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EPR and Absorption Spectra of Singly Reduced Mono- and Dinuclear Diorganoplatinum Complexes of Heterocyclic α -Diimines

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The diorganoplatinum(II) complexes [(bpy)Pt(Ph)₂] (I), [(bpym)Pt(Ph)₂] (II), [(μ -bpym)(Pt(*p*-tol)₂)₂] (III), and [(μ -bpym)(PtAd₂)₂] (IV) (bpy = 2,2'-bipyridine; bpym = 2,2'-bipyrimidine; Ph = phenyl; *p*-tol = *p*-tolyl; Ad = 1-adamantylmethyl) were subjected to two successive one-electron reductions, and the one-electron reduction products were studied in situ by UV-vis-near-IR and EPR spectroscopy. The first reduction is at the heterocyclic ligand, in possible contrast to the metal-centered reductions in such closely similar species as [Pt(bpy)(py)₂]²⁺ (py = pyridine) (V). We attribute this difference to the greater ligand field strength of carbanionic as opposed to neutral N-bound ligands. While the EPR signals of the paramagnetic species show sizable *g* anisotropy (1.92–2.02) in frozen solution due to the large spin-orbit coupling constant of the metal, the rhombic *g* pattern, the low isotropic values (*g*_{iso} < 2), and the isotropic hyperfine coupling as observed and reproduced in the case of [(bpym)Pt(Ph)₂]⁻ all suggest a predominant localization of the unpaired electron at the α -diimine ligand.

Introduction

There has been considerable interest recently in the nature of the Pt to carbon σ -bond in alkyl- and aryl-Pt(II) complexes.^{1,2} In the latter, the Pt(II) atom act as both σ -acceptor and π -donor toward the aryl group.³ In the near-IR-visible-UV region, the spectra of these complexes exhibit intense metal-to-ligand charge-transfer (MLCT) absorptions.⁴ Solution spectroelectrochemistry has been successful in assigning redox orbitals as ligand- or metal-based.⁵ Only a few examples of radical complexes containing platinum or organoplatinum fragments have been reported.^{6,7} EPR studies involving other platinum metal containing radicals have shown that the high spin-orbit coupling constants and the rotation-slowing mass of these heavy elements can cause poor EPR hyperfine resolution and significant *g* anisotropy.^{8,9} In this paper, we describe the formation, EPR spectra, and absorption spectra of the reduced species of the diorganoplatinum(II) complexes [(bpy)Pt(Ph)₂] (I), [(bpym)Pt(Ph)₂] (II), [(μ -bpym)(Pt(*p*-tol)₂)₂] (III), and [(μ -bpym)(PtAd₂)₂] (IV) (bpy = 2,2'-bipyridine; bpym = 2,2'-bipyrimidine; Ph = phenyl; *p*-tol = *p*-tolyl; Ad = 1-adamantylmethyl).

Experimental Section

Materials. The complexes, donated by Dr. G. Brent Young (Imperial College, London), had been prepared by literature methods.^{2d,4} HPLC grade dichloromethane as purchased from Aldrich was dried with P₂O₅ under argon and stored over molecular sieves. Tetrahydrofuran (THF) and dimethoxyethane (DME) were distilled from potassium. DMF was stored over molecular sieves (4 Å) and distilled from anhydrous CuSO₄ under vacuum. Tetra-*n*-butylammonium tetrafluoroborate ((TBA)BF₄), perchlorate ((TBA)ClO₄), and hexafluorophosphate ((TBA)PF₆) were prepared from the aqueous acid and hydroxide, recrystallized from ethyl acetate/pentane, and washed repeatedly with water.

Instrumentation. Cyclic Voltammetry was performed under argon using a PAR 173 potentiostat and 175 signal generator, results being recorded on a JJ X-Y recorder, Model 151 (the same potentiostat was then used for controlled-potential electrolysis in the spectroelectrochemistry experiments). In the reference electrode for work in dichloromethane solution, Ag/0.01 M AgNO₃ + 0.09 M (TBA)BF₄ in acetonitrile was used in the inner compartment and 0.1 M (TBA)BF₄/dichloromethane in the outer compartment. The reference electrode for DMF/0.1 M (TBA)PF₆ was Ag/AgCl; no correction was attempted for liquid-liquid junction potentials. Potentials are referred to the ferrocene/ferrocenium(1+) potential obtained under identical conditions. The absorption spectra of the reduced species were recorded as previously described⁹ on a Perkin-Elmer Lambda 9 UV-vis-near-IR spectrophotometer, and EPR measurements were performed using a Bruker ESP 300 spectrometer. Chemical and electrochemical generation of singly reduced complexes in EPR experiments was carried out as described previously.¹⁰

Results and Discussion

Electrochemistry. All the complexes show the usual¹¹ ligand-based reductions. The first reduction of I-IV is a chemically and

Table I. Reduction Potentials of Diorganoplatinum Complexes in CH₂Cl₂/(TBA)BF₄ and DMF/(TBA)PF₆ Solutions at 25 °C^a

complex	conditions	<i>E</i> _{red} ^(0/-)	<i>E</i> _{red} ^(-/2-)
I	CH ₂ Cl ₂ /(TBA)BF ₄	-1.84 (0.064) ^b	-2.45 (irr) ^c
II	CH ₂ Cl ₂ /(TBA)BF ₄	-1.51 (0.061)	-2.12 (irr) ^c
	DMF/(TBA)PF ₆	-1.53 (0.065)	-2.29 (irr) ^c
III	CH ₂ Cl ₂ /(TBA)BF ₄	-0.94 (0.068)	-1.50 (0.079)
	DMF/(TBA)PF ₆	-1.07 (0.060)	-1.83 (0.060)
IV	CH ₂ Cl ₂ /(TBA)BF ₄	-1.25 (0.062)	-1.71 (0.075)
	DMF/(TBA)PF ₆	-1.27 (0.070)	-2.09 (irr) ^c

^aData from cyclic voltammetry at 200 mV s⁻¹; potentials in volts vs ferrocene/ferrocenium(1+) in stated solvent. ^b*E*_{pa} - *E*_{pc} (V). ^cDenotes (chemically) irreversible redox processes with peak potentials given (scan rate 200 mV s⁻¹).

Table II. Main Absorption Maxima of Diorganoplatinum(II) Complexes As Measured in CH₂Cl₂ and Their Assignments [λ /nm ($\nu/10^3$ cm⁻¹) (10⁻³ε/L mol⁻¹ cm⁻¹)]

parent	$\pi \rightarrow \pi^*$	MLCT (λ_2)	MLCT (λ_1)
I	292 (34.2) (20.0)	309 (32.4) sh ^a	441 (22.7) (5.7)
II	301 (33.2) (15.5)	326 (30.7) sh	462 (21.6) (6.5)
III	301 (33.2) (15.9)	395 (25.3) (18.5)	576 (17.4) (8.0)
			520 (19.2) (8.3)
IV	309 (32.4) (16.5)	410 (24.4) (20.5)	595 (16.8) (8.4)
			535 (18.7) (8.8)
parent(1-)	$\pi(6) \rightarrow \pi(7)$	$\pi(7) \rightarrow \pi(10)^b$	$\pi(7) \rightarrow \pi(9)^b$
I ⁻	367 (27.3) (14.8)	520 (19.2) (5.8)	965 ^c (10.4) (2.4)
II ⁻	369 (27.1) (17.7)	495 (20.2) (7.7)	821 (12.2) (3.2)
III ⁻	376 (26.6) (17.5)	507 (19.7) (10.3)	912 (11.0) (3.3)
IV ⁻	373 (26.8) (18.0)	501 (20.0) (10.7)	892 (11.2) (3.5)

^aShoulder. ^bVibrational structure (ca. 1500 cm⁻¹ spacing); most intense component indicated. ^c $\pi(7) \rightarrow \pi(8,9)$ transitions.

electrochemically reversible one-electron process and is in the range expected for the reduction of a coordinated bipyridine or bi-

- (1) Song, J.-I. Ph.D. Thesis, University of Glasgow, 1982.
- (2) (a) Stewart, R. P.; Treichel, P. M. *J. Am. Chem. Soc.* **1970**, *92*, 2710. (b) Clark, H. C.; Ward, J. E. H. *J. Am. Chem. Soc.* **1974**, *96*, 1741. (c) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. (d) Bochmann, M.; Wilkinson, G.; Young, G. B. *J. Chem. Soc., Dalton Trans.* **1980**, 1879. (e) Lanza, S. *Inorg. Chim. Acta* **1983**, *75*, 131. (f) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 1538. (g) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1986**, *5*, 2522. (h) Ankaniec, B. C.; Young, G. B. *Polyhedron* **1989**, *8*, 57. (i) Kelly, R. D.; Young, G. B. *J. Organomet. Chem.* **1989**, *361*, 123. (j) Christou, V.; Young, G. B. *J. Organomet. Chem.* **1989**, *368*, 391.
- (3) Chaudhury, N.; Puddephatt, R. J. *J. Organomet. Chem.* **1975**, *84*, 105.
- (4) Sutcliffe, V. F.; Young, G. B. *Polyhedron* **1984**, *3*, 87 and reference therein.
- (5) Braterman, P. S.; Song, J.-I. *Inorg. Chim. Acta* **1991**, *183*, 131.
- (6) von Zelewsky, A.; Daul, C.; Schläpfer, C. W. Radicals in metal complexes. *Landolt-Börnstein, New Series, II/17a*; Springer-Verlag: Berlin, 1986; p 199.
- (7) Klingler, R. J.; Huffman, R. J.; Kochi, J. K. *J. Am. Chem. Soc.* **1982**, *104*, 2147.

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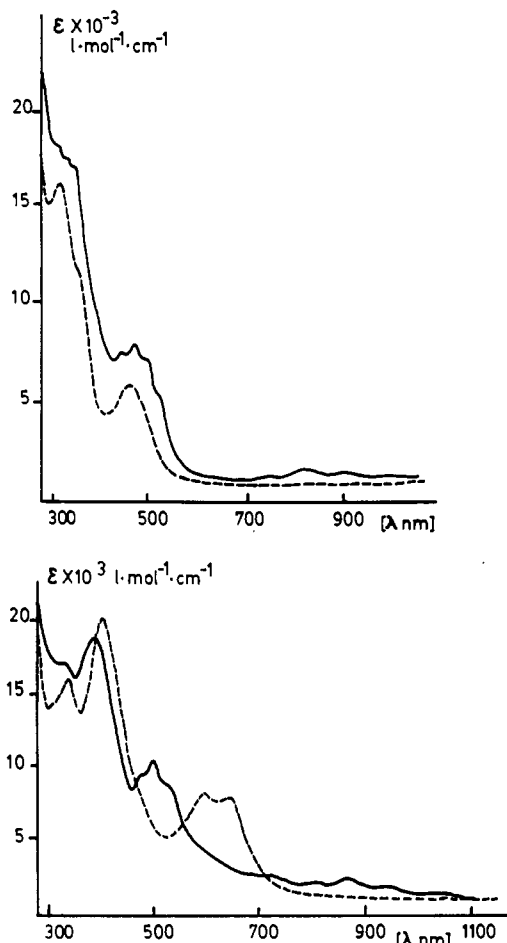


Figure 1. Electronic absorption spectra of neutral and reduced diorganoplatinum(II) complexes in $\text{CH}_2\text{Cl}_2/(\text{TBA})\text{BF}_4$ solution at 25 °C [volts vs ferrocene/ferrocenium(1+)]: (top) $[\text{Pt}(\text{bpym})(\text{Ph})_2]^{0/-}$ (II) and reduction product at -1.356 V; (bottom) $[(\mu\text{-bpym})(\text{PtAd}_2)_2]$ (IV) and reduction product at -1.100 V; (---) parent; (—) singly reduced species.

pyrimidine attached to a divalent organometal center.^{9,13} A second reduction at more negative potentials was chemically irreversible under our conditions except for the reductions of III and IV (in dichloromethane). The observed potentials are collected in Table I. Three trends are clear in these data; bpym complexes are more easily reduced than those by bpy, bridged bpym complexes more easily than those in which bpym is coordinated to only one metal center, and aryl complexes more easily than their alkyl analogues. The completely irreversible anodic waves at E_p varying from +0.4 to +1.1 V are assigned to Pt-centered oxidations, followed by fast chemical processes, possibly involving reaction with solvent.

Spectroelectrochemistry. The spectral data for I–IV and the corresponding singly reduced species, between 200 and 1200 nm, are summarized in Table II, and representative results are shown in Figure 1. The parent spectra exhibit three main absorptions, which are assigned to the intraligand $\pi(6) \rightarrow \pi(7)$ transition and to two MLCT transitions (λ_1, λ_2). The higher of the two in energy, λ_2 , is often obscured by the more intense intraligand $\pi \rightarrow \pi^*$ transitions. The lower energy absorption, λ_1 , can be observed at

Table III. EPR Data for Singly Reduced Diorganoplatinum Complexes

complex	g_{iso}	solvent/ counterion	complex	g_{iso}	solvent/ counterion
I ⁻	1.9933	THF/ Bu_4N^+	III ⁻	1.9891 ^c	DME/ K^+
II ⁻	1.9945 ^{a,b}	DME/ K^+	IV ⁻	1.9937	DME/ K^+

^a Hyperfine structure at 293 K: $a(^{14}\text{N}) = 0.24$ mT (4 N), $a(^1\text{H}) = 0.48$ mT (2 H, H-5,5'). ^b g components at 100 K: $g_1 = 2.0219$, $g_2 = 2.0043$, $g_3 = 1.9532$. ^c g components at 100 K: $g_1 = 2.0178$, $g_2 = 1.9979$, $g_3 = 1.9221$.

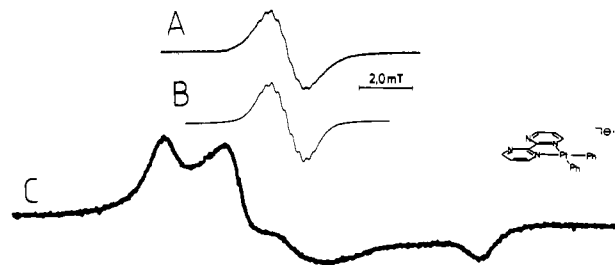


Figure 2. (A) Experimental isotropic EPR spectrum of $\text{K}^+[(\text{bpym})\text{Pt}(\text{Ph})_2]^-$ at 293 K in DME solution. (B) Computer simulation using the coupling constants from Table I and 0.3-mT line width. (C) EPR spectrum at 100 K in glassy frozen DME.

130–160 nm to longer wavelength of λ_2 .⁴ The MLCT energy is considerably higher for I than for the bpym complexes, as expected from the difference in ligand electronegativities. For the dinuclear complexes, the first MLCT absorption occurs at longer wavelength than in the corresponding mononuclear complexes, and this band comprises two peaks of about equal intensity with 40–60-nm separation between the maxima.

The electronic absorption spectra of all the singly reduced diorganoplatinum(II) complexes I–IV⁻ show characteristic $[\text{L}]^-$ (L = bpym or bpy) intraligand $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow \pi^*$ transitions in the region between 280 and 1000 nm. When compared with our previous findings,^{5,10} these results are consistent with the added electron being localized in the π^* orbital of the coordinated ligand (L). In the neutral ligand, the lowest transition is $\pi(6) \rightarrow \pi(7)$,¹² in the range 260–310 nm. This transition still occurs in the reduced species, in which $\pi(7)$ is half-full, but lower energy transitions from $\pi(7)$ to $\pi(8-11)$ are now also possible.

The band of I⁻ centered at 367 nm is assigned to the HOMO \rightarrow LUMO [$\pi(6) \rightarrow \pi(7)$] transition of the coordinated $[\text{bpy}]^-$. The structured band in the near-infrared region between 700 and 1100 nm is assigned as a $\pi(7) \rightarrow \pi(8,9)$ transition of $[\text{bpy}]^-$ (the $\pi(7) \rightarrow \pi(8)$ transition of $[\text{bpym}]^-$ is formally allowed in I⁻ but forbidden both in the free ligand and in the bridged complexes III and IV), and another structured band appears in the visible region at approximately 520 nm, as expected for the $\pi(7) \rightarrow \pi(10)$ transition.¹² Similar results are found for the other reduced diorganoplatinum complexes. These results agree well with those from spectroelectrochemistry of other complexes containing bipyridyl or bipyrimidyl anion radicals as ligands.^{10,11a,b}

The absorption spectrum of singly reduced I⁻ shows a shoulder at 309 nm, which we tentatively assign to the $(\text{bpy})[\pi(7)] \rightarrow \text{Pt(II)}[d_{xy}]$ charge-transfer transition. The d_{xy} orbital is destabilized in organoplatinum complexes and lies at higher energy than the lowest ligand π^* orbitals. When I becomes reduced, the $\pi(7)$ orbital of $[\text{bpy}]^-$ acts as the HOMO, and we may expect to see the LMCT transition from the $\pi^*([\text{bpy}]^-) \rightarrow d[\text{Pt(II)}]$ orbitals. This band is not found in the $\text{Pt(II)}-[\text{bpym}]^-$ complexes, presumably because of the lower energy of $\pi(7)$ in these.

While these organoplatinum compounds show ligand-based reductions, there is evidence that the first reductions of such closely related pyridine complexes as $[\text{Pt}(\text{bpy})(\text{py})_2]^{2+}$ (V) occur at the metal.¹ We ascribe these differences to ligand field strength effects. In the organoplatinum compounds, the strong field of the carbanionic ligands raises the metal $d(\sigma^*)$ orbital above the π^* orbital of the bipyridine and bipyrimidine; in the isoelectronic pyridine complexes, the opposite ordering is found.

- (8) Kohlmann, S.; Kasack, V.; Roth, E.; Kaim, W. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 4047.
 (9) Kaim, W.; Ernst, S.; Kasack, V. *J. Am. Chem. Soc.* **1990**, *112*, 173. See also: Ernst, S. D.; Kaim, W. *Inorg. Chem.* **1989**, *28*, 1520.
 (10) Braterman, P. S.; Song, J.-I.; Kohlmann, S.; Vogler, C.; Kaim, W. *J. Organomet. Chem.* **1991**, *411*, 207.
 (11) (a) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *J. Chem. Soc., Chem. Commun.* **1981**, 287. (b) Heath, G. A.; Yellowlees, L. J.; Braterman, P. S. *Chem. Phys. Lett.* **1982**, *92*, 646. (c) Braterman, P. S.; Song, J.-I. *Inorg. Chim. Acta* **1991**, *180*, 145.
 (12) König, E.; Kremer, S. *Chem. Phys. Lett.* **1970**, *5*, 87.
 (13) (a) Schultz, A.; Kaim, W. *Chem. Ber.* **1991**, *124*, 129. (b) Stahl, T. *Diplom. Thesis, University of Frankfurt*, 1988.

EPR Spectroscopy. The two mononuclear diphenylplatinum complexes of bpy and bpym and the two dinuclear complexes of bis(*p*-tolyl)- and bis(1-adamantylmethyl)platinum with μ -bpym were reduced chemically at room temperature with potassium in 1,2-dimethoxyethane (II–IV) or electrolytically in THF/0.1 M Bu₄NClO₄ (I) for EPR spectroscopy. The results are summarized in Table III. II⁻ was the only species to show some hyperfine structure. This could be reproduced using the ¹⁴N and ¹H (H-5,5') coupling constants previously shown^{9,14} to be typical of the bpym anion radical and its homo- and heterodinuclear complexes (Figure 2A,B). In addition, the slight broadening of the wing sections of the experimental signal relative to the simulated spectrum (Figure 2A,B) puts an upper limit of about 2.5 mT on the ¹⁹⁵Pt coupling (nuclear spin $I = 1/2$, 33.8% natural abundance). In view of the very large elemental isotropic hyperfine constant A_{iso} of 370.9 mT for this isotope,¹⁵ a value of 2.5 mT or less for $a(\text{Pt})$ is rather small and confirms the assignment as bpym⁻ and marginally perturbed Pt(II); for comparison, rhenium(I) complexes of such anion-radical ligands display similar metal splittings (^{185,187}Re: $A_{\text{iso}} = 320$ mT).¹⁶ Although a larger platinum hyperfine coupling of $a(\text{Pt}) = 6.0$ mT was reported for the related dichloroplatinum radical complex [(bpy)PtCl₂]⁻,⁷ the smaller value found here is more in agreement with the range of 1–2 mT observed for $a(^{195}\text{Pt})$ of *o*-semiquinone complexes of organoplatinum(II).^{6,17}

Unfortunately, the other paramagnetic complexes studied did not exhibit a structured EPR spectrum in solution at room temperature. However, the g anisotropy of II⁻ and III⁻ was observed in frozen solutions at 100 K; Figure 2C shows one such rhombic spectrum. The isotropic g factors and the g anisotropy of these species help to clarify the electronic structure. Both complexes exhibit rhombic signals (Figure 2C) with rather small low- g components (Table III). This pattern is incompatible with square-planar platinum(I), since a d^9 configuration at the metal should then be characterized by an axial spectrum with $g_{\parallel} > g_{\perp} > 2.0023$.^{15,18} The g_{iso} values of all four species are smaller than $g(\text{electron}) = 2.0023$, a situation which is typical both for bpym⁺ complexes¹⁴ and many heavy-metal radical complexes^{8,9} but which would be atypical for d^9 systems.^{15,18} Also, rhombic signals are quite normal for π radical ions.¹⁹ The unusually large²⁰ anisotropy and deviation Δg_{iso} (eq 1) are then a result of the very large

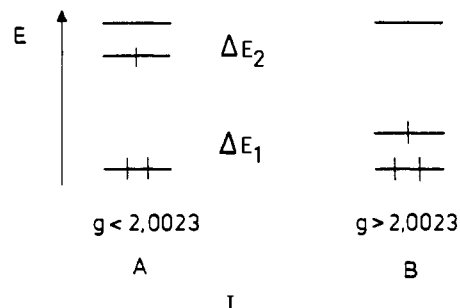
$$\Delta g = g - g(\text{electron}) = g - 2.0023 = k \cdot \zeta (1/\Delta E_1 - 1/\Delta E_2) \quad (1)$$

ζ : spin orbit coupling constant

spin-orbit coupling constant of $\zeta \approx 5000$ cm⁻¹ for platinum(II),¹⁵ which is a factor in Stone's approximation (1) for g ;^{14,21} a small

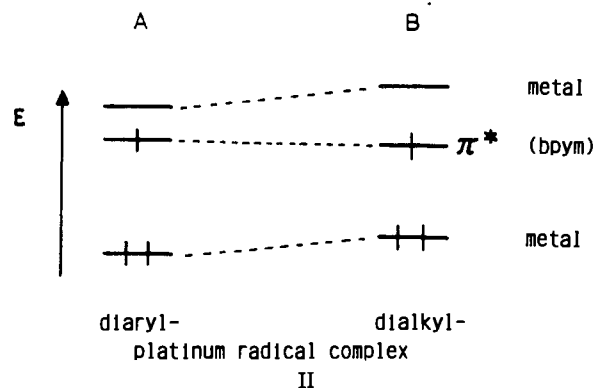
contribution of this metal to the singly occupied molecular orbital (SOMO) by way of spin polarization²⁰ can thus have a significant effect on g factors.

According to (1), the relation $g < g(\text{electron})$ should occur if higher excited paramagnetic states are rather close in energy; in a molecular orbital description it suggests a situation resembling that in IA rather than IB.^{9,14}



Single-crystal optical studies of neutral complexes such as (bpym)PtCl₂²² do indeed suggest the presence of several states lying close to the first MLCT excited state; again, the very large spin-orbit coupling factor and the availability of 6p orbitals for platinum are responsible for such a special situation.²²

The smaller isotropic g factor and larger g anisotropy of the bis(diarylplatinum) radical anion as compared to the mononuclear bpym⁻ complex (Table III) simply reflect the double participation of the heavy metal at the SOMO. On the other hand, the comparison between the two dinuclear paramagnetic complexes must take into account the different charge-transfer excitation energies of the neutral complexes (Table II) and the established donor character of the adamantylmethyl group relative to a *p*-tolyl substituent. The lower isotropic g factor (according to IIA) for



the radical anion III⁻ and the higher $d \rightarrow \pi^*$ MLCT transition energy of neutral III both agree with IIA, as opposed to IIB, for the alkyl analogue IV⁻: relative to the $\pi^*(\text{bpym})$ orbital, all the metal-based orbitals are destabilized in the bis((adamantylmethyl)platinum) dimer IV.

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- (14) (a) Kaim, W. *Inorg. Chem.* **1984**, *23*, 3365. (b) Vogler, C.; Hausen, H.-D.; Kaim, W.; Kohlmann, S.; Kramer, H. E. A.; Rieker, J. *Angew. Chem.* **1989**, *101*, 1734; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1659. (c) Matheis, W.; Kaim, W. *Inorg. Chim. Acta* **1991**, *181*, 15. (d) Matheis, W.; Kaim, W. *Z. Anorg. Allg. Chem.* **1991**, *593*, 147.
- (15) Goodman, B. A.; Raynor, J. B. *Adv. Inorg. Chem. Radiochem.* **1970**, *13*, 136.
- (16) Kaim, W.; Kohlmann, S. *Inorg. Chem.* **1990**, *29*, 2909.
- (17) Abakumov, G. A.; Teplova, I. A.; Cherkasov, V. K.; Shalnova, K. G.; Razuvaev, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1984**, 1402.
- (18) Symons, M. *Chemical and Biochemical Aspects of Electron-spin Resonance*; Van Nostrand Reinhold Co.: New York, 1978.
- (19) Cf.: Harrison, S. R.; Pilkington, R. S.; Sutcliffe, L. H. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 669.
- (20) Kaim, W. *Coord. Chem. Rev.* **1987**, *76*, 187.
- (21) Fischer, H. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. II, p 452.

- (22) Biedermann, J.; Gliemann, G.; Klement, U.; Range, K.-J.; Zabel, M. *Inorg. Chim. Acta* **1990**, *169*, 63.