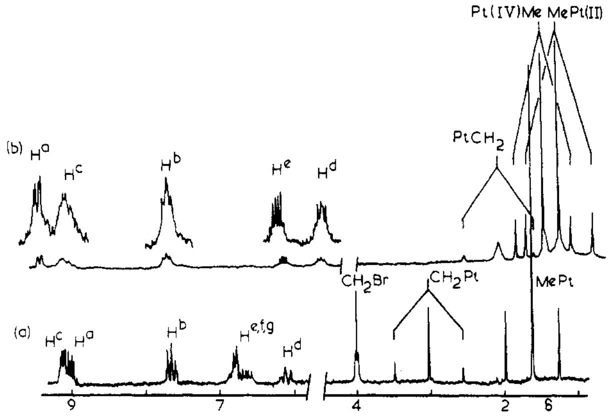

**Figure 3.** $^1H$ NMR spectra (100 MHz) of (a) complex **6** and (b) complex **18** (note the unusual chemical shifts of protons $H^d$ and $H^e$ and the breadth of the $CH_2Pt$ resonance). Assignments are given above the spectra.

Complexes **17** and **18** were also characterized by their $^1H$ NMR spectra, and the spectrum of **18** is shown in Figure 3b. There are two methylplatinum resonances of equal intensity corresponding to the $Me_2Pt^{II}$ groups [$^2J$(PtH) = 90 Hz] and the $Me_2Pt^{IV}$ groups [$^2J$(PtH) = 74 Hz]. A very broad signal was observed for the $PtCH_2$ protons, attributed to the effects of restricted rotation about the Pt–$CH_2$ bonds. The resonances due to the bipym protons were also broad, presumably for the same reason. Again the signals $H^d$ and $H^e$ (the aryl protons of the xylyl group) were strongly shielded, probably as a result of this aromatic ring being sandwiched between the two bipym rings. The spectrum clearly defines the structure **18**.

The platinum(II) centers of **17** and **18** are electron-rich and can take part in further oxidative addition. For example, reaction with excess methyl iodide gave the orange complexes $[\{PtIMe_3(\mu\text{-bipym})PtIMe_2\}_2\{\mu\text{-}(CH_2)_5\}]$ (**19**) and $[\{PtIMe_3(\mu\text{-bipym})PtIMe_2\}_2\{\mu\text{-}o\text{-}CH_2C_6H_4CH_2\}]$ (**20**).

## Conclusions

A strategy has been devised for the stepwise synthesis of high nuclearity organometallic complexes. The utility of the system has been illustrated by the easy synthesis of binuclear and tetranuclear complexes containing both platinum(II) and platinum(IV) centers. It is apparent that the method can readily be applied to the synthesis of still higher nuclearity complexes and also to high nuclearity complexes containing two or more different metal centers. By using other bis(chelate) ligands, it should be possible to prepare complexes in which two metal centers are held in different orientations (with bipym the metal centers are approximately coplanar) and with different separations between the metal centers. These will be useful in mechanistic studies, and, in favorable cases, intramolecular oxidative addition of complexes analogous to **10** may be expected.

The success of this method relies on the high reactivity of the $Me_2Pt(II)$ centers to oxidative addition in diimine complexes and is aided by the ease of characterization of the products by $^1H$ NMR spectroscopy. Further studies of synthesis, reactivity, and mechanism in this system are in progress.

## Experimental Section

$^1H$ NMR spectra were recorded on Varian XL100 and XL200 spectrometers in $CD_2Cl_2$ solvent unless stated otherwise. Chemical shifts are given with respect to $Me_4Si$. IR spectra were recorded on a Beckman IR4250 spectrometer as Nujol mulls between NaCl plates. UV–vis spectra were recorded on both Varian Cary 118 and Varian Cary 2290 spectrometers in $CH_2Cl_2$ solution unless stated otherwise. Mass spectra were recorded on a Varian MAT Bremen mass spectrometer MAT311A. Elemental analyses were performed by Guelph Chemical Laboratories Ltd.

Complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ and $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ were prepared as previously described.[9,20]

**[PtMe$_2$(bipym)] (2).** A solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.500 g) in $CH_2Cl_2$ (30 mL) was added rapidly to a stirring solution containing 5 equiv per Pt of 2,2′-bipyrimidine (1.380 g) in $CH_2Cl_2$ (20 mL). The solution immediately turned dark red. After $^1/_2$ h the dark brown precipitate of $[Pt_2Me_4(\mu\text{-bipym})]$ was filtered off, and the resulting clear red solution was evaporated to dryness. Recrystallization from acetone yielded the monomer as a dark red crystalline solid: yield 83%; mp 120 °C dec. Anal. Calcd for $C_{10}H_{12}N_4Pt$: C, 31.3; H, 3.2; N, 14.6. Found: C, 31.8; H, 3.3; N, 14.6. $^1H$ NMR: 1.03 [s, 6 H, $^2J(PtH)$ = 88 Hz, MePt], 9.41 [dd, 2 H, $^3J(H^aH^b)$ = 5.5 Hz, $^4J(H^aH^c)$ = 2.5 Hz, $^3J(PtH^a)$ = 20.5 Hz, $H^a$], 7.66 [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $^4J(PtH^b)$ = 3.0 Hz, $H^b$], 9.29 ppm [dd, 2 H, $^3J(H^cH^b)$ = 5.0 Hz, $^4J(H^cH^a)$ = 2.5 Hz, $^5J(PtH^c)$ = 1.5 Hz, $H^c$]. IR: 1570 and 1548 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: $\lambda_{max}$ 480 nm.

**[Pt$_2$Me$_4$($\mu$-bipym)] (3).** To a solution of [PtMe$_2$(bipym)] (0.079 g) in $CH_2Cl_2$ (10 mL) was added a solution containing 0.5 equiv of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.059 g) in $CH_2Cl_2$ (10 mL). The product precipitated as a dark brown insoluble solid. The solid was washed with $CH_2Cl_2$ and dried under vacuum: yield 90%; mp 185 °C dec. Anal. Calcd for $C_{12}H_{18}N_4Pt_2$: C, 23.7; H, 3.0; N, 9.2. Found: C, 23.8; H, 3.0; N, 9.6. Complex **3** is too insoluble to obtain $^1H$ NMR or UV–vis spectra. IR: 1568 cm$^{-1}$ [$\nu$(C=N)].

**[PtIMe$_3$(bipym)] (4a).** To a solution of [PtMe$_2$(bipym)] (0.090 g) in acetone (50 mL) was added an excess of MeI (0.5 mL). The solution immediately turned pale yellow. The solution was concentrated under vacuum, and the product was precipitated as a pale yellow solid by adding pentane: yield 93%; mp 255 °C dec. Anal. Calcd for $C_{11}H_{15}N_4IPt$: C, 25.2; H, 2.9; N, 10.7. Found: C, 25.5; H, 3.0; N, 10.4. $^1H$ NMR: 1.56 [s, 6 H, $^2J(PtH)$ = 72 Hz, MePt trans to N], 0.67 [s, 3 H, $^2J(PtH)$ = 72 Hz, MePt trans to I], 9.19 [dd, 2 H, $^3J(H^aH^b)$ = 5.5 Hz, $^4J(H^aH^c)$ = 2.0 Hz, $^3J(PtH^a)$ = 13.0 Hz, $H^a$], 7.78 [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $^4J(PtH^b)$ = 2.5 Hz, $H^b$], 9.23 ppm [dd, 2 H, $^3J(H^cH^b)$ = 5.0 Hz, $^4J(H^cH^a)$ = 2.5 Hz, $^5J(PtH^c)$ = 1.0 Hz, $H^c$]. IR: 1567 and 1546 cm$^{-1}$ [$\nu$(C=N)]. The following were prepared in a similar way. [PtIMe$_2$(Et)(bipym)] (**4b**): orange solid; yield 86%; mp 235 °C dec. Anal. Calcd for $C_{12}H_{17}N_4IPt$: C, 26.7; H, 3.2; N, 10.4. Found: C, 26.5; H, 3.0; N, 10.5. $^1H$ NMR: 1.49 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N], 0.12 [t, 3 H, $^3J(HH)$ = 7.0 Hz, $^3J(PtH)$ = 68 Hz, $CH_3$], 9.22 [m, br, 4 H, $H^a$ and $H^c$], 7.79 ppm [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $H^b$]. IR: 1567 and 1544 cm$^{-1}$ [$\nu$(C=N)]. [PtIMe$_2$($n$-Pr)(bipym)] (**4c**): orange solid; yield 89%; mp 210 °C dec. Anal. Calcd for $C_{13}H_{19}N_4IPt$: C, 28.2; H, 3.5; N, 10.1. Found: C, 28.1; H, 3.4; N, 10.0. $^1H$ NMR: 1.51 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N], 0.63 [t, br, 3 H, $^3J(HH)$ = 6.0 Hz, $CH_3$], 9.20 [m, br, 4 H, $H^a$ and $H^c$], 7.80 ppm [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $H^b$]. IR: 1570 and 1548 cm$^{-1}$ [$\nu$(C=N)].

**[PtIMe$_2$($i$-Pr)(bipym)] (4d).** A solution of [PtMe$_2$(bipym)] (0.120 g) in acetone (75 mL) was degassed by bubbling $N_2$ through the solution for 3 h. To this solution was added an excess of $i$-PrI (2.0 mL). $N_2$ was bubbled through the solution for another $^1/_2$ h, and then the solution under $N_2$ atmosphere was placed in direct sunlight. The color changed to bright yellow in 0.5 h. The solvent was reduced to 5 mL, and the product precipitated as a yellow solid by addition of pentane: yield 89%; mp 240 °C dec. Anal. Calcd for $C_{13}H_{19}N_4IPt$: C, 28.2; H, 3.5; N, 10.1. Found: C, 28.6; H, 3.5; N, 10.0. $^1H$ NMR: 1.50 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N], 0.33 [d, 6 H, $^3J(HH)$ = 7.0 Hz, $^3J(PtH)$ = 62 Hz, $CH_3$], 1.75 [spt, 1 H, $^3J(HH)$ = 7.0 Hz, CH], 9.17 [dd, 2 H, $^3J(H^aH^b)$ = 5.5 Hz, $^4J(H^aH^c)$ = 2.5 Hz, $^3J(PtH)$ = 12.0 Hz, $H^a$], 7.78 [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $^4J(PtH^b)$ = 2.0 Hz, $H^b$], 9.25 ppm [dd, 2 H, $^3J(H^cH^b)$ = 5.0 Hz, $^4J(H^cH^a)$ = 2.5 Hz, $^5J(PtH^c)$ = 1.0 Hz, $H^c$]. IR: 1573 and 1547 cm$^{-1}$ [$\nu$(C=N)].

**[PtIMe$_2${(CH$_2$)$_3$I}(bipym)] (5a).** To a solution of [PtMe$_2$(bipym)] (0.079 g) in acetone (75 mL) was added an excess of 1,3-diiodopropane (1.0 mL). After 2 h the solution turned pale orange. The solvent was reduced under vacuum, and the product precipitated as an orange solid by addition of diethyl ether. The product was washed with ether and dried under vacuum: yield 78%; mp 185 °C dec. Anal. Calcd for $C_{13}H_{18}N_4I_2Pt$: C, 23.0; H, 2.7; N, 8.3. Found: C, 23.0; H, 2.7; N, 8.2. $^1H$ NMR: 1.52 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N], 2.86 [t, 2 H, $^3J(HH)$ = 7 Hz, $CH_2I$], 9.17 [dd, 2 H, $^3J(H^aH^b)$ = 5.5 Hz, $^4J(H^aH^c)$ = 2.5 Hz, $^3J(PtH^a)$ = 13.0 Hz, $H^a$], 7.81 [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $H^b$], 9.27 ppm [m, 2 H, $H^c$]. IR: 1568 and 1547 cm$^{-1}$ [$\nu$(C=N)]. The following complexes were prepared in a similar way. [PtIMe$_2${(CH$_2$)$_4$I}(bipym)] (**5b**): orange solid; yield 83%; mp 175 °C dec. Anal. Calcd for $C_{14}H_{20}N_4I_2Pt$: C, 24.3; H, 2.9; N, 8.1. Found: C, 24.3; H, 2.9; N, 7.9. $^1H$ NMR: 1.50 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N], 2.94 [t, 2 H, $^3J(HH)$ = 7 Hz, $CH_2I$], 9.18 [dd, 2 H, $^3J(H^aH^b)$ = 5.5 Hz, $^4J(H^aH^c)$ = 2.5 Hz, $^3J(PtH^a)$ = 12.5 Hz, $H^a$], 7.80 [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $H^b$], 9.28 ppm [m, 2 H, $H^c$]. IR: 1568 and 1548 cm$^{-1}$ [$\nu$(C=N)]. [PtIMe$_2${(CH$_2$)$_5$I}(bipym)] (**5c**): orange solid; yield 76%; mp 185 °C dec. Anal. Calcd for $C_{15}H_{22}N_4I_2Pt$: C, 25.5; H, 3.1; N, 7.9. Found: C, 25.4; H, 3.1; N, 7.8. $^1H$ NMR: 1.49 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N], 2.87 [t, 2 H, $^3J(HH)$ = 7 Hz, $CH_2I$], 9.17 [dd, 2 H, $^3J(H^aH^b)$ = 5.5 Hz, $^4J(H^aH^c)$ = 2.5 Hz, $^3J(PtH^a)$ = 13.0 Hz, $H^a$], 7.79 [dd, 2 H, $^3J(H^bH^a)$ = 5.5 Hz, $^3J(H^bH^c)$ = 5.0 Hz, $H^b$], 9.30 ppm [m, 2 H, $H^c$]. IR: 1568 and 1549 cm$^{-1}$ [$\nu$(C=N)]. [PtIMe$_2${CH$_2$)$_6$I}(bipym)] (**5d**): orange solid; yield 71%; mp 168 °C dec. Anal. Calcd for $C_{16}H_{24}N_4I_2Pt$: C, 26.6; H, 3.4; N, 7.8. Found: C, 26.5; H, 3.2; N, 7.6. $^1H$ NMR (acetone-$d_6$): 1.46 [s, 6 H, $^2J(PtH)$ = 74 Hz, MePt trans to N],

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[20] Lashanizadehgan, M.; Rashidi, M.; Hux, J. E.; Puddephatt, R. J.; Ling, S. S. M. *J. Organomet. Chem.* **1984**, *269*, 317.

3.10 [t, 2H, $^3J$(HH) = 7 Hz, CH$_2$I], 9.36 [m, 4 H, H$^a$ and H$^c$], 8.07 ppm [dd, 2 H, $^3J$(H$^b$H$^a$) = 5.5 Hz, $^3J$(H$^b$H$^c$) = 5.0 Hz, H$^b$]. IR: 1570 and 1547 cm$^{-1}$ [$\nu$(C=N)]. [PtBrMe$_2$(2-BrCH$_2$C$_6$H$_4$CH$_2$)(bipym)] (**6**): yellow solid; yield 68%; mp 220 °C dec. Anal. Calcd for C$_{18}$H$_{20}$N$_4$Br$_2$Pt: C, 33.4; H, 3.1; N, 8.7. Found: C, 33.3; H, 3.1; N, 8.5. $^1$H NMR 1.63 [s, 6 H, $^2J$(PtH) = 72 Hz, MePt trans to N], 3.02 [s, 2 H, $^2J$(PtH) = 92 Hz, H$_2$CPt], 3.90 [s, 2 H, $^5J$(PtH) = 6 Hz, CH$_2$Br], 9.02 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.5 Hz, $^4J$(H$^a$H$^c$) = 2.5 Hz, $^3J$(PtH$^a$) = 12.0 Hz, H$^a$], 7.74 [dd, 2H, $^3J$(H$^b$H$^a$) = 5.5 Hz, $^3J$(H$^b$H$^c$) = 5.0 Hz, H$^b$], 9.13 [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.5 Hz, H$^c$], 6.12 [m, 1 H, H$^d$], 6.64 [m, 2 H, H$^e$ and H$^f$], 6.80 ppm [m, 1 H, H$^g$]. IR: 1568 and 1550 cm$^{-1}$ [$\nu$(C=N)]. [PtBrMe$_2$(4-BrCH$_2$C$_6$H$_4$CH$_2$)(bipym)] (**7**): yellow solid; yield 84%; mp 205 °C dec. Anal. Calcd for C$_{18}$H$_{20}$N$_4$Br$_2$Pt: C, 33.4; H, 3.1; N, 8.7. Found: C, 33.0; H, 3.2; N, 8.5. $^1$H NMR: 1.54 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt trans to N], 2.84 [s, 2 H, $^2J$(PtH) = 91 Hz, H$_2$CPt], 4.24 [s, 2 H, $^7J$(PtH) = 5.0 Hz, CH$_2$Br], 6.32 [d, 2 H, $^3J$(H$^d$H$^e$) = 8.5 Hz, $^4J$(PtH$^d$) = 5.0 Hz, H$^d$], 6.72 [d, 2 H, $^3J$(H$^e$H$^d$) = 8.5 Hz, $^5J$(PtH$^e$) = 2.5 Hz, H$^e$], 8.81 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.5 Hz, $^4J$(H$^a$H$^c$) = 2.5 Hz, $^3J$(PtH$^a$) = 11.5 Hz, H$^a$], 7.60 [dd, 2 H, $^3J$(H$^b$H$^a$) = 5.5 Hz, $^3J$(H$^b$H$^c$) = 5.0 Hz, H$^b$], 9.12 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.5 Hz, H$^c$]. IR: 1569 and 1550 cm$^{-1}$ [$\nu$(C=N)].

**[PtClMe$_3$(bipym)] (4e).** To a solution of [PtIMe$_3$(bipym)] (0.203 g) in acetone (75 mL) was added 1 equiv of AgNO$_3$ (0.066 g) as an acetone solution (100 mL). There was an immediate precipitation of AgI, and the mixture was allowed to stir for 1 h. AgI was removed by filtration leaving a pale yellow solution to which was added 1 equiv of LiCl (0.017 g) as an acetone solution (25 mL). After $^1/_2$ h the solvent was removed. The platinum complex was extracted into CH$_2$Cl$_2$, and the remaining salts were filtered off. The solvent was reduced and the yellow product precipitated out by addition of pentane: yield 64%; mp 242 °C dec. Anal. Calcd for C$_{11}$H$_{15}$N$_4$ClPt: C, 30.5; H, 3.5; N, 12.9. Found: C, 30.2; H, 3.5; N, 12.5. $^1$H NMR: 1.20 [s, 6 H, $^2J$(PtH) = 72 Hz, MePt trans to N], 0.38 [s, 3 H, $^2J$(PtH) = 74 Hz, MePt trans to Cl], 9.04 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.5 Hz, $^4J$(H$^a$H$^c$) = 2.5 Hz, $^3J$(PtH$^a$) = 13.0 Hz, H$^a$], 7.71 [dd, 2 H, $^3J$(H$^b$H$^a$) = 5.5 Hz, $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 2.0 Hz, H$^b$], 9.13 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.5 Hz, $^5J$(PtH$^c$) = 1.0 Hz, H$^c$]. IR: 1571 and 1551 cm$^{-1}$ [$\nu$(C=N)]. In a similar way was prepared [PtBrMe$_3$(bipym)] (**4f**): yellow solid; yield 74%; mp 230 °C dec. Anal. Calcd for C$_{11}$H$_{15}$N$_4$BrPt: C, 27.6; H, 3.2; N, 11.7. Found: C, 27.2; H, 3.3; N, 11.2. $^1$H NMR: 1.40 [s, 6 H, $^2J$(PtH) = 68 Hz, MePt trans to N], 0.58 [s, 3 H, $^2J$(PtH) = 72 Hz, MePt trans to Br], 9.15 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.5 Hz, $^4J$(H$^a$H$^c$) = 2.5 Hz, $^3J$(PtH$^a$) = 13.0 Hz, H$^a$], 7.80 [dd, 2 H, $^3J$(H$^b$H$^a$) = 5.5 Hz, $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 2.0 Hz, H$^b$], 9.24 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.5 Hz, $^5J$(PtH$^c$) = 1.0 Hz, H$^c$]. IR: 1570 and 1550 cm$^{-1}$ [$\nu$(C=N)].

**[PtIMe$_3$($\mu$-bipym)PtMe$_2$] (8a).** To a solution of [PtIMe$_3$(bipym)] (0.300 g) in CH$_2$Cl$_2$ (15 mL) was added 0.5 equiv of [Pt$_2$Me$_4$($\mu$-SMe$_2$)$_2$] (0.164 g) as a CH$_2$Cl$_2$ solution (10 mL). The solution immediately turned dark green. After $^1/_2$ h the solvent volume was reduced, and the product was precipitated as a dark greenish brown solid by addition of diethyl ether. The product was washed with ether and dried under vacuum: yield 96%; mp 280°C dec. Anal. Calcd for C$_{13}$H$_{21}$N$_4$IPt$_2$: C, 20.8; H, 2.8; N, 7.5. Found: C, 20.6; H, 2.8; N, 7.4. $^1$H NMR: 1.63 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt$^{IV}$ trans to N], 0.70 [s, 3 H, $^2J$(PtH) = 70 Hz, MePt$^{IV}$ trans to I], 1.34 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 9.69 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 20.0 Hz, H$^a$], 8.00 ppm [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 2.0 Hz, H$^b$], 9.52 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 12.0 Hz, H$^c$]. IR: 1559 and 1552 cm$^{-1}$ [$\nu$(C=N)]. UV–vis (acetone): $\lambda_{max}$ 570 nm (Pt$^{II}$ → bipym CT). The following complexes were prepared in a similar way. [PtIMe$_2$(Et)($\mu$-bipym)PtMe$_2$] (**8b**): green solid; yield 84%; mp 240 °C dec. Anal. Calcd for C$_{14}$H$_{23}$N$_4$IPt$_2$: C, 22.0; H, 3.0; N, 7.3. Found: C, 22.0; H, 3.1; N, 7.1. $^1$H NMR: 1.58 [s, 6 H, $^2J$(PtH) = 75 Hz, MePt$^{IV}$], 1.35 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 0.21 [t, 3 H, $J$(HH) = 7.0 Hz, CH$_3$], 9.73 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 19.0 Hz, H$^a$], 7.99 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, H$^b$], 9.51 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 13.0 Hz, H$^c$]. IR: 1563 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: $\lambda_{max}$ 572 nm (Pt$^{II}$ → bipym CT). [PtIMe$_2$($n$-Pr)($\mu$-bipym)PtMe$_2$] (**8c**): green solid; yield 88%; mp 210 °C dec. Anal. Calcd for C$_{15}$H$_{25}$N$_4$IPt$_2$: C, 23.1; H, 3.2; N, 7.2. Found: C, 23.2; H, 3.2; N, 7.1. $^1$H NMR: 1.59 [s, 6 H, $^2J$(PtH) = 75 Hz, MePt$^{IV}$], 1.35 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 0.66 [t, br, 3 H, $J$(HH) = 6.0 Hz, *CH*$_3$], 9.72 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 19.5 Hz, H$^a$], 8.00 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, H$^b$], 9.50 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 12.5 Hz, H$^c$]. IR: 1560 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: $\lambda_{max}$ 570 nm (Pt$^{II}$ → bipym CT). [PtIMe$_2$($i$-Pr)($\mu$-bipym)PtMe$_2$] (**8d**): green solid; yield 78%; mp 215 °C dec. Anal. Calcd for C$_{15}$H$_{25}$N$_4$IPt$_2$: C, 23.1; H, 3.2; N, 7.2. Found: C, 23.5; H, 3.4; N, 7.4. $^1$H NMR (acetone-$d_6$): 1.57 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt$^{IV}$], 1.22 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 0.61 [d, 6 H, $J$(HH) = 8.0 Hz, $^3J$(PtH) = 62 Hz, CH$_3$], 9.84 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 18.5 Hz, H$^a$], 8.36 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 3.0 Hz, H$^b$], 9.80 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 12.0 Hz, H$^c$]. IR: 1562 cm$^{-1}$ [$\nu$(C=N)]. UV–vis (acetone): $\lambda_{max}$ 566 nm (Pt$^{II}$ → bipym CT). [PtClMe$_3$($\mu$-bipym)PtMe$_2$] (**8e**): green solid; yield 89%; mp 260 °C dec. Anal. Calcd for C$_{13}$H$_{21}$N$_4$ClPt$_2$: C, 23.7; H, 3.2; N, 8.5. Found: C, 24.0; H, 3.3; N, 8.4. $^1$H NMR (acetone-$d_6$): 1.36 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$ trans to N], 0.65 [s, 3 H, $^2J$(PtH) = 72 Hz, MePt$^{IV}$ trans to Cl], 1.21 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 9.82 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 19.0 Hz, H$^a$], 8.36 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 3.0 Hz, H$^b$], 9.69 [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 12.0 Hz, H$^c$]. IR: 1565 cm$^{-1}$ [$\nu$(C=N)]. UV–vis (acetone): $\lambda_{max}$ 558 nm (Pt$^{II}$ → bipym CT). [PtBrMe$_3$($\mu$-bipym)PtMe$_2$] (**8f**): green solid; yield 79%; mp 245 °C dec. Anal. Calcd for C$_{13}$H$_{21}$N$_4$Pt$_2$: C, 22.2; H, 3.0; N, 8.0. Found: C, 22.7; H, 3.3; N, 7.8. $^1$H NMR (acetone-$d_6$): 1.44 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$ trans to N], 0.74 [s, 3 H, $^2J$(PtH) = 73 Hz, MePt$^{IV}$ trans to Br], 1.21 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 9.81 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 20.0 Hz, H$^a$], 8.36 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 3.0 Hz, H$^b$], 9.71 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 12.0 Hz, H$^c$]. IR: 1564 cm$^{-1}$, $\nu$(C=N). UV–vis (acetone): $\lambda_{max}$ 564 nm (Pt$^{II}$ → bipym CT). [PtIMe$_2${(CH$_2$)$_3$I}($\mu$-bipym)PtMe$_2$] (**10a**): green solid; yield 93%; mp 270 °C dec. Anal. Calcd for C$_{15}$H$_{24}$N$_4$I$_2$Pt$_2$: C, 19.9; H, 2.7; N, 6.2. Found: C, 20.2; H, 2.8; N, 6.4. $^1$H NMR: 1.61 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$], 1.40 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 2.86 ppm [t, 2 H, $^3J$(HH) = 7 Hz, CH$_2$I]. IR: 1568 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: 571 nm (Pt$^{II}$ → bipym CT). [PtIMe$_2${(CH$_2$)$_4$I}($\mu$-bipym)PtMe$_2$] (**10b**): green solid; yield 91%; mp 240 °C dec. Anal. Calcd for C$_{16}$H$_{26}$N$_4$I$_2$Pt$_2$: C, 20.9; H, 2.9; N, 6.1. Found: C, 20.9; H, 2.8; N, 6.0. $^1$H NMR: 1.60 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt$^{IV}$], 1.37 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 2.92 ppm [t, 2 H, $^3J$(HH) = 7 Hz, CH$_2$I]. IR: 1565 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: $\lambda_{max}$ 570 nm (Pt$^{II}$ → bipym CT). [PtIMe$_2${(CH$_2$)$_5$I}($\mu$-bipym)PtMe$_2$] (**10c**): green solid; yield 83%; mp 250 °C dec. Anal. Calcd for C$_{17}$H$_{28}$N$_4$I$_2$Pt$_2$: C, 21.9; H, 3.0; N, 6.0. Found: C, 22.0; H, 3.0; N, 6.0. $^1$H NMR: 1.58 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$], 1.35 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 3.00 [t, 2 H, $^3J$(HH) = 7 Hz, CH$_2$I], 9.72 [m, 2 H, H$^a$], 8.00 [m, 2 H, H$^b$], 9.50 ppm [m, 2 H, H$^c$]. IR: 1568 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: $\lambda_{max}$ 570 nm (Pt$^{II}$ → bipym C.T.). [PtIMe$_2${(CH$_2$)$_6$I}($\mu$-bipym)PtMe$_2$] (**10d**): green solid; yield 78%; mp 215 °C dec. Anal. Calcd for C$_{18}$H$_{30}$N$_4$I$_2$Pt$_2$: C, 22.8; H, 3.2; N, 5.9. Found: C, 23.3; H, 3.2; N, 6.0. $^1$H NMR: 1.48 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$] 1.26 [s, 6 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 2.97 [t, 2 H, $^3J$(HH) = 8 Hz, CH$_2$I], 9.58 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 19.0 Hz, H$^a$], 7.89 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 3.0 Hz, H$^b$], 9.36 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 11.0 Hz, H$^c$]. IR: 1567 cm$^{-1}$ [$\nu$(C=N)]. UV–vis: $\lambda_{max}$ 569 nm (Pt$^{II}$ → bipym C.T.).

**[PtMe$_4$($\mu$-bipym)PtMe$_2$] (9).** To a solution of [PtMe$_2$(bipym)] (0.046 g) in acetone (25 mL) was added $^1/_2$ equiv of [Pt$_2$Me$_8$($\mu$-SMe$_2$)$_2$] (0.038 g) in acetone (10 mL). The solution turned deep purple, and after 1 h the solvent was removed. The product was obtained as a green solid which was washed with diethyl ether: yield 93%; mp 165 °C dec. Anal. Calcd for C$_{14}$H$_{24}$N$_4$Pt$_2$: C, 26.3; H, 3.8; N, 8.8. Found: C, 26.1; H, 4.1; N, 9.3. $^1$H NMR (acetone-$d_6$): 1.01 [s, 6 H, $^2J$(PtH) = 77 Hz, MePt$^{IV}$ trans to N], –0.52 [s, 6 H, $^2J$(PtH) = 44 Hz, MePt$^{IV}$ trans to Me], 1.20 [s, 6 H,

$^2J$(PtH) = 90 Hz, MePt$^{II}$], 9.72 [dd, 2 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 19.0 Hz, H$^a$], 8.22 [t, 2 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, $^4J$(PtH$^b$) = 3.0 Hz, H$^b$], 9.67 ppm [dd, 2 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, $^3J$(Pt$^{IV}$H$^c$) = 13.0 Hz, H$^c$]. IR: 1555 cm$^{-1}$ [$\nu$(C=N)]. UV-vis (acetone): $\lambda_{max}$ 556 nm (Pt$^{II}$ → bipym CT).

**[PtIMe$_2$(bipym){$\mu$-(CH$_2$)$_3$}PtIMe$_2$(bipym)] (15a).** To a solution of [PtIMe$_2${(CH$_2$)$_3$I}(bipym)] (0.049 g) in acetone (10 mL) was added 1 equiv of [PtMe$_2$(bipym)] (0.028 g) as an acetone solution (25 mL). After 24 h the product precipitated as a yellow solid. The product was collected by filtration and washed with acetone: yield 64%; mp 220 °C dec. Anal. Calcd for C$_{23}$H$_{30}$N$_8$I$_2$Pt$_2$: C, 26.0; H, 2.9; N, 10.6. Found: C, 26.0; H, 2.8; N, 10.6. IR: 1565 and 1545 cm$^{-1}$ [$\nu$(C=N)]. The following complexes were prepared in an analogous manner; however, with complexes **5c** and **5d** the reaction mixture was warmed at 40 °C for 2 days. With complex **5e** the reaction was complete within 2 h. With **5c–e** the products had to be precipitated from acetone by addition of pentane due to their greater solubility. [PtIMe$_2$(bipym){$\mu$-(CH$_2$)$_4$}PtIMe$_2$(bipym)] (**15b**): yellow solid; yield 72%; mp 240 °C dec. Anal. Calcd for C$_{24}$H$_{32}$N$_8$I$_2$Pt$_2$: C, 26.8; H, 3.0; N, 10.4. Found: C, 26.9; H, 3.1; N, 10.0. IR: 1566 and 1546 cm$^{-1}$ [$\nu$(C=N)]. [PtIMe$_2$(bipym){$\mu$-(CH$_2$)$_5$}PtIMe$_2$(bipym)] (**15c**): orange solid; yield 76%; mp 235 °C dec. Anal. Calcd for C$_{25}$H$_{34}$N$_8$I$_2$Pt$_2$: C, 27.5; H, 3.1; N, 10.3. Found: C, 27.7; H, 3.3; N, 9.9. $^1$H NMR: 1.37 [s, 12 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$], 9.17 [m, 8 H, H$^a$ and H$^c$], 7.76 ppm [t, br, 4 H, $^3J$(HH) = 5.0 Hz, H$^b$]. IR: 1568 and 1546 cm$^{-1}$ [$\nu$(C=N)]. [PtIMe$_2$(bipym){$\mu$-(CH$_2$)$_6$}PtIMe$_2$(bipym)] (**15d**): orange solid; yield 72%; mp 225 °C dec. Anal. Calcd for C$_{26}$H$_{36}$N$_8$I$_2$Pt$_2$: C, 28.3; H, 3.3; N, 10.1. Found: C, 28.3; H, 3.2; N, 10.1. $^1$H NMR: 1.42 [s, 12 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$], 9.10 [dd, 4 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(PtH$^a$) = 11.0 Hz, H$^a$], 7.78 [t, 4 H, $^3J$(H$^b$H$^a$) = $^3J$(H$^b$H$^c$) = 5.0 Hz, H$^b$], 9.23 ppm [dd, 4 H, $^3J$(H$^c$H$^b$) = 5.0 Hz, $^4J$(H$^c$H$^a$) = 2.0 Hz, H$^c$]. IR: 1569 and 1547 cm$^{-1}$ [$\nu$(C=N)]. [PtBrMe$_2$(bipym){$\mu$-*o*-(CH$_2$)$_2$C$_6$H$_4$}PtBrMe$_2$(bipym)] (**16**): yellow solid; yield 68%; mp 190 °C dec. Anal. Calcd for C$_{28}$H$_{32}$N$_8$Br$_2$Pt$_2$: C, 32.6; H, 3.1; N, 10.9. Found: C, 32.5; H, 3.0; N, 10.6. $^1$H NMR: 1.33 [s, 12 H, $^2J$(PtH) = 72 Hz, MePt$^{IV}$], 1.98 [s, 4 H, $^2J$(PtH) = 94 Hz, CH$_2$Pt$^{IV}$], 8.77 [m, br, 4 H, H$^a$], 7.53 [m, br, 4 H, H$^b$], 9.02 [m, br, 4 H, H$^c$], 5.71 and 6.11 ppm [m, br, 4 H, H$^d$ and H$^e$]. IR: 1569 and 1550 cm$^{-1}$ [$\nu$(C=N)].

**[{PtIMe$_2$($\mu$-bipym)PtMe$_2$}$_2${$\mu$-(CH$_2$)$_5$}] (17a).** To a solution of [PtIMe$_2$(bipym){$\mu$-(CH$_2$)$_5$}PtIMe$_2$(bipym)] (0.017 g) in CH$_2$Cl$_2$ (50 mL) was added 1 equiv of [Pt$_2$Me$_4$($\mu$-SMe$_2$)$_2$] (0.009 g) as a CH$_2$Cl$_2$ solution. The solution immediately turned dark green, and after 1 h the solvent was reduced and the product precipitated as a green solid by addition of diethyl ether: yield 96%; mp 265 °C dec. Anal. Calcd for C$_{29}$H$_{46}$N$_8$I$_2$Pt$_4$: C, 22.6; H, 3.0; N, 7.3. Found: C, 22.9; H, 2.9; N, 7.1. IR: 1561 cm$^{-1}$ [$\nu$(C=N)]. UV-vis: $\lambda_{max}$ 570 nm (Pt$^{II}$ → bipym CT). The following complexes were prepared in the same manner. [{PtIMe$_2$($\mu$-bipym)PtMe$_2$}$_2${$\mu$-(CH$_2$)$_6$}] (**17b**): green solid; yield 93%; mp 235 °C dec. Anal. Calcd for C$_{30}$H$_{48}$N$_8$I$_2$Pt$_4$: C, 23.2; H, 3.1; N, 7.2. Found: C, 23.7; H, 3.3; N, 6.9. $^1$H NMR: 1.38 [s, 12 H, $^2J$(PtH) = 76 Hz, MePt$^{IV}$], 1.09 [s, 12 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 9.42 [dd, br, 4 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 20.0 Hz, H$^a$], 7.74 [t, br, 4 H, $^3J$(HH) = 5.0 Hz, H$^b$], 9.20 ppm [m, br, 4 H, H$^c$]. IR: 1565 cm$^{-1}$ [$\nu$(C=N)]. UV-vis: $\lambda_{max}$ 572 nm (Pt$^{II}$ → bipym CT). [{PtBrMe$_2$($\mu$-bipym)PtMe$_2$}$_2${$\mu$-*o*-(CH$_2$)$_2$C$_6$H$_4$}] (**18**): green solid; yield 89%; mp 290 °C dec. Anal. Calcd for C$_{32}$H$_{44}$N$_8$Br$_2$Pt$_4$: C, 26.0; H, 3.0; N, 7.6. Found: C, 25.9; H, 2.9; N, 7.2. $^1$H NMR: 1.45 [s, 12 H, $^2J$(PtH) = 74 Hz, MePt$^{IV}$], 1.23 [s, 12 H, $^2J$(PtH) = 90 Hz, MePt$^{II}$], 2.07 [s, 4 H, $^2J$(PtH) = 92 Hz, CH$_2$Pt$^{IV}$], 9.44 [dd, br, 4 H, $^3J$(H$^a$H$^b$) = 5.0 Hz, $^4J$(H$^a$H$^c$) = 2.0 Hz, $^3J$(Pt$^{II}$H$^a$) = 20.0 Hz, H$^a$], 7.74 [t, br, 4 H, $^3J$(HH) = 5.0 Hz, H$^b$], 9.14 [m, br, 4 H, H$^c$], 5.63 and 6.16 ppm [m, br, 4 H, H$^d$ and H$^e$]. IR: 1567 cm$^{-1}$ [$\nu$(C=N)]. UV-vis: $\lambda_{max}$ 576 nm (Pt$^{II}$ → bipym CT).

**[{PtIMe$_2$($\mu$-bipym)PtIMe$_3$}$_2${$\mu$-(CH$_2$)$_5$}] (19a).** To a solution of [{PtIMe$_2$($\mu$-bipym)PtMe$_2$}$_2${$\mu$-(CH$_2$)$_5$}] (0.050 g) in CH$_2$Cl$_2$ (75 mL) was added an excess of MeI (0.5 mL). The solution immediately turned orange and the product precipitated as an orange solid. The solvent was removed and the product washed with acetone: yield 98%; mp 170 °C dec. Anal. Calcd for C$_{31}$H$_{52}$N$_8$I$_4$Pt$_4$: C, 20.4; H, 2.9; N, 6.1. Found: C, 20.4; H, 2.8; N, 6.5. IR: 1566 cm$^{-1}$ [$\nu$(C=N)]. The following complexes were prepared analogously. [{PtIMe$_2$($\mu$-bipym)PtIMe$_3$}$_2${$\mu$-(CH$_2$)$_6$}] (**19b**): orange solid; yield 94%; mp 165 °C dec. Anal. Calcd for C$_{32}$H$_{54}$N$_8$I$_4$Pt$_4$: C, 20.9; H, 3.0; N, 6.1. Found: C, 20.9; H, 3.0; N, 6.2. IR: 1563 cm$^{-1}$ [$\nu$(C=N)]. [{PtBrMe$_2$($\mu$-bipym)PtIMe$_3$}$_2${$\mu$-*o*-(CH$_2$)$_2$C$_6$H$_4$}] (**20**): orange solid; yield 97%; mp 165 °C dec. Anal. Calcd for C$_{34}$H$_{50}$N$_8$Br$_2$I$_2$Pt$_4$: C, 23.1; H, 2.9; N, 6.4. Found: C, 23.6; H, 3.1; N, 6.2. IR: 1568 cm$^{-1}$ [$\nu$(C=N)].

**[Pt$_2$Me$_8$($\mu$-bipym)].** To a solution of bipym (0.021 g) in acetone (10 mL) was added 1 equiv of [Pt$_2$Me$_8$($\mu$-SMe$_2$)$_2$] (0.084 g) as an acetone solution (10 mL). The solution initially turned red in color and after $^1/_2$ h turned green. After 1 h the solvent was removed, and the product obtained as a dark green solid was washed with diethyl ether: yield 73%; mp 150 °C dec. Anal. Calcd for C$_{16}$H$_{30}$N$_4$Pt$_2$: C, 28.7; H, 4.5; N, 8.4. Found: C, 28.4; H, 4.4; N, 8.4. $^1$H NMR (acetone-$d_6$): 1.05 [s, 12 H, $^2J$(PtH) = 76 Hz, MePt trans to N], −0.52 ppm [s, 12 H, $^2J$(PtH) = 44 Hz, MePt trans to Me]. IR: 1562 cm$^{-1}$ [$\nu$(C=N)]. UV-vis (acetone): 570 nm.

***cis*- and *trans*-[Pt$_2$I$_2$Me$_6$($\mu$-bipym)] (13a and 14a).** To a solution of [PtIMe$_3$($\mu$-bipym)PtMe$_2$] (0.050 g) in acetone (40 mL) was added an excess of MeI (0.5 mL). The solution immediately turned pale orange. The solvent was removed, and the product was obtained as an orange solid in quantitative yield: mp 240 °C dec. Anal. Calcd for C$_{14}$H$_{24}$N$_4$I$_2$Pt$_2$: C, 18.8; H, 2.7; N, 6.3. Found: C, 18.5; H, 2.7; N, 6.1. $^1$H NMR (acetone-$d_6$): cis and trans, 1.65 ppm [s, 12 H, $^2J$(PtH) = 76 Hz, MePt trans to N; signals for both isomers are superimposed], cis; 0.82 ppm [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I]; trans, 0.73 [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I], 9.71 [m, br, 4 H, H$^a$], 8.51 ppm [m, br, 2 H, H$^b$]. IR: 1567 cm$^{-1}$ [$\nu$(C=N)]. The following complexes were analogously prepared. *trans*-[PtIMe$_2$(*i*-Pr)($\mu$-bipym)PtIMe$_3$] (**14e**): orange solid; yield, quantitative; mp 210 °C dec. Anal. Calcd for C$_{16}$H$_{28}$N$_4$I$_2$Pt$_2$: C, 20.9; H, 3.1; N, 6.1. Found: C, 21.1; H, 3.0; N, 5.9. $^1$H NMR (acetone-$d_6$): 1.63 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt trans to N], 1.59 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt trans to N], 0.87 [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I], 0.49 [d, 6 H, $J$(HH) = 7.0 Hz, $^3J$(PtH) = 60 Hz, CH$_3$], 9.72 [m, br, 4 H, H$^a$], 8.50 ppm [t, br, 2 H, $^3J$(HH) = 5.0 Hz, H$^b$]. IR: 1568 cm$^{-1}$ [$\nu$(C=N)]. [PtClMe$_3$($\mu$-bipym)PtMe$_3$I] (**13b** and **14b**): orange solid; yield, quantitative; mp 230 °C dec. Anal. Calcd for C$_{14}$H$_{24}$N$_4$ClIPt$_2$: C, 21.0; H, 3.0; N, 7.0. Found: C, 21.5; H, 3.0; N, 7.1. $^1$H NMR (acetone-$d_6$): cis and trans, 1.76 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt trans to N on the I side] and 1.40 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt trans to N on the Cl side; these signals are superimposed for both isomers]; cis, 0.82 [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I], 0.60 ppm [s, 3 H, $^2J$(PtH) = 73 Hz, MePt trans to Cl]; trans, 0.84 [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I], 0.62 [s, 3 H, $^2J$(PtH) = 73 Hz, MePt trans to Cl], 9.68 [m, br, 4 H, H$^a$], 8.51 ppm [t, br, 2 H, $^3J$(HH) = 5.0 Hz, H$^b$]. IR: 1567 cm$^{-1}$ [$\nu$(C=N)]. [PtBrMe$_3$($\mu$-bipym)PtIMe$_3$] (**13c** and **14c**): orange solid; yield, quantitative; mp 240 °C dec. Anal. Calcd for C$_{14}$H$_{24}$N$_4$BrIPt$_2$: C, 19.9; H, 2.9; N, 6.6. Found: C, 19.8; H, 2.8; N, 7.0. $^1$H NMR (acetone-$d_6$): cis and trans, 1.63 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt trans to N on the I side] and 1.49 ppm [s, 6 H, $^2J$(PtH) = 77 Hz, MePt trans to N on the Br side; these signals are superimposed for both isomers]; cis, 0.82 [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I], 0.69 ppm [s, 3 H, $^2J$(PtH) = 72 Hz, MePt trans to Br]; trans, 0.72 ppm [s, 3 H, $^2J$(PtH) = 72 Hz, MePt trans to Br]; trans, 0.72 ppm [s, 3 H, $^2J$(PtH) = 70 Hz, MePt trans to I], 0.61 [s, 3 H, $^2J$(PtH) = 72 Hz, MePt trans to Br], 9.68 [m, br, 4 H, H$^a$], 8.51 ppm [t, br, 2 H, $^3J$(HH) = 5.0 Hz, H$^b$]. IR: 1568 cm$^{-1}$ [$\nu$(C=N)]. [PtMe$_4$($\mu$-bipym)PtIMe$_3$] (**12**): brown solid; yield, quantitative; mp 185 °C dec. Anal. Calcd for C$_{15}$H$_{27}$N$_4$IPt$_2$: C, 23.1; H, 3.5; N, 7.2. Found: C, 23.2; H, 3.6; N, 6.9. $^1$H NMR (acetone-$d_6$): 1.62 [s, 6 H, $^2J$(PtH) = 74 Hz, MePt trans to N on the I side], 1.05 [s, 6 H, $^2J$(PtH) = 76 Hz, MePt trans to N on the Me side], 0.80 [s, 3 H, $^2J$(PtH) = 71 Hz, MePt trans to I], −0.53 [s, 3 H, $^2J$(PtH) = 44 Hz, MePt trans to Me], −0.56 [s, 3 H, $^2J$(PtH) = 44 Hz, MePt trans to Me], 9.58 [m, br, 4 H, H$^a$], 8.33 ppm [t, br, 2 H, $^3J$(HH) = 5.0 Hz, H$^b$]. IR: 1566 cm$^{-1}$ [$\nu$(C=N)].

**Acknowledgment.** We thank NSERC (Canada) for financial support.

**Registry No.** **1**, 79870-64-7; **2**, 90144-57-3; **3**, 90191-00-7; **4a**, 93708-89-5; **4b**, 93708-90-8; **4c**, 93708-91-9; **4d**, 102614-93-7; **4e**, 102614-94-8; **4f**, 102614-95-9; **5a**, 93708-92-0; **5b**, 93708-93-1; **5c**, 93708-94-2; **5d**, 102614-96-0; **6**, 93709-02-5; **7**, 102614-97-1; **8a**, 93708-95-3; **8b**, 93708-96-4; **8c**, 93708-97-5; **8d**, 102614-98-2; **8e**, 102614-99-3; **8f**, 102615-00-9; **9**, 102615-01-0; **10a**, 93708-98-6; **10b**, 93708-99-7; **10c**, 93709-00-3; **10d**, 102615-02-1; **12**, 102615-03-2; **13a**, 93709-05-8; **13b**, 102615-05-4; **13c**, 102615-06-5; **13d**, 102615-07-6; **14a**, 102680-25-1; **14b**, 102680-26-2; **14c**, 102680-27-3; **14d**, 102680-28-4; **15a**, 93753-21-0; **15b**, 102680-29-5; **15c**, 93753-22-1; **15d**, 102615-09-8; **16**, 102615-08-7; **17a**, 102615-14-5; **17b**, 102615-11-2; **17c**, 93709-04-7; **17d**, 102615-13-4; **18**, 102615-10-1; **19a**, 102648-60-2; **19b**, 102615-16-7; **20**, 102615-15-6; [$\text{Pt}_2\text{Me}_8(\mu\text{-bipym})$], 102615-17-8; [$\text{Pt}_2\text{Me}_8(\mu\text{-SMe}_2)_2$], 102615-18-9.

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# $^{125}$Te Coupling to $^{1}$H, $^{13}$C, and $^{125}$Te Nuclei in NMR Studies of $^{125}$Te-Enriched 1,3-Ditellurole

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*Received January 23, 1986*

Detailed $^{13}$C, $^{1}$H, and $^{125}$Te NMR studies of 1,3-ditellurole enriched to 80% in the $^{125}$Te isotope ($I$ = $^1/_2$) gave $^1J(^{125}\text{Te}-^{13}\text{CH}_2)$ = 178.7 Hz, $^1J(^{125}\text{Te}-^{13}\text{CH})$ = 288.3 Hz, $^2J(^{125}\text{Te}-^{13}\text{CH})$ = 12.3 Hz, $^2J(^{125}\text{Te}-\text{C}^1H_2)$ = 25.9 Hz, $^2J(^{125}\text{Te}-\text{C}^1H)$ = 126.5 Hz, $^3J(^{125}\text{Te}-\text{C}^1H)$ = 33.5 Hz, $^2J(^{125}\text{Te}-^{125}\text{Te})$ = 260.3 Hz, and $^3J(^1\text{H}-^1\text{H})$ = 8.12 Hz. The $^{125}$Te–$^{125}$Te coupling is comparable in magnitude to $^1J(^{125}\text{Te}-^{125}\text{Te})$ in diorgano ditellurides. The magnitude of the $^{125}$Te–$^{125}$Te coupling may include contributions from two- and three-bond couplings as well as direct coupling of $^{125}$Te nuclei, which are less than the sum of the van der Waals radii apart. The experimental spectra were matched by computer simulation to a root-mean-square error of 0.35. The $^{125}$Te–$^{125}$Te coupling was determined by an iterative process to be 260.3 ± 0.3 Hz.

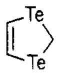
## Introduction

Although tellurium-125 is a spin $^1/_2$ nucleus with ~7% natural abundance and a frequency 0.28 times that of $^1$H, little is known about the $^{125}$Te–$^{125}$Te coupling in organotellurium compounds.[1] In symmetric species, $^1J(^{125}\text{Te}-^{123}\text{Te})$ couplings have been measured by using $^{123}$Te NMR ($I$ = $^1/_2$, natural abundance 0.89%),[2] from which $^1J(^{125}\text{Te}-^{125}\text{Te})$ can be calculated by using the magnetogyric ratios of $^{125}$Te ($\gamma = -8.453 \times 10^7$ rad T$^{-1}$ s$^{-1}$) and $^{123}$Te ($\gamma = -7.011$ rad T$^{-1}$ s$^{-1}$).[3] In unsymmetrical diaryl ditellurides, $^1J(^{125}\text{Te}-^{125}\text{Te})$ couplings were measured directly by using satellites in the $^{125}$Te spectrum; they were between 170 and 207 Hz and were concentration and solvent dependent.[2c] In symmetrical ditellurides, $^1J(^{125}\text{Te}-^{123}\text{Te})$ couplings were concentration dependent and in the range 213–269 Hz.[2c,3] No longer range Te–Te couplings for organotellurium compounds have been reported.

Inorganic Te cations have yielded values for longer range Te–Te couplings. The square-planar Te$^{2+}$ cation gave $^2J(^{125}\text{Te}-^{123}\text{Te})$ of 602–604 Hz,[2a,b] comparable to $^1J(^{125}\text{Te}-^{123}\text{Te})$ of 608–676 Hz[2a,b] in the same system. In the Te$^{4+}$ cation, a distorted trigonal prism, $^2J(^{125}\text{Te}-^{123}\text{Te})$ was determined to be 701 Hz, again comparable to $^1J(^{125}\text{Te}-^{123}\text{Te})$ in this cation of 791 and 1196 Hz.[2b] In the cubic Te$_2$Se$^{2+}$ cation, $^3J(^{125}\text{Te}-^{123}\text{Te})$ was determined to be 120 Hz from a sample of Te$_2$Se$^{2+}$ enriched to 77.3% in $^{125}$Te.[4]

The large values of $^2J(^{125}\text{Te}-^{123}\text{Te})$ relative to $^1J(^{125}\text{Te}-^{123}\text{Te})$ suggest that three-center bonding may be important in the compounds described above. Three-center bonds would, in effect, lead to a partial bond between the tellurium nuclei. Additional measurements of tellurium coupling constants are needed to establish whether two-bond couplings are generally comparable to one-bond couplings.

During studies of the 1,3-ditellurole radical cation, we prepared 1,3-ditellurole (1) that was enriched in the $^{125}$Te isotope.[5] Herein we report a detailed analysis of $^{125}$Te–$^1$H and $^{125}$Te–$^{13}$C couplings in this system as well as the first multibond $^{125}$Te–$^{125}$Te coupling in an organotellurium compound.



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## Results and Discussion

1,3-Ditellurole (1) was prepared from tellurium powder that was enriched to 80% in the $^{125}$Te isotope. This isotope enrichment produced a 2:1 mixture of the doubly and singly $^{125}$Te-labeled ditelluroles, respectively.

The $^1$H NMR spectrum of 1 prepared from unenriched tellurium consists of two singlets centered at $\delta$ 8.86 and 4.73 for the olefinic and methylene protons, respectively. In the enriched sample, the methylene protons display a triplet from the doubly $^{125}$Te-labeled ditellurole and a doublet from the singly $^{125}$Te-labeled ditellurole with $^2J(^{125}\text{Te}-\text{C}^1H_2)$ of 25.9 Hz (Table I).

The olefinic protons display a more complicated splitting pattern, as shown in Figure 1. The doubly $^{125}$Te-labeled ditellurole shows four lines of similar intensity, whereas the singly $^{125}$Te-labeled ditellurole has an eight-line pattern that appears to be composed of two AB quartets, one to

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0276-7333/86/2305-1544$01.50/0