Reaction of 6 with 20% H_3PO_4 and $[(CH_3)_3O]BF_4$. Solutions of 1 in THF were treated with $Li[BEt_3H]$ and allowed to stand for 24 h to generate 6 in situ. Procedures identical with those used for the reactions of 4 with the title reagents were used with 6, but complex 1 was isolated as the only product in 90–94% yields following the reactions.

Synthesis of $(CO)_4Cr(\mu\text{-}PPh_2)(\eta^2(P,C)\text{-}\mu\text{-}PPh_2CH(OMe))Os(CO)_2(PMePh_2)$ (8). A solution of 5 in 10 mL of THF, generated from 3 (223 mg, 0.221 mmol) and $Li[BEt_3H]$ (500 μL of a 1 M THF solution), was reduced in vacuo to a yellow oil and redissolved in 25 mL of CH_3NO_2. This orange solution was transferred via cannula to a 100-mL Schlenk flask containing $[(CH_3)_3O]BF_4$ (120 mg, 0.80 mmol). The solution turned red immediately and was stirred for 45 min. The CH_3NO_2 was removed in vacuo and the residue dissolved in a minimum of CH_2Cl_2 and loaded onto two SiO_2 chromatography plates (25 g). Elution with 20% acetone/hexane afforded an orange band of complex 8 on each. Complex 8 was isolated as an orange band of complex 8 on each. Complex 8 was isolated as an orange, air-stable, microcrystalline solid in 34% yield (81 mg, 0.075 mmol) by solvent removal from these fractions. 8: IR (CH_2Cl_2) ν_{CO} 2026 (s), 1993 (vs), 1950 (s), 1900 (m) cm^{-1}. Anal. Calcd for $C_{45}H_{36}CrO_7OsP\cdot(CH_3)CO$: C, 53.28; H, 3.88. Found: C, 53.53; H, 3.69.

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A Comparison of the Reactivities toward Oxidative Addition of the Dimethylplatinum(II) Units in Mononuclear and Binuclear Complexes with Bis(diimine) Ligands

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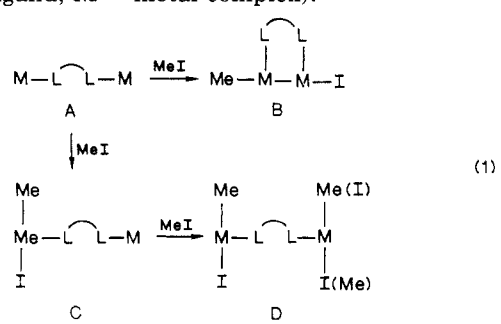
A study of the reactivity toward oxidative addition of methyl iodide of some mononuclear and binuclear dimethylplatinum(II) complexes with the binucleating bis(diimine) ligands 2,2′-bipyrimidine (bipym), 2,3-bis(2-pyridyl)pyrazine (pypz), and bis(2-pyridinal)ethylenediimine (pyen) has been made. In this series of binucleating ligands, the metals are held progressively further apart and the coordination planes of the two metal centers vary from rigidly coplanar to slightly and almost completely flexible with respect to one another. In all cases, the binuclear complexes react more slowly than the mononuclear complexes. This is believed to be primarily an electronic effect for the bipym and pypz complexes, but steric effects may dominate for the pyen complexes. The effect is greatest for the bipym complexes in which, as deduced from the UV–visible spectra, there is strongest conjugation between the two diimine donor units. However, there is no correlation between the reactivity to oxidative addition and the energy of a metal-to-ligand charge-transfer band in the UV–visible spectra, and reasons for this are discussed. Within the series of mixed oxidation state complexes $[Me_2RXPt(\mu\text{-bipym})PtMe_2]$, the trend in reactivity of the platinum(II) center to oxidative addition depends primarily on steric effects of R and X, giving the reactivity series R, X = Me, Cl > Me, Br > Me, I > *i*-Pr, I. Several of the μ-pypz complexes undergo a novel disproportionation reaction. For example, the complexes $[Me_3IPt(\mu\text{-pypz})PtMe_n]$, n = 2 or 4, disproportionate readily to the corresponding symmetrical complexes $[Me_3IPt(\mu\text{-pypz})PtIMe_3]$ and $[Me_nPt(\mu\text{-pypz})PtMe_n]$. Evidence, from variable-temperature ^1H NMR spectroscopy, is presented that the μ-pypz complexes adopt a twisted structure but are fluxional, with a planar transition state between two equivalent but less symmetrical twisted forms.

Introduction

Binuclear complexes can exhibit patterns of organometallic reactivity which are significantly different from those of mononuclear complexes. For bridged binuclear complexes, oxidative addition reactions with alkyl halides can occur to yield three types of products,[1] and each of these reactions can be reversible or irreversible (eq 1, L–L = bridging ligand, M = metal complex).[2-4]



(1)

Complexes of general type B are formed by binuclear oxidative addition, in which the oxidation state of each metal center increases by one unit,[5-7] complexes C by oxidative addition at a single metal center, and complexes D by double oxidative addition.[3,4,8] In principle, complexes D could be formed from either B or C, but only formation from C appears to be known in alkyl halide additions.[1-7] Two isomers of D are often possible, as illustrated in eq 1.

In systems which react along the pathway A ⇌ C ⇌ D, it appears that the first oxidative addition occurs more

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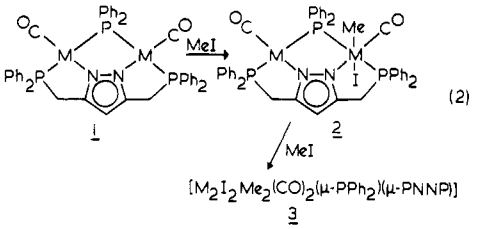
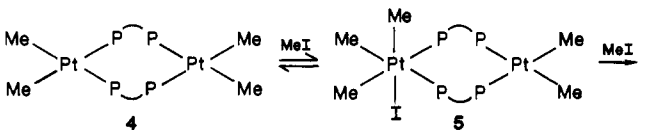
readily than the second.[3,4,9] For the planar complexes $[M_2(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}PNNP)]$ (1, M = Rh or Ir), in which the metal centers are separated by ~3.8 Å, the lower reactivity of **2** compared to **1** was deduced, with convincing evidence, to be largely an electronic effect (eq 2) with charge being transferred from the M(I) to the M(III) center of **2** through the bridging ligand.[3]



(2)

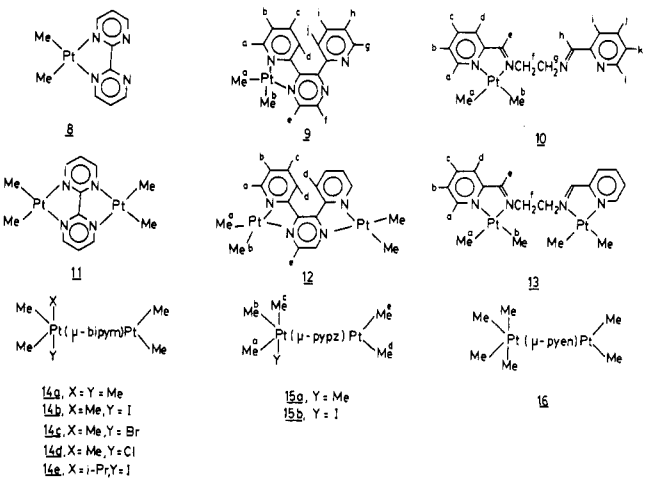
On the other hand, the lower reactivity of **5** compared to **4**, in which the metal centers are separated by ~4.3 Å, was thought to be due largely to steric effects (eq 3, P⌒P = $Et_2PCH_2PEt_2$). These results may appear to be con-



(3)

tradictory but are not, since the reactivity of each binuclear system will depend on a different combination of steric and electronic effects. Some of the factors which are likely to be significant are the following. (1) Is the bridging ligand capable of transmitting electronic effects between metal centers? Single atom bridges such as μ-PPh_2 or μ-SMe_2 or conjugated unsaturated ligands such as μ-pyrazine should be capable of transmitting electronic effects, but saturated ligands such as μ-$R_2PCH_2PR_2$ may not. (2) For a given metal–metal separation, relative steric effects in C compared to A are likely to be lower when the binuclear molecule is approximately planar (e.g., **1** and **2**)[3] than when the coordination planes of the metal centers are tilted with respect to one another (e.g., **4** and **5**).[4] Relative steric effects should decrease as the metal–metal separation increases.

With these principles in mind and with the knowledge that complexes of general formula $[PtMe_2(\text{diimine})]$ (diimine = 2,2′-bipyridine, **6**, or 1,10-phenanthroline, **7**) are very reactive in oxidative addition,[10] a study of the relative reactivities of complexes **8–16** toward methyl iodide, which is a typical electrophile in oxidative addition, was planned. The three binucleating diimine ligands used were 2,2′-bypyrimidine (bipym, complexes **8**, **11**, and **14**), bis(2-pyridyl)pyrazine (pypz, complexes **9**, **12**, and **15**), and bis(2-pyridinal)ethylenediimine (pyen, complexes **10**, **13**, and **16**). The ligands bipym and pypz differ in the metal–metal separation in the binuclear complexes, which are expected to be ~5.7 and ~7.0 Å, respectively. This should lead to lower steric effects in **15** compared to **14** and should also lead to weaker transmission of electronic effects between the metal centers. The latter effect would be magnified by any twisting of the pyridyl groups in **12** or **15** to relieve steric hindrance between the hydrogen atoms H^d–H^d in **12**. In pyen the two diimine units are separated by the C_2H_4 bridge, and so transmission of electronic effects through the ligand is not expected. Unlike bipym and pypz, this ligand is flexible and it is expected that the coordination planes of the dimethylplatinum(II) centers in **13** will be tilted and able to move with respect to one another.



Synthetic routes to the bipym complexes **8**, **11**, and **14**, including a number of derivatives **14** with differing electronic and steric properties of substituents X and Y, have been reported earlier.[11,12]

Results and Discussion

Synthesis of the Complexes. The syntheses of complexes **12** and **13** were carried out by a similar method to that described earlier for **11**, by reaction of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$[13] with the required ligand in a 1:1 molar ratio.[12] The syntheses of **9** and **10** were more difficult than for **8**, because the pairs of compounds **9**, **12** and **10**, **13** could not be separated. Hence it was necessary that none of the binuclear derivative **12** or **13** should be formed as a by-product in the synthesis of the mononuclear derivative **9** or **10**. This was achieved by adding a dilute solution of *cis*-$[PtMe_2(SMe_2)_2]$ to a large excess of the ligand pypz or pyen, followed by separation of the product **9** or **10** from the excess ligand.

The octamethyldiplatinum(IV) complexes **17a–19a** were prepared by reaction of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$[14] with the required ligand in a 1:1 mole ratio. In addition, reaction of **8** or **9** with $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ gave the mixed oxidation state complex **14a**[12] or **15a**, respectively, each containing both Me_4Pt^{IV} and Me_2Pt^{II} units, but attempts to prepare **16** by this method were unsuccessful.

The complexes **17c**, **18b**, and **19b** could be prepared, as a mixture of isomers, by double oxidative addition of MeI to the binuclear complexes **11**, **12**, and **13**, respectively. The isomers arise due to the two different faces at which the second oxidative addition could occur, giving cis and trans isomers. These isomeric forms are illustrated in structures **17–19**.

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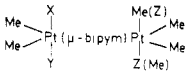
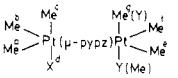
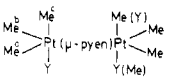
Complexes **8**, **9**, and **10** reacted readily with MeI to give **20**, **21**, and **22**, respectively, and reaction of **20** with



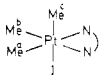
17a, X = Y = Z = Me
17b, X = Y = Me, Z = I
17c, X = Me, Y = Z = I
17d, X = Me, Y = Br, Z = I
17e, X = Me, Y = Cl, Z = I
17f, X = *i*-Pr, Y = Z = I



18a, X = Y = Me
18b, X = Y = I
18c, X = Me, Y = I



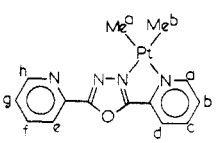
19a, Y = Me
19b, Y = I



20, NN = bipym
21, NN = pypz
22, NN = pyen

$[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ then gave **14b**. In a similar way, $[Me_3IPt(\mu\text{-pypz})PtMe_2]$ (**15b**) could be prepared from **21**, but then a slower disproportionation reaction occurred to give the Pt(IV)–Pt(IV) and Pt(II)–Pt(II) dimers **18b** and **12**, respectively. This is a remarkable observation since the reaction appears to involve the reversible dissociation of a bidentate diimine ligand from platinum. In contrast, **15a** is thermally stable and does not disproportionate. However, reaction of **15a** with MeI gave $[Me_4Pt(\mu\text{-pypz})PtIMe_3]$ (**18c**) which did disproportionate to give the symmetrical derivatives **18a** and **18b**. The mechanism of these disproportionation reactions is unclear, but, empirically, the reaction appears to occur only when $PtMe_3I$ groups are present. Perhaps the unfavorable steric effects between H^d and $H^{d'}$ when pypz acts as a binucleating ligand, and which cause the twisting effect illustrated in eq 4 (see later), also make it easier for one of the metals to dissociate than would be expected for chelating diimine ligand. Other possible mechanisms could involve methyl–iodide exchange for **18c** or an intermolecular redox reaction for **15b**, and these cannot be eliminated.

Attempts have been made to extend the series of complexes studied, but with limited success. Using the ligand 2,5-bis(2-pyridyl)-1,3,4-oxadiazole, pyox, complexes **23** and **24** were prepared, but it was not possible to synthesize binuclear derivatives. Presumably steric interactions prevent a second dimethylplatinum center from being incorporated. Complex **25** could be prepared by using



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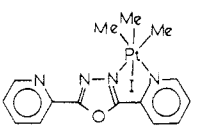

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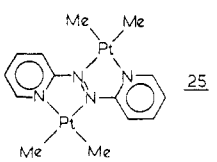


25

2,2′-azopyridine, azpy, but it was too insoluble to be useful in further syntheses. In this case, attempts to prepare mononuclear derivatives were unsuccessful. Both pyox and azpy were designed to give a wider range of separations of the two platinum centers in binuclear derivatives.

Attempts were made to use 1,8-naphthyridine as a binucleating ligand, designed to hold two dimethylplatinum(II) centers in a face-to-face configuration, but no pure products could be obtained.

Characterization of the New Complexes. In most cases the new complexes could be characterized unambiguously by elemental analysis and by NMR spectroscopy. Details are given in the Experimental Section, and only typical examples are discussed below.

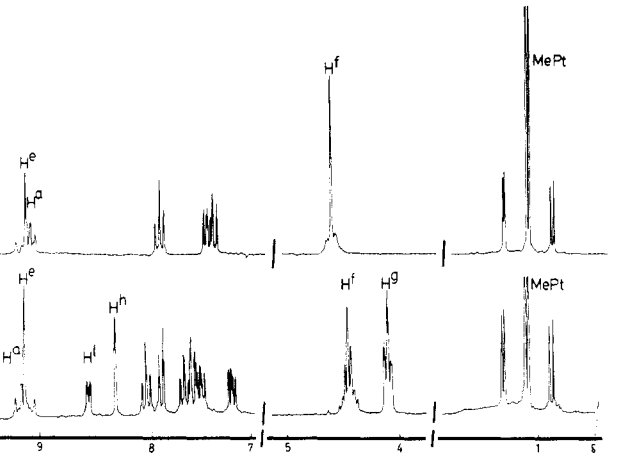


Figure 1. ^1H NMR spectra (200 MHz) of $[PtMe_2(pyen)]$ (**10**; below) and $[Pt_2Me_4(\mu\text{-pyen})]$ (**13**; above).

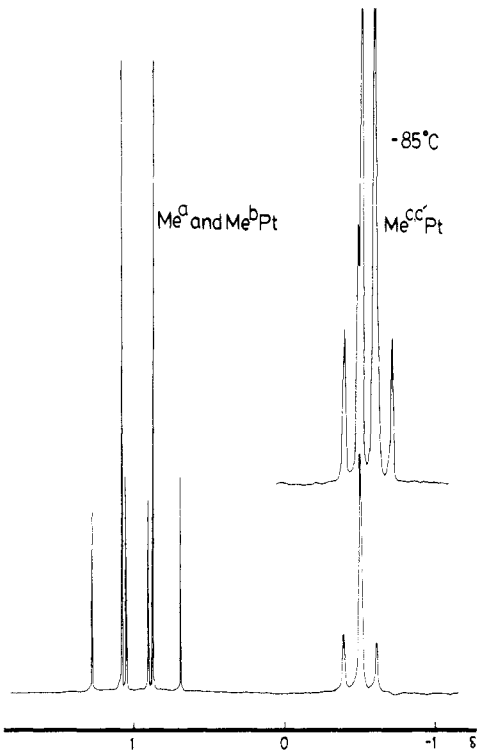


Figure 2. ^1H NMR spectra (200 MHz) of $[Pt_2Me_8(\mu\text{-pypz})]$ (**18a**) at 25 °C (below) and at −85 °C (above).

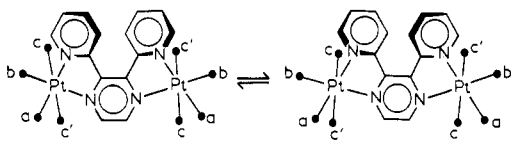
Figure 1 shows the ^1H NMR spectra of complexes **10** and **13**, as examples of mononuclear and binuclear dimethylplatinum(II) complexes. Each complex gives, as expected, two equal intensity methylplatinum signals with coupling constants $^2J(PtH)$ in the region 84–88 Hz. In **10** the two CH_2 groups of the pyen ligand are nonequivalent and occur as the multiplets labeled H^f and H^g, whereas in **13** the CH_2 groups are equivalent and occur as a singlet. The aromatic resonances were complex, and no attempt was made to assign all peaks. However, the pyridinal protons and the ortho hydrogen atoms appeared at highest δ and were readily assigned, especially since the $^3J(PtH)$ couplings were resolved for these protons.

An interesting example is provided by the binuclear complex **18a**, whose ^1H NMR spectrum is shown in Figure 2. In the room-temperature spectrum, the signals due to the equatorial methyl groups Me^a and Me^b occur as sharp singlets, with satellites due to coupling to ^{195}Pt, but the signal due to the axial methyl groups, Me^c, occur as a broad

Table I. MLCT Maxima and Second-Order Rate Constants for Reaction of Complexes 8, 14a–e, 9, 12, 15a,b, 10, and 13 with MeI at 25.0 °C

	MLCT band			
complex	λ_{max}, nm	ϵ, L mol^{-1} cm^{-1}	k_2, L mol^{-1} s^{-1}	solv
$[PtMe_2(bipym)]$ (**8**)	482	1960	9.7	acetone
$[PtMe_2(\mu\text{-bipym})PtIMe_3]$ (**14b**)	570	2020	1.4	acetone
$[PtMe_2(\mu\text{-bipym})PtBrMe_3]$ (**14c**)	564	1720	1.5	acetone
$[PtMe_2(\mu\text{-bipym})PtClMe_3]$ (**14d**)	558	1530	1.65	acetone
$[PtMe_2(\mu\text{-bipym})PtI(i\text{-Pr})Me_2]$ (**14e**)	566	1860	1.1	acetone
$[PtMe_2(\mu\text{-bipym})PtMe_4]$ (**14a**)	556	1690	2.0	acetone
$[PtMe_2(pypz)]$ (**9**)	504	3290	8.4	acetone
	534	3570	1.7	toluene
$[PtMe_2(\mu\text{-pypz})PtMe_2]$ (**12**)	538	9730	4.9	acetone
	572	8220	0.76	toluene
$[PtMe_2(\mu\text{-pypz})PtMe_4]$ (**15a**)	528	5210	5.15	acetone
$[PtMe_2(\mu\text{-pypz})PtIMe_3]$ (**15b**)			2.9	acetone
$[PtMe_2(pyen)]$ (**10**)	510	2020	21	acetone
$[PtMe_2(\mu\text{-pyen})PtMe_2]$ (**13**)	511	7231	8.2	acetone
$[PtMe_2(phen)]$ (**7**)	438	1600	69	acetone
$[PtMe_2(bipy)]$ (**6**)	461	3400	47	acetone

singlet. At low temperature this signal splits into two equal intensity singlets, each with satellites due to coupling to ^{195}Pt. This proves that the molecule is not planar but presumably twists in order to reduce steric hindrance between the aromatic protons H^d and $H^{d'}$. The fluxional process, in which the transition state has a planar pypz ligand, is shown in eq 4. This twisted structure is expected



(4)

for all of the pypz complexes but can only be proved by NMR spectroscopy when the twisting causes nonequivalence of axial methyl groups. A similar effect was observed for **15a** and for the cis isomer of **18b**. However, for the trans isomer of **18b**, the twisting does not cause nonequivalence of the two axial methylplatinum groups and a sharp singlet was observed for these protons in the ^1H NMR spectrum which was unchanged at low temperature. Hence only one of the two possible conformers is present in detectable quantity.

The magnitudes of coupling constants $^2J(PtCH_3)$ and $^3J(PtNCH)$ were useful in characterization, as discussed in greater detail elsewhere.[10,12] For example, in the platinum(II) and platinum(IV) derivatives **9** and **21** the couplings $^2J(PtCH_3)$ were 86–88 and 72 Hz, respectively, and the couplings $^3J(PtNCH)$ were 21–23 and 14–16 Hz, respectively. This reduction in coupling constants on oxidation of Pt(II) to Pt(V) is a general effect.[10–14]

The complexes containing a Me_2Pt^{II}–diimine unit were all intensely colored, the colors ranging from green to red. The colors are useful in monitoring oxidative addition reactions, and the peaks in the visible region have been assigned as $5d_\pi(Pt) \rightarrow \pi^*$(diimine) MLCT bands. There was a considerable shift in the band energy for the binuclear compared to the mononuclear complexes when diimine = bipym, a smaller shift when diimine = pypz, and no significant shift when diimine = pyen (see Table I). For example, the red shift on going from $[Me_2Pt(bipym)]$ to $[Me_2Pt(\mu\text{-bipym})PtMe_4]$ was $\sim$2800 cm^{-1}, but on going from $[Me_2Pt(pypz)]$ to $[Me_2Pt(\mu\text{-pypz})PtMe_4]$ the shift was only $\sim$900 cm^{-1}. The large shift for the bipym complexes can be understood in terms of the qualitative MO diagram of Figure 3.[15,16] In the mononuclear complex 8

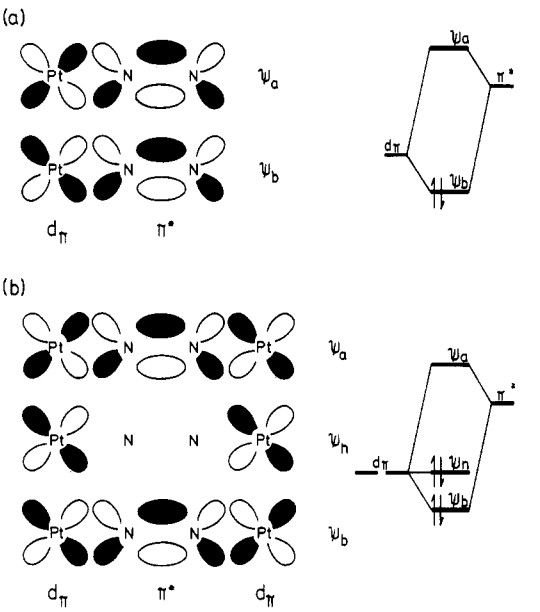


Figure 3. Qualitative MO energy level diagrams showing the $5d_\pi$ levels for (a) a mononuclear complex such as $[PtMe_2(bipym)]$ (**8**) and (b) a binuclear complex such as $[Pt_2Me_4(\mu\text{-bipym})]$ (**11**).

the transition is $\psi_b \rightarrow \psi_a$ whereas in the binuclear **14a** it is $\psi_n \rightarrow \psi_a$ and hence of lower energy (for simplicity, Figure 3 refers to a Pt(II)–Pt(II) dimer but will apply in a qualitative manner to the more complex Pt(II)–Pt(IV) dimers also). The difference of 2800 cm^{-1} may approximate the d_π–π^* back-bonding energy.[15] A strong interaction is expected for the planar bipym complexes. However, for binuclear pypz complexes the metal atoms are further apart, and, perhaps more importantly, the twisting of the ligand (see eq 4) will reduce the interaction between the $5d_\pi$ orbitals of the metal centers. Hence a much smaller shift is observed in this case. In the pyen complexes the metals are insulated from each other by the saturated $N(CH_2)_2N$ group, and hence no interaction of d_π orbitals on the two metal centers of **13** can occur. These spectra therefore give direct evidence that transmission of electronic effects between the two platinum centers follows the series diimine = bipym > pypz > pyen.

Reactivity toward Oxidative Addition. Whenever possible, the kinetics of oxidative addition of methyl iodide

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(16) Ruminski, R. R.; Peterson, J. D. *Inorg. Chem.* **1982**, *21*, 3706.

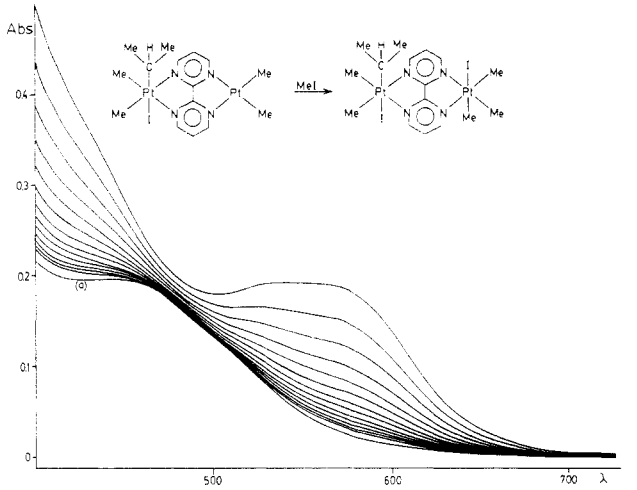

Figure 4. UV–visible absorption spectra recorded during one reaction of MeI with [*i*-PrMe$_2$IPt(μ-bipym)PtMe$_2$] in acetone solution. Spectra were recorded at 4-min intervals and at completion of reaction (spectrum a). Absorbance decreased with time.

to the dimethylplatinum(II) centers of the complex were studied. Previous studies have shown that such oxidative additions occur by the S_N2 mechanism, that is by initial displacement of iodide from methyl iodide by the metal-centered nucleophile.[10e-g] The observation (Table I) that the rates are much higher in the more polar acetone than in toluene is fully consistent with this mechanism.[10g] The reactions were carried out by using a large excess of methyl iodide in acetone solution and were monitored by UV–visible spectrophotometry. Typical changes in spectra during a kinetic run are shown in Figure 4, and the reactions were found to be first order in platinum complex reagent. The observed first-order rate constants, k_{obsd}, were directly proportional to the concentration of methyl iodide (Figure 5), and hence overall the second-order rate constants, k_2, were determined and are listed in Table I. Unfortunately, complex **11** was insufficiently soluble for kinetic studies. A discussion of the trends in reactivity is given below.

For the mononuclear complexes, the reactivity series is [PtMe$_2$(phen)] (**7**) > [PtMe$_2$(bpy)] (**6**) > **10** > **8** > **9**. This is consistent with the extra electronegative nitrogen atoms in bipym and pypz compared to bpy, causing these ligands to be slightly weaker donors and hence leading to lower reactivity in oxidative addition for **8** and **9** compared to [PtMe$_2$(bpy)]. The lower reactivity of **10** compared to **6** or **7** is ascribed to increased steric hindrance by the nonplanar pyen ligand compared to the planar bpy or phen ligands.

In every case studied, the binuclear complex was less reactive in oxidative addition than the corresponding mononuclear complex. For example, the rate of reaction of [PtMe$_2$(pypz)] (**9**) was almost twice that for [Pt$_2$Me$_4$(μ-pypz)] (**12**) despite the fact that **12** has two dimethylplatinum units and so, from a statistical basis only, might be expected to react twice as fast. Since **12** is roughly planar, the difference in this case cannot be due to extra steric hindrance to reaction with MeI for **12** compared to **9**. Indeed steric effects should be higher for **9** since the free pyridyl group will adopt a conformation in which it is approximately perpendicular to the plane of the platinum(II) center. It is likely that an electronic effect is important, due to the μ-pypz ligand being a weaker donor to each platinum center in **12** than the monochelating pypz ligand in **9**. This argument is less convincing for the pyen complexes **10** and **13**, and, in this case, steric effects probably play a part since the molecule is nonplanar.

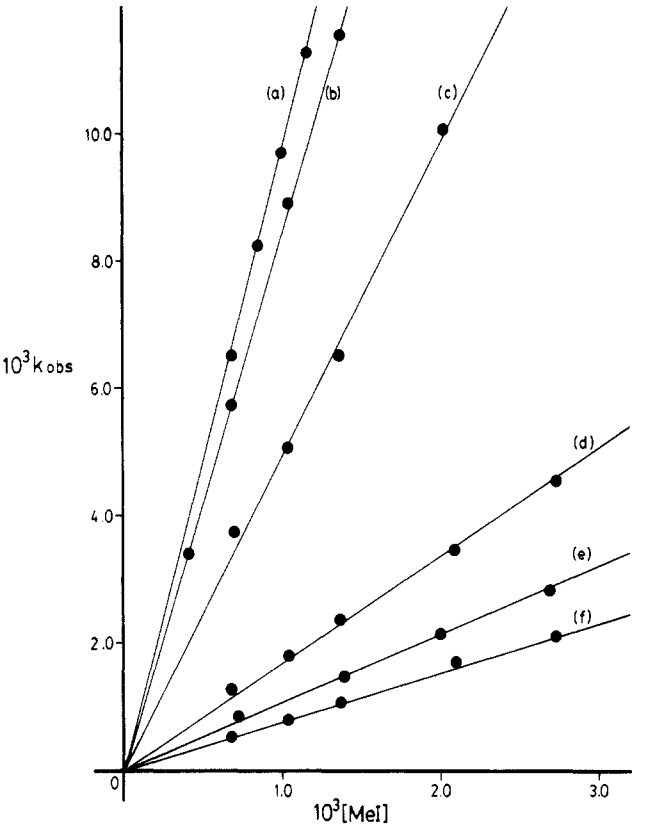

Figure 5. Typical plots of first-order rate constants, k_{obsd}, vs. concentration of methyl iodide for (a) complex **8** in acetone, (b) complex **9** in acetone, (c) complex **12** in acetone, (d) complex **9** in toluene, (e) complex **14e** in acetone, and (f) complex **12** in toluene.

Differential solvation effects between the ground and transition states for the mononuclear and binuclear complexes could also be significant. There was no correlation between the rates of reaction and the energy of the first MLCT band in the UV–visible spectra (Table I). The MLCT band involves the 5d$_\pi$ (5d$_{xz}$ and 5d$_{yz}$) orbitals of platinum, and, as discussed above, there is a higher energy component for the binuclear complexes and hence a lower energy MLCT band (Figure 3). However, it is the 5d$_{z^2}$ electron pair on platinum(II) which acts as the nucleophile in oxidative addition. The energy of this orbital is expected to be determined by σ-bonding effects rather than the π-bonding effects shown in Figure 3. The lack of a correlation between rate of oxidative addition and MLCT band energy is therefore not surprising. Increasing the oxidation state of the second platinum center in the binuclear complexes does not cause a decrease in the rate of reaction for the μ-pypz complexes, as seen by comparison of the rates for **12** and **15a** (Table I). Since **12** has two platinum(II) centers, the platinum(II) center in **15a** is actually about twice as reactive as the platinum(II) centers in **12**.

Steric effects are expected to be most important in the μ-bipym complexes, since the two platinum atoms are closest together, and there is good evidence that the differences in the rates of oxidative addition to the Pt(II)–Pt(IV) complexes **14a–e** are primarily due to steric effects. Thus, the reactivity series **14d** > **14c** > **14b** > **14e** is the opposite of the order expected from electronic effects but is the expected order if steric effects are dominant. Figure 6 shows that there is a correlation of the values of log k_2, for reaction of MeI with complexes **14**, with the average cone angle of the axial ligands X and Y ($\theta_{av} = 0.5(\theta_X + \theta_Y)$].[17] In addition, the steric effects determine the ratio

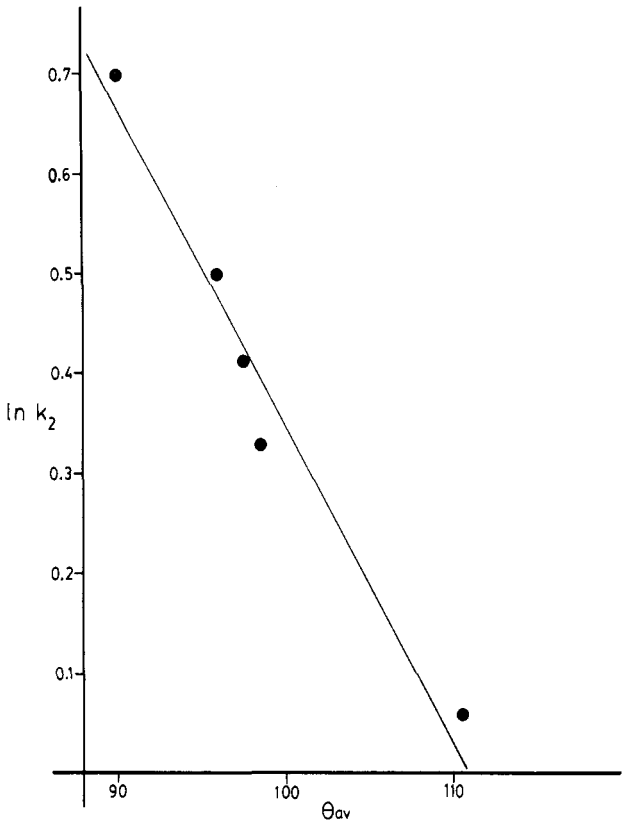

Figure 6. Correlation of second-order rate constants for reaction with methyl iodide with average cone angle of the axial substituents X and Y in complexes **14**.

of isomers of **17** formed in the reactions. The ratio of isomers with axial Me and X (= Me or *i*-Pr) groups mutually cis or trans followed the sequence **17c > 17d > 17e ≫ 17f**,[12b] as expected if S_N2 attack on MeI occurs from the least hindered face of complex **14**. For complexes **17c–e**, when both cis and trans isomers were formed, the experimentally determined isomer ratios[12b] could be used to factor the overall rate constants, k_2, into the contributions due to attack of methyl iodide on either the face of **14b–d** cis to alkyl or trans to alkyl. The values for $(k_2)_{cis}$ were 1.0, 1.0, and 0.9 and for $(k_2)_{trans}$ were 0.4, 0.5, and 0.75 L mol^{-1} s^{-1}, respectively, for **14b**, **14c**, and **14d**. The $(k_2)_{cis}$ values, for attack on the methyl side, are equal, within experimental error, to each other and to $0.5k_2$ for complex **14a** (k_2 = 2.0 L mol^{-1} s^{-1}), which has axial methyl groups on *both* sides. The $(k_2)_{trans}$ value for attack on the halide side is greatest for the least bulky chloride derivative **14d**. Again, these results strongly suggest that steric effects are responsible for the observed trends.

Experimental Section

^{1}H NMR spectra were recorded by using a Varian XL200 spectrometer. Chemical shifts are given with respect to Me_4Si. UV–visible spectra and kinetic data were obtained by using a Varian Cary 2290 UV–visible spectrometer equipped with a DS-15 data station and a PolyScience Series 900 constant-temperature fluid circulator. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, Canada.

Complexes $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$, *cis*-$[PtMe_2(SMe_2)_2]$, $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$, **8**, and **14a–e** were prepared as described previously.[12-14] The ligand pypz was purchased from Aldrich Chemical Co., and pyen, pyox, azpy, and 1,8-naphthyridine were prepared by literature methods.[18-21]

Kinetic Studies. These studies were carried out by using a large excess of MeI monitoring the decay of the MLCT band of the starting material at the appropriate λ_{max} in a cell thermostated to 25.0 ± 0.1 °C. For example, a 10.0-mL aliquot of 1.37 × 10^{-3} M solution of MeI in acetone was added to a 10.0-mL aliquot of 1.33 × 10^{-4} M solution of *cis*-$[PtMe_2(bipym)]$ in acetone at 25.0 °C. The solution was transferred to a 1.0-cm cuvette and placed in the thermostated cell compartment and the DS-15 engaged to collect 88 data points over 16.0 min at λ = 482 nm during which time the reaction went to completion. Computer treatment of the data gave good first-order kinetics from which the observed first-order rate constants were obtained. The linear plots of k_{obsd} vs. [MeI] then gave the second-order rate constants k_2 (Figure 4). The same general method, but varying the data collection time as appropriate, was used for all reactions.

Preparation of the Complexes. $[PtMe_2(pypz)]$ (9). $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.105 g) was converted to *cis*-$[PtMe_2(SMe_2)_2]$ by reaction with excess Me_2S (30 μL) in acetone (150 mL). This solution was rapidly added to a stirring acetone solution containing 10 equiv per Pt of pypz (0.860 g in 50 mL). The solution turned deep red over 0.5 h, and after 2 h, the solvent was removed. The solid obtained was extracted with diethyl ether (6 × 50 mL). The ether was decanted off and collected after each washing. The product was isolated as a bright red solid by filtration and was washed with ether: yield 77%; mp 180 °C dec. Anal. Calcd for $C_{16}H_{16}N_4Pt$: C, 41.8; H, 3.5; N, 12.2. Found: C, 41.4; H, 3.7; N, 11.8. ^{1}H NMR (CD_2Cl_2): δ 1.22 [s, 3 H, ^2J(PtH) = 88 Hz, Me_a or Me_bPt], 1.08 [s, 3 H, ^2J(PtH) = 86 Hz, Me_a or Me_bPt], 9.26 [d, br, 1 H, $^3J(H^aH^b)$ = 6 Hz, $^3J(PtH^a)$ = 21 Hz, H^a], 9.29 [d, 1 H, $^3J(H^eH^f)$ = 3 Hz, $^3J(PtH^e)$ = 23 Hz, H^e], 8.76 [d, 1 H, $^3J(H^fH^e)$ = 3 Hz, $^4J(PtH^f)$ = 3 Hz, H^f], 8.63 [ddd, 1 H, $^3J(H^gH^h)$ = 6 Hz, $^4J(H^gH^i)$ = 3 Hz, $^5J(H^gH^j)$ = 1 Hz, H^g], 6.92 [ddd, 1 H, $^3J(H^jH^i)$ = 6 Hz, $^4J(H^jH^h)$ = 3 Hz, $^5J(H^jH^g)$ = 1 Hz, H^j], 7.45–8.02 [m, 5 H, $H^{b-d,h,i}$].

The contaminated excess ligand was purified by slowly passing a CH_2Cl_2 solution through a 12-in. column packed with Florisil, eluting with a 2:1 mixture of CH_2Cl_2/acetone. Pypz passes through and *cis*-$[PtMe_2(pypz)]$ decomposes on the column.

$[PtMe_2(\mu\text{-pypz})PtMe_2]$ (12). $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.265 g) was dissolved in acetone (50 mL), and to this solution was added one equivalent of pypz (0.108 g) as an acetone solution (25 mL). The solution immediately turned dark red, and after 1 h the product precipitated as a dark purple solid. The solvent was removed, and the product was washed with acetone and dried under vacuum: yield 97%; mp 186 °C dec. Anal. Calcd for $C_{18}H_{22}N_4Pt_2$: C, 31.6; H, 3.2; N, 8.2. Found: C, 32.0; H, 3.3; N, 8.6. ^{1}H NMR (acetone-d_6): δ 1.28 [s, 6 H, ^2J(PtH) = 88 Hz, Me^a or Me^bPt], 1.07 [s, 6 H, ^2J(PtH) = 86 Hz, Me^a or Me^bPt], 9.30 [s, 2 H, $^3J(PtH^e)$ = 21 Hz, H^e], 9.27 [d, br, 2 H, $^3J(H^aH^b)$ = 5 Hz, ^3J(PtH) = 22 Hz, H^a], 7.78 [ddd, 2 H, $^3J(H^bH^a)$ = 5 Hz, $^3J(H^bH^c)$ = 8 Hz, $^4J(H^bH^d)$ = 1.5 Hz, H^b], 8.14 [td, 2 H, $^3J(H^cH^b)$ = 8 Hz, $^3J(H^cH^d)$ = 8 Hz, $^4J(H^cH^a)$ = 1.5 Hz, H^c], 8.35 [d, br, 2 H, $^3J(H^dH^c)$ = 8 Hz, H^d]. Note that good ^{1}H NMR spectra of **12** could only be obtained from supersaturated solutions obtained during its formation. **12** could also be prepared by reaction of **9** with $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$.

$[PtIMe_3(pypz)]$ (21). $[PtMe_2(pypz)]$ (0.050 g) was dissolved in acetone (20 mL), and to this solution was added an excess of MeI (0.5 mL). The red solution immediately turned orange, and after 0.5 h the solvent was removed to give the product as an organe solid; yield, quantitative; mp 235 °C dec. Anal. Calcd for $C_{17}H_{19}N_4IPt$: C, 34.0; H, 3.2; N, 9.3. Found: C, 33.9; H, 3.3; N, 9.1. ^{1}H NMR (CD_2Cl_2): δ 1.60 [s, 3 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], 1.49 [s, 3 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], 0.69 [s, 3 H, ^2J(PtH) = 72 Hz, Me^cPt], 8.99 [d, br, 1 H, $^3J(H^aH^b)$ = 5 Hz, ^3J(PtH) = 16 Hz, H^a], 8.97 [d, ^1H, $^3J(H^eH^f)$ = 3 Hz, $^3J(PtH^e)$ = 14 Hz, H^e], 8.89 [d, 1 H, $^3J(H^fH^e)$ = 3 Hz, $^4J(PtH^f)$ = 1.5 Hz, H^f], 8.62 [dt, 1 H, $^3J(H^gH^h)$ = 5 Hz, $^4J(H^gH^i)$ = $^5J(H^gH^j)$ = 1.5 Hz, H^g], 7.15 [dt, 1 H, $^3J(H^jH^i)$ = 8 Hz, $^4J(H^jH^h)$ = $^5J(H^jH^g)$ = 1.5 Hz, H^j], 7.49–8.05 [m, 5 H, $H^{b-d,h,i}$].

$[PtMe_4(\mu\text{-pypz})PtMe_2]$ (15a). $[PtMe_2(pypz)]$ (0.044 g) was dissolved in acetone (25 mL), and to this solution was added an

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acetone solution containing 0.5 equiv of $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ (0.032 g in 25 mL). The solution immediately turned deep purple, and after 20 min the solvent was removed. The product was washed with diethyl ether and dried under vacuum: yield 73%; mp 163 °C dec. Anal. Calcd for $C_{20}H_{28}N_4Pt_2$: C, 33.6; H, 4.0; N, 7.8. Found: C, 33.7; H, 4.3; N, 7.6. ^{1}H NMR (acetone-d_6): δ 1.08 [s, 3 H, ^2J(PtH) = 74 Hz, Me^a or Me^bPt^{IV}], 0.87 [s, 3 H, ^2J(PtH) = 73 Hz, Me^a or Me^bPt^{IV}], −0.49 [s, br, 6 H, ^2J(PtH) = 44 Hz, Me^c and $Me^{c\prime}Pt^{IV}$], 1.13 [s, 3 H, ^2J(PtH) = 87 Hz, Me^d or Me^ePt^{II}], 1.40 [s, 3 H, ^2J(PtH) = 87 Hz, Me^d or Me^ePt^{II}], 9.02 [d, br, 1 H, $^3J(H^aH^b)$ = 5 Hz, $^3J(Pt^{IV}H^a)$ = 14 Hz, H^a], 8.34 [d, br, 1 H, $^3J(H^dH^c)$ = 8 Hz, H^d], 9.00 [d, 1 H, $^3J(H^eH^f)$ = 3 Hz, $^3J(Pt^{IV}H^e)$ = 14 Hz, H^e], 9.44 [d, 1 H, $^3J(H^fH^e)$ = 3 Hz, $^3J(Pt^{II}H^f)$ = 22 Hz, $^4J(Pt^{IV}H^f)$ = 1 Hz, H^f], 9.38 [d, br, 1 H, $^3J(H^gH^a)$ = 5 Hz, $^3J(Pt^{II}H^g)$ = 22 Hz, H^g], 8.60 [d, br, 1 H, $^3J(H^jH^i)$ = 8 Hz, H^j], 7.78–8.28 [m, 4 H, $H^{b,c,h,i}$]. Low-temperature ^{1}H NMR shows non-equivalence of Me^c and $Me^{c\prime}$ (see text).

[$PtMe_4(\mu$-pypz)$PtMe_4$] (18a). $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ (0.055 g) was dissolved in acetone (15 mL), and to this solution was added 1 equivalent of pypz (0.020 g) as an acetone solution (10 mL). The solution immediately turned deep purple. After 20 min the solvent was removed, and the solid purple product was washed with diethyl ether and dried under vacuum: yield 84%; mp 177 °C dec. Anal. Calcd for $C_{22}H_{34}N_4Pt_2$: C, 35.5; H, 4.6; N, 7.5. Found: C, 35.5; H, 4.7; N, 7.7. ^{1}H NMR (acetone-d_6): δ 1.10 [s, 6 H, ^2J(PtH) = 74 Hz, Me^a or Me^bPt], 0.88 [s, 6 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], −0.49 [s, br, 12 H, ^2J(PtH) = 44 Hz, Me^c and $Me^{c\prime}Pt$], 8.98 [d, br, 2 H, $^3J(H^eH^b)$ = 6 Hz, $^3J(PtH^a)$ = 15 Hz, H^a], 7.80 [ddd, 2 H, $^3J(H^bH^a)$ = 6 Hz, $^3J(H^bH^c)$ = 8 Hz, $^4J(H^bH^d)$ = 1.5 Hz, H^b], 8.04 [td, 2 H, $^3J(H^cH^d)$ = 8 Hz, $^3J(H^cH^b)$ = 8 Hz, $^4J(H^cH^a)$ = 1.5 Hz, H^c], 8.45 [d, br, 2 H, $^3J(H^dH^c)$ = 8 Hz, H^d], 9.00 [s, 2 H, $^3J(PtH^e)$ = 12 Hz, H^e]. Low-temperature ^{1}H NMR shows nonequivalence of Me^c and $Me^{c\prime}$ (see text).

[$PtIMe_3(\mu$-pypz)$PtMe_2$] (15b). [$PtIMe_3$(pypz)] (0.045 g) was dissolved in acetone (20 mL) and the solution cooled to 0 °C. To this solution was added 0.5 equiv of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ as an acetone solution (0.022 g in 20 mL). The solution turned deep red over 0.5 h. The solvent was removed, and the dark red product was washed with ether and dried under vacuum. At 0 °C disproportionation is slow while coordination of Me_2Pt^{II} proceeds more rapidly. At 25 °C disproportionation is rapid (see text): yield 74%; mp 163 °C dec. Anal. Calcd for $C_{19}H_{25}N_4IPt_2$: C, 27.6; H, 3.0; N, 6.8. Found: C, 26.4; H, 2.8; N, 6.7. ^{1}H NMR (acetone-d_6): δ 1.64 [s, 3 H, ^2J(PtH) = 73 Hz, Me^a or Me^bPt^{IV}], 1.44 [s, 3 H, ^2J(PtH) = 71 Hz, Me^a or Me^bPt^{IV}], 1.46 [s, 3 H, ^2J(PtH) = 88 Hz, Me^d or Me^ePt^{II}], 1.16 [s, 3 H, ^2J(PtH) = 88 Hz, Me^d or Me^ePt^{II}], 0.81 [s, br, 3 H, ^2J(PtH) = 72 Hz, Me^cPt^{IV}].

[$PtIMe_3(\mu$-pypz)$PtIMe_3$] (18b). This complex could be prepared by three different routes: (1) by addition of excess MeI to a solution of [$PtMe_2(\mu$-pypz)$PtMe_2$] in acetone; (2) by addition of excess MeI to an acetone solution containing [$PtIMe_3(\mu$-pypz)$PtMe_2$] and its disproportionation products, and by the following reaction. (3) $[PtIMe_3]_4$ (0.032 g) was dissolved in toluene (25 mL), and to this solution was added 0.5 equiv of pypz (0.010 g) as a toluene solution (25 mL). The solution was warmed to 60 °C and the reaction allowed to proceed for 24 h, during which time the colorless solution turned bright yellow. The solvent was removed, and the product was dissolved in toluene and precipitated by addition of diethyl ether, giving an orange solid: yield 87%; mp 215 °C dec. Anal. Calcd for $C_{20}H_{28}N_4I_2Pt_2$: C, 24.8; H, 2.9; N, 5.8. Found: C, 25.3; H, 3.1; N, 5.4. ^{1}H NMR (acetone-d_6): **18b**-*cis* δ 1.69 [s, 6 H, ^2J(PtH) = 74 Hz, Me^a or Me^bPt], 1.45 ppm [s, 6 H, ^2J(PtH) = 71 Hz, Me^a or Me^bPt], 0.80 ppm [s, br, 6 H, ^2J(PtH) = 72 Hz, Me^cPt]; **18b**-*trans*, δ 1.70 [s, 6 H, ^2J(PtH) = 74 Hz, Me^a or Me^bPt], 1.46 [s, 6 H, ^2J(PtH) = 71 Hz, Me^a or Me^bPt], 0.82 [s, 6 H, ^2J(PtH) = 72 Hz, Me^cPt].

[$PtMe_4(\mu$-pypz)$PtIMe_3$] (18c). To an acetone solution (25 mL) of [$PtMe_4(\mu$-pypz)$PtMe_2$] (0.025 g) was added an excess of MeI (0.25 mL) at 0 °C (to minimize disproportionation of the product). The red solution turned orange, and after 15 min the solvent was removed. The orange solid was washed with pentane and dried under vacuum: yield 91%; mp 195 °C dec. Anal. Calcd for $C_{21}H_{31}N_4IPt_2$: C, 29.4; H, 3.7; N, 6.5. Found: C, 28.9; H, 3.5; N, 6.7. Disproportionation in solution complicated all aspects of the ^{1}H NMR spectrum of **18c**. However, the MePt resonances could be identified. ^{1}H NMR (acetone-d_6): δ 1.68 [s, 3 H, ^2J(PtH) = 72 Hz, Me^e or Me^fPt], 1.46 [s, 3 H, ^2J(PtH) = 71 Hz, Me^e or Me^fPt], 1.19 [s, 3 H, ^2J(PtH) = 73 Hz, Me^a or Me^bPt], 0.90 [s, 3 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], 0.83 [s, 3 H, ^2J(PtH) = 72 Hz, Me^gPt], −0.47 [s, br, 6 H, ^2J(PtH) = 44 Hz, Me^c and Me^dPt].

[$PtMe_2$(pyen)] (10). $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.110 g) was converted to *cis*-$[PtMe_2(SMe_2)_2]$ by reaction with excess Me_2S (30 μL) in acetone (150 mL). This solution was rapidly added to a stirring acetone solution containing 10 equiv per Pt of pyen (0.912 g in 50 mL). Over 0.5 h the solution turned deep orange, and after 2 h the solvent was removed, giving an orange oil. The crude product was solidified by precipitation out of a minimum of CH_2Cl_2 with 50:50 Et_2O/pentane. The excess ligand was removed by extracting with warm low boiling petroleum ether (5 × 25 mL). The orange solid product was collected by filtration and washed with petroleum ether and dried under vacuum: yield 68%; mp 59 °C dec. Anal. Calcd for $C_{16}H_{20}N_4Pt$: C, 41.5; H, 4.4; N, 12.1. Found: C, 41.1; H, 4.8; N, 11.9. ^{1}H NMR (CD_2Cl_2): δ 1.13 [s, 3 H, ^2J(PtH) = 84 Hz, Me^a or Me^bPt], 1.10 [s, 3 H, ^2J(PtH) = 88 Hz, Me^a or Me^bPt], 4.12 [t, 2 H, $^3J(H^gH^f)$ = 6 Hz, $^4J(H^gH^h)$ = 1 Hz, H^g], 4.47 [t, 2 H, $^3J(PtH^f)$ = 21 Hz, $^3J(H^fH^g)$ = 6 Hz, $^4J(H^fH^e)$ = 1 Hz, H^f], 8.17 [d, 1 H, $^4J(H^hH^g)$ = 1 Hz, H^h], 8.57 (ddd, 1 H, $^3J(H^lH^k)$ = 5 Hz, $^4J(H^lH^j)$ = 3 Hz, $^3J(H^lH^i)$ = 1 Hz, H^l], 9.14 [s, br, 1 H, $^3J(PtH^e)$ = 35 Hz, H^e], 9.15 [d, br, 1 H, $^3J(H^aH^b)$ = 5 Hz, $^3J(PtH^a)$ = 20 Hz, H^a], 7.24–8.12 [m, 6 H, $H^{b-d,i-k}$].

[$PtMe_2(\mu$-pyen)$PtMe_2$] (13). A solution of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$ (0.065 g) in benzene (10 mL) was combined with a solution containing 1 equiv of pyen (0.027 g) in diethyl ether (10 mL). The solution immediately turned deep orange-red, and the product precipitated as dark red crystals over several hours. The product was collected by filtration, washed with ether, and dried under vacuum: yield 89%; mp 185 °C dec. Anal. Calcd for $C_{18}H_{26}N_4Pt_2$: C, 31.4; H, 3.8; N, 8.1. Found: C, 31.7; H, 4.1; N, 7.9. ^{1}H NMR (CD_2Cl_2): δ 1.12 [s, 6 H, ^2J(PtH) = 84 Hz, Me^a or Me^bPt], 1.09 [s, 6 H, ^2J(PtH) = 88 Hz, Me^a or Me^bPt], 4.65 [s, 4 H, ^3J(PtH) = 16 Hz, H^f], 9.13 [d, br, 2 H, $^3J(H^aH^b)$ = 6 Hz, $^3J(PtH^a)$ = 16 Hz, H^a], 9.16 [s, br, 2 H, $^3J(PtH^e)$ = 34 Hz, H^e], 7.44–8.02 [m, 6 H, H^{b-d}]. **13** could also be prepared by reaction of **10**, with 0.5 equiv of $[Pt_2Me_4(\mu\text{-}SMe_2)_2]$.

[$PtIMe_3$(pyen)] (22). [$PtMe_2$(pyen)] (0.074 g) was dissolved in acetone (25 mL), and to this solution was added 1 equiv of MeI (10 μL). The orange solution turned bright yellow, and the solvent was removed after 4 h. The yellow solid was dried under vacuum: yield, quantitative; mp 176 °C dec. Anal. Calcd for $C_{17}H_{23}N_4IPt$: C, 33.7; H, 3.8; N, 9.3. Found: C, 33.6; H, 4.2; N, 9.8. ^{1}H NMR (acetone-d_6): δ 1.41 [s, 3 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], 1.37 [s, 3 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], 0.60 [s, 3 H, ^2J(PtH) = 72 Hz, Me^cPt], 9.15 [s, br, 1 H, $^3J(PtH^e)$ = 30 Hz, H^e], 8.92 [d, br, 1 H, $^3J(H^aH^b)$ = 5 Hz, $^3J(PtH^a)$ = 14 Hz, H^a], 8.55 [ddd, 1 H, $^3J(H^lH^k)$ = 5 Hz, $^4J(H^lH^j)$ = 3 Hz, $^5J(H^lH^i)$ = 1 Hz, H^l], 8.47 [s, br, 1 H, H^h], 7.32–8.25 [m, 6 H, $H^{b-d,i-k}$], 4.45 [m, 2 H, $H^{f,f\prime}$], 4.18 [m, 2 H, $H^{g,g\prime}$]. It was found that at high concentrations of MeI, quaternization of the ligand occurred, and hence the use of excess MeI was avoided when preparing **22**.

[$PtMe_4(\mu$-pyen)$PtMe_4$] (19a). $[Pt_2Me_8(\mu\text{-}SMe_2)_2]$ (0.053 g) was dissolved in acetone (20 mL), and to this solution was added 1 equiv of pyen (0.020 g). The solution turned orange, after 0.5 h the solvent was removed, and the solid orange product was washed with diethyl ether and dried under vacuum: yield 93%; mp 148 °C dec. Anal. Calcd for $C_{22}H_{38}N_4Pt_2$: C, 35.3; H, 5.1; N, 7.5. Found: C, 35.3; H, 5.1; N, 7.6. ^{1}H NMR (acetone-d_6): δ 0.91 [s, 6 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], 0.84 [s, 6 H, ^2J(PtH) = 72 Hz, Me^a or Me^bPt], −0.52 [s, 12 H, ^2J(PtH) = 44 Hz, Me^cPt], 9.14 [s, br, 2 H, $^3J(PtH^e)$ = 30 Hz, H^e], 8.89 [d, br, 2 H, $^3J(H^aH^b)$ = 5 Hz, $^3J(PtH^a)$ = 14 Hz, H^a], 7.74 and 8.17 [m, 6 H, H^{b-d}], 4.45 [s, 4 H, $^3J(H^fH^f)$ = 4 Hz, $^3J(H^fH^f)$ = 1 Hz, $^3J(PtH^f)$ = 12 Hz, H^f].

[$PtIMe_3(\mu$-pyen)$PtIMe_3$] (19b). To a solution of [$PtMe_2(\mu$-pyen)$PtMe_2$] (0.053 g) in acetone (200 mL) was added an excess of MeI (1 mL). The solution turned yellow, and after 1 h the solvent was removed. The solid yellow product was dried under vacuum: yield, quantitative; mp 210 °C dec. Anal. Calcd for $C_{20}H_{32}N_4I_2Pt_2$: C, 24.7; H, 3.3; N, 5.8. Found: C, 24.5; H, 3.6; N, 5.4. ^{1}H NMR (acetone-d_6): first isomer, δ 1.45 [s, 6 H, ^3J(PtH) = 71 Hz, Me^a or Me^bPt], 1.41 [s, 6 H, ^3J(PtH) = 72 Hz, Me^a or Me^bPt], 0.66 [s, 6 H, ^3J(PtH) = 73 Hz, Me^cPt], 10.05 [s, br, 2 H,

$^3J(PtH^e)$ = 30 Hz, H^e], 8.98 [d, br, 2 H, $^3J(PtH^a)$ = 13 Hz, H^a]; second isomer, δ 1.44 [s, 6 H, $^3J(PtH)$ = 71 Hz, Me^a or Me^bPt], 1.20 [s, 6 H, $^3J(PtH)$ = 72 Hz, Me^a or Me^bPt], 0.68 [s, 6 H, $^3J(PtH)$ = 72 Hz, Me^cPt], 9.43 [s, br, 2 H, $^3J(PtH^e)$ = 30 Hz, H^e]; the signal for H^a is superimposed with the signal for H^a listed above. The spectrum containing both isomers **19b** also have multiplets due to H^{b-d} between 7.81 and 8.29 ppm and due to the nonequivalent methylene protons at 4.55–4.87 ppm.

[PtMe$_2$(pyox)] (23). To a solution of pyox (0.103 g) in CH_2Cl_2 (5 mL) was added 0.5 equiv of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (0.132 g) as a CH_2Cl_2 (10 mL) solution. The solution immediately turned dark orange, and on standing for 1 h some of the prodduct precipitated from solution. The solvent was removed, and the orange product was washed with diethyl ether and dried under vacuum: yield 97%; mp 186 °C dec. Anal. Calcd for $C_{14}H_{14}N_4OPt$: C, 37.4; H, 3.1; N, 12.5. Found: C, 37.3; H, 2.9; N, 12.1. ^1H NMR (CD_2Cl_2) δ 1.03 [s, 3 H, $^2J(PtH)$ = 92 Hz, Me^aPt], 1.03 ppm [s, 3 H, $^2J(PtH)$ = 90 Hz, Me^bPt], 9.20 [d, br, 1 H, $^3J(PtH)$ = 19.5 Hz, $^3J(H^aH^b)$ = 6 Hz, H^a], 8.82 [ddd, 1 H, $^3J(H^hH^g)$ = 6 Hz, $^4J(H^hH^f)$ = 3 Hz, $^5J(H^hH^e)$ = 1 Hz, H^h], 7.54–8.42 [m, 6 H, H^{b-d}, H^{e-g}]; the labels Me^a and Me^b may be interchanged.

[PtIMe$_3$(pyox)] (24). To a solution of [$PtMe_2$(pyox)] (0.063 g) in CH_2Cl_2 (15 mL) was added an excess of MeI (0.5 mL). The orange solution immediately turned bright yellow, and after 0.5 h the solvent was removed. The solid yellow product was washed with *n*-pentane and dried under vacuum: yield, quantitative ; mp 237 °C dec. Anal. Calcd for $C_{15}H_{17}H_4OIPt$: C, 30.5; H, 2.9; N, 9.5. Found: C, 30.1; H, 2.9; N, 9.3. ^1H NMR (CD_2Cl_2): δ 1.77 [s, 3 H, $^2J(PtH)$ = 76 Hz, Me^aPt], 1.57 [s, 3 H, $^2J(PtH)$ = 72 Hz, Me^bPt], 0.79 [s, 3 H, $^2J(PtH)$ = 72 Hz, Me^cPt], 9.00 [d, br, 1 H, $^3J(PtH)$ = 14 Hz, $^3J(H^aH^b)$ = 6 Hz, H^a], 8.83 [d, br, 1 H, $^3J(H^hH^g)$ = 6 Hz, H^h], 7.55–8.47 [m, 6 H, H^{b-d}, H^{e-g}]; the assignments Me^a and Me^b may be reversed.

[Pt$_2$Me$_4$(μ-azpy)] (25). To a solution of azpy (0.026 g) in acetone (10 mL) was added 1 equiv of [$Pt_2Me_4(\mu$-$SMe_2)_2$] (0.080 g) as an acetone solution (15 mL). The solution immediately turned dark brown, and the product precipitated from solution over 1 h. The brown solid product was collected by filtration, washed with acetone, and dried under vacuum: yield 94%; mp 205 °C dec. Anal. Calcd for $C_{14}H_{20}N_4Pt_2$: C, 26.5; H, 3.2; N, 8.8. Found: C, 27.0; H, 3.6; N, 8.8. This complex is insoluble in all common organic solvents. Attempts to prepare the mononuclear [$PtMe_2$(azpy)] were unsuccessful.

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Heats of Reaction of (Toluene)Mo(CO)$_3$ with Substituted Arenes, Sodium Cyclopentadiene, Nitriles, Isocyanides, and Other Ligands. Solution Thermodynamic Study of Ligand Exchange in the Complexes *fac*-L$_3$Mo(CO)$_3$

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The results of solution calorimetric studies are used to measure the relative stability in solution of the following complexes: (arene)Mo(CO)$_3$ (arene = *o*-xylene, *m*-xylene, *p*-xylene, *N,N*-dimethylaniline, *p*-bis(dimethylamino)benzene, (trimethylsilyl)benzene, sodium tetraphenylborate, and sodium cyclopentadiene), L$_3$Mo(CO)$_3$ (L = acetone, acetonitrile, benzonitrile, *tert*-butyl cyanide, *tert*-butyl isocyanide, cyclohexyl isocyanide, piperidine, and tributylphosphine oxide), and L*Mo(CO)$_3$ (L* = bis(methoxyethyl) ether and potassium hydridotris(pyrazoyl)borate). The enthalpy of deprotonation of H–Mo(CO)$_3$C$_5$H$_5$ by NaC$_5$H$_5$ has been measured and used to complete a thermochemical cycle comparing the heats of reaction of (toluene)Mo(CO)$_3$ with C$_5$H$_6$ and NaC$_5$H$_5$. These results are combined with earlier data to yield enthalpies of ligand exchange: $L_nMo(CO)_3 + nL' \rightarrow L'_nMo(CO)_3 + nL$ which span over 50 kcal/mol and encompass a broad range of organometallic ligands. Factors involved in controlling Mo–L bond strengths are discussed.

Introduction

Knowledge of metal–ligand bond strengths is fundamental to understanding organometallic chemistry. Dissociation of a ligand to generate a vacant site at a metal center is a required step in many reactions of importance to catalysis.[1] An active catalyst, due to low-energy barriers with regard to ligand exchange and interconversion, may be subject to thermodynamic constraints within a limited domain of reactivity. Solution thermochemistry can provide essential information in understanding and predicting such behavior. Despite an increased interest in this area,[2] there are few studies of the thermochemistry of organometallic reactions in solution.

Several methods are available to generate metal–ligand bond strength estimates, particularly in the gas phase.[3]

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