Electrochemical Reactions of Dichlorobis(aryl isocyanide)platinum(II) Complexes†

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Electrochemical reduction of *cis*-$[PtCl_2(RNC)_2]$ [(**1a**), R = 2,4-Bu^t_2-6-MeC_6H_2; (**1c**), R = 2,4,6-$Bu^t_3C_6H_2$] produced $[Pt_2Cl_2(RNC)_4]$ (**2**) or $[Pt_3(RNC)_6]$ (**4**), depending on the charge consumed and reduction potential. Potentiostatic reduction of $[PtCl_2(2,6\text{-}Me_2C_6H_3NC)_2]$ (**1b**) gave $[Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ (**3b**) *via* a two-electron transfer process. $[Pt_2Cl_2(RNC)_4]$ (**2**) was formed by the chemical reaction of *cis*-$[PtCl_2(RNC)_2]$ with zero-valent complexes (**3**) or (**4**) which were obtained by the above electrochemical process. The structure of compound (**2**) consists of two perpendicular $PtCl(RNC)_2$ planes joined by a Pt–Pt bond; extended Hückel molecular orbital calculations on $[Pt_2Cl_2(HNC)_4]$ indicate that the perpendicular geometry is more stable than the planar one. Reaction of binuclear complexes (**2**) with isocyanide in the presence of $[NH_4][PF_6]$ or $NaClO_4$ gave $[Pt_2(RNC)_6][X]_2$ (**8**) (X = PF_6 or ClO_4). In the electronic spectra of the binuclear complexes (**2**) and (**8**) the absorption near 320 nm is assigned to a σ–σ* excitation.

Electrochemical studies give useful information on the electronic configuration of metal complexes and the mechanism of redox reactions. Furthermore, electrochemical methods can be used for selective preparation of transition metal complexes in higher or lower oxidation states. Several polarographic studies have been made for square-planar isocyanide complexes of palladium and platinum. Electroreduction of *cis*- and *trans*-dichlorobis(alkyl isocyanide)platinum(II) at platinum electrodes have been demonstrated to occur with two irreversible processes.[1] Zanello *et al.*[2] have reported that *cis*-$[MCl_2(p\text{-}XC_6H_4NC)(PMePh_2)]$ (M = Pd or Pt, X = Cl or MeO) was electrochemically reduced to give zero-valent species. However, no discrete complexes have been isolated in their reactions. Recently we reported that the reduction of dichlorobis(2,6-xylyl isocyanide)platinum(II) with sodium amalgam gave new homonuclear and mixed-metal clusters such as $[Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}]$[3] and $[Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ (**3b**).[4] We present here an electrochemical reduction of isocyanide complexes of platinum(II) in comparison with the chemical reduction by sodium amalgam.

A preliminary account of this work has appeared recently.[5]

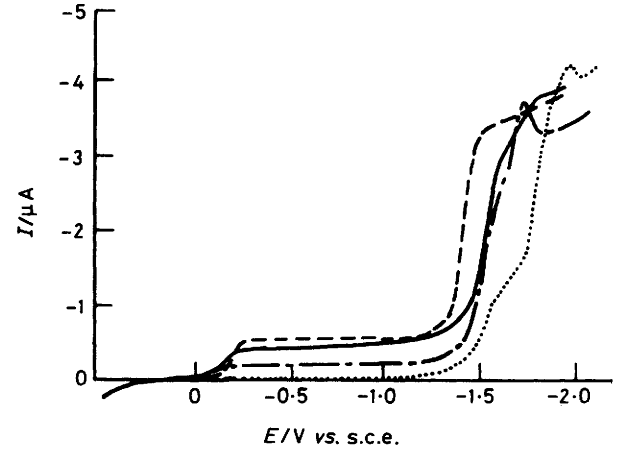

Figure 1. Polarograms of $[PtCl_2(RNC)_2]$ (**1**) and $[Pt_2Cl_2(RNC)_4]$ (**2**) in 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$–MeCN: (**1a**), R = 2,4-Bu^t_2-6-MeC_6H_2 (*ca.* 0.7 mmol dm^{-3}) (———); (**1b**), R = 2,6-$Me_2C_6H_3$ (*ca.* 0.7 mmol dm^{-3}) (— — —); (**1c**), R = 2,4,6-$Bu^t_3C_6H_2$ (*ca.* 0.6 mmol dm^{-3}) (- — - —); (**2a**), R = 2,4-Bu^t_2-6-MeC_6H_2 (*ca.* 0.4 mmol dm^{-3}) (····)

Results and Discussion

Polarograms of *cis*-$[PtCl_2(RNC)_2]$ [(**1a**), R = 2,4-Bu^t_2-6-MeC_6H_2; (**1b**), R = 2,6-$Me_2C_6H_3$; (**1c**), R = 2,4,6-$Bu^t_3C_6H_2$] in 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$–MeCN solution were measured at a dropping mercury electrode (d.m.e.) to investigate the conditions of a macroscopic electrochemical reduction and showed two reduction waves (Figure 1). The waves at *ca.* −0.2 V whose waveheights are independent of the concentrations of Pt^{II} complexes, were attributed to reduction of adsorbed species of Pt^{II} complexes on Hg electrodes. The waves at −1.5 V correspond to the main reduction of Pt^{II} complexes and to a two-electron one-step process. The shapes of the waves indicated that the electrochemical reactions were polarographically irreversible.

Potentiostatic electroreduction was carried out in a *ca.* 10 mmol dm^{-3} acetonitrile solution of the complex by means of a mercury pool electrode (m.p.e.). The electrochemical reduction of (**1a**) consumed 2 F (F = 96.5 kC) of charge per mole of complex at −2.0 V (a limiting current region), giving a green solution, from which a green solid, (**3a**), was obtained. Since the electronic spectrum of the green solid was similar to that found for the known green complex, $[Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ (**3b**),[4] (**3a**) is assumed to be $[Hg\{Pt_3(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6\}_2]$. We could not isolate (**3a**) as an analytically pure sample because of partial loss of mercury (see Experimental section). Finally the only isolated product was the brown-yellow triangular complex $[Pt_3(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6]$ (**4a**).

A similar reaction of (**1a**) consumed 2 F at −1.7 V, giving a yellow-green solution. Work-up of the solution gave two complexes, $[Pt_2Cl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4]$ (**2a**) (20%) and (**4a**) (41%). The i.r. spectrum of (**2a**) showed a peak at 2 142 cm^{-1}, due to terminal isocyanide ligands, which is lower in energy by *ca.* 50 cm^{-1} from that of (**1a**). The ^1H n.m.r. spectrum in $CDCl_3$ showed three characteristic singlets at δ 1.19, 1.53, and 2.56 (intensity ratio 3:3:1), which are assigned to the 4-Bu^t, 2-Bu^t, and 6-Me groups, respectively. The electronic spectrum showed a similar pattern to that of dichlorotetrakis(6-methyl-

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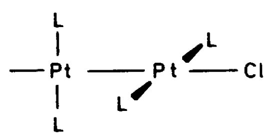
† *Non-S.I. units employed:* F ≈ 96.5 kC, eV ≈ 1.60 × 10^{-19} J.

Table 1. Electrochemical reduction of $[PtCl_2(RNC)_2]^a$

Complex	*E*/V	n^b	Yield (%)	Product^c
(1a)	−1.70	1	95	**(2a)**
	−1.60	1	87	**(2a)**
	−1.55	1	48	**(2a)**
	−1.70	2	20, 41	**(2a)**, **(4a)**
	−2.0	2	86	**(4a)**
(1b)^d	−1.50	1	24	**(3b)**
	−1.50	2	77	**(3b)**
	−1.70	2	92	**(3b)**
(1c)^d	−1.50	1	89	**(2c)**
	−1.70	2	86	**(4c)**

^{a} Complex concentration 0.1 mol dm^{-3}; supporting electrolyte 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$–MeCN (30 cm^3). ^{b} Theoretical electron number reduced by the electrolysis. ^{c} Formulae: $[Pt_2Cl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4]$ **(2a)**, $[Pt_2Cl_2(2,4,6\text{-}Bu^t_3C_6H_2NC)_4]$ **(2c)**, $[Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ **(3b)**, $[Pt_3(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6]$ **(4a)**, $[Pt_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6]$ **(4c)**. ^{d} The complex was suspended and the solution is in a saturated state.



(I) L = RNC

2,4-di-t-butylphenyl isocyanide)dipalladium(I). From the spectroscopic data and by analogy with the structure of the binuclear palladium complex,[6] complex **(2a)** has a metal–metal-bonded structure in which two square-planar $PtClC_2$ planes are joined by a Pt–Pt bond,[5] structure (I).

When 1 F of charge per mole of **(1a)** was passed at −1.7 V, **(2a)** was isolated in a nearly quantitative yield. On lowering of reductive potentials (Table 1), yields of **(2a)** decrease, indicating a decrease in current efficiency.

Two possible routes to formation of the binuclear complex **(2a)** are generally assumed to be as follows: (*a*) directly produced by a one-electron reduction of **(1a)** [equation (1)]; (*b*) **(3a)** is initially produced by a two-electron reduction of **(1a)** and subsequently **(2a)** is formed by a reaction between **(1a)** and **(3a)** [equations (2) and (3)].

$$[PtCl_2(RNC)_2] \xrightarrow{+e} [Pt_2Cl_2(RNC)_4] \quad (1)$$

$$[PtCl_2(RNC)_2] \xrightarrow{+Hg,\ +2e} [Hg\{Pt_3(RNC)_6\}_2] \quad (2)$$

$$[Hg\{Pt_3(RNC)_6\}_2] + [PtCl_2(RNC)_2] \xrightarrow{-Hg} [Pt_2Cl_2(RNC)_4] \quad (3)$$

It was observed in the electroreduction at −1.7 V that the solution on the surface of the mercury pool electrode changed from yellow to green and the green colour rapidly changed back to yellow by diffusion of the green complex toward the bulk with stirring. Since the appearance of the green colour suggested the formation of $[Hg\{Pt_3(RNC)_6\}_2]$, a disproportionation reaction [equation (3)] was assumed to be operative in this process. Since only **(2a)** was isolated from the reaction system, reaction (3) must be fast.

The electrochemical reduction of **(2a)** to the zero-valent complex **(3a)** will also occur in the reaction at −1.70 V, as

$$[Pt_2Cl_2(RNC)_4] \xrightarrow{+Hg,\ +e} [Hg\{Pt_3(RNC)_6\}_2] \quad (4)$$

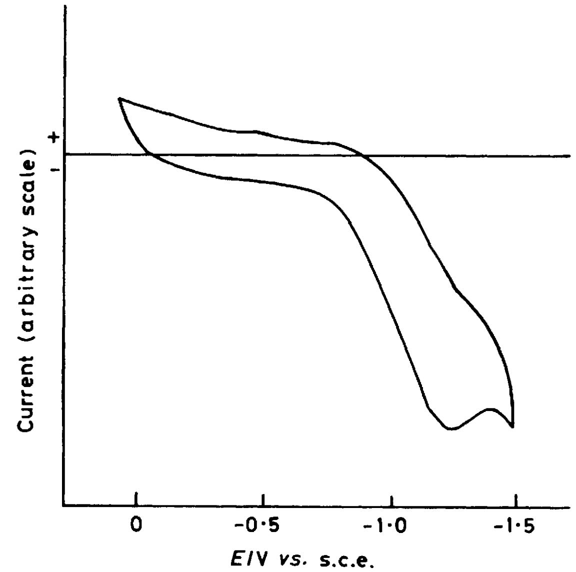


Figure 2. Cyclic voltammogram of $[PtCl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_2]$ **(1a)** (10 mmol dm^{-3}) in MeCN

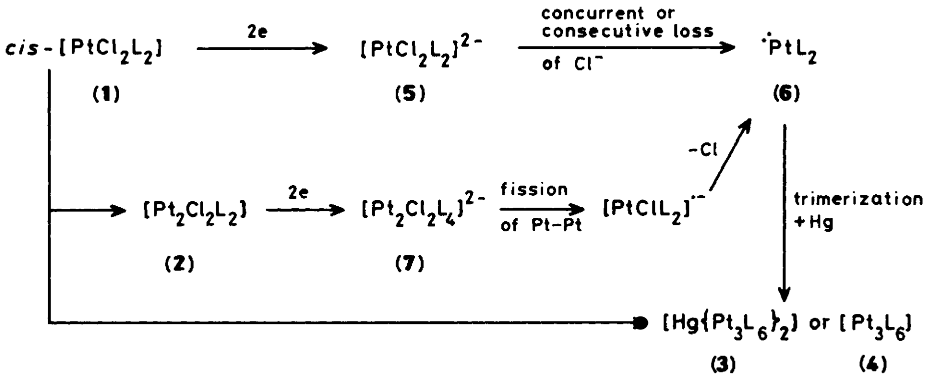
shown in the polarogram of the binuclear complex **(2a)** [equation (4) and Figure 1]. In the initial stage of the reduction, the two-electron reduction of **(1a)** to **(3a)** proceeds. As the reaction progresses, the binuclear complex **(2a)**, accumulated by the chemical reaction (3), is also reduced electrochemically to regenerate **(3a)**.

Thus two electrochemically reductive processes [equations (2) and (4)] are operative simultaneously. Reaction (4) was confirmed by the observation that the reduction of **(2a)** at −1.7 V resulted in the isolation of **(4a)** in 45% yield. A similar reaction at −2.0 V gave **(4a)** in quantitative yield. When a suspension of $[PtCl_2(2,6\text{-}Me_2C_6H_3NC)_2]$ **(1b)** in acetonitrile was electrolysed, consuming 2 F of charge at a limiting current range (at −1.7 V), $[Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ **(3b)** was isolated in 92% yield as a dark green precipitate.

The charge-controlled electrolyses at −1.50 V (near an apparent half-wave potential) consumed 1 and 2 F of charge per mole of **(1b)**, resulting in the isolation of **(3b)**, where the yield of the former reaction is 24% and that of the latter, 77%. No binuclear complex **(2b)** was isolated. This reaction was inhibited since **(3b)** was formed as the precipitate in the reaction system. In the former reaction (1 F of charge), the starting complex **(1b)** was recovered in *ca.* 45% yield. These electrochemical reductions are assumed to be two-electron one-step processes.

One-electron reduction of $[PtCl_2(2,4,6\text{-}Bu^t_3C_6H_2NC)_2]$ **(1c)** consumed 1 F of charge at −1.5 V (near a half-wave potential) and gave $[Pt_2Cl_2(2,4,6\text{-}Bu^t_3C_6H_2NC)_4]$ **(2c)** in high yield, probably *via* reaction (3). The reduction consuming 2 F of charge, near a limiting current range (at −1.7 V), gave the triplatinum complex $[Pt_3(2,4,6\text{-}Bu^t_3C_6H_2NC)_6]$ **(4c)** in 86% yield. A two-electron reduction is operative. In these reactions, no green colour (the appearance of which would suggest the formation of a mixed Hg–Pt cluster) was observed. The formation or not of a mixed Hg–Pt cluster may be related to the bulkiness of the ligands. The steric crowding in the complex having bulky 2,6-Bu^t_2 disubstituted phenyl isocyanide ligands would prevent incorporation of a mercury atom between two triangular platinum cores.

Electroreduction of **(1a)** at Pt electrodes was performed; the cyclic voltammogram of **(1a)** was measured on a *ca.* 10 mmol dm^{-3} solution in MeCN (Figure 2). An irreversible wave appeared at *ca.* −1.20 V (E_{pc}), corresponding to a two-electron



Scheme. Electrochemical reduction pathway for $[PtCl_2(RNC)_2]$ (L = RNC)

transfer. In the controlled potential electrolyses at −1.60 V, charges of 1 or 2 F per mole of (**1a**) were passed at Pt electrodes; the former reaction gave (**2a**) in 57% yield and the latter, (**4a**) in 53% yield. The cyclic voltammogram and controlled electrolyses agreed with those at Hg electrodes, but the current efficiency at Pt electrodes is lower. This is due to the formation of a coating on the surface of the Pt electrodes, whereas the surface of the Hg electrodes was freshly maintained with stirring. The synthetic method at Hg electrodes was more useful than that at Pt electrodes.

Electrochemical Process.—The overall reaction path is as shown in the Scheme. The electrochemical reduction was initiated by a two-electron transfer to *cis*-$[PtCl_2(RNC)_2]$ to give an 18-electron species, $[PtCl_2L_2]^{2-}$ (**5**) (L = RNC). The reaction is followed by consecutive or concurrent loss of Cl^- ions to produce a d^{10} PtL_2 fragment (**6**) (a 14-electron species). The d^{10} PtL_2 fragment is isolobal with CH_2; $Pt(PR'_3)_2$ (R′ = Ph or Me) has been proposed as a reactive transient species in many reactions.[7] Recently we suggested the presence of $Pt(RNC)_2$ in the reaction of $[Pt_2(dppm)_2(RNC)_2]^{2+}$ [dppm = bis(diphenylphosphino)methane] with $[Hg\{Pt_3(RNC)_6\}_2]$ to give an A-frame complex, $[Pt_3(dppm)_2(RNC)_4]^{2+}$.[8] The reaction was completed by trimerization of the $Pt(RNC)_2$ fragment; the incorporation of Hg probably occurs at this stage. In another route, the binuclear complex (**2**) was produced by the reaction of (**1**) with a zero-valent complex (**3**) or (**4**), and was reduced by an electron transfer to produce (**7**). The species (**6**) was obtained by fission of the metal–metal bond in (**7**) and loss of a Cl^- ion; the reaction was accomplished by trimerization of (**6**).

Properties and Reactions of the Dimeric Complexes.—As we could not obtain $[Pt_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_4]$ (**2b**) by electrochemical reduction, the chemical reaction between (**3b**) and (**1b**) was carried out in CH_2Cl_2 and gave (**2b**) as expected, in high yield.

When (**2a**) was treated with 6-methyl-2,4-di-t-butylphenyl isocyanide in the presence of $[NH_4][PF_6]$ at room temperature, the cationic complex $[Pt_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6][PF_6]_2$ (**8a**) was obtained quantitatively. Analogous complexes $[Pt_2(RNC)_6][PF_6]_2$ [(**8b**), R = $2,6\text{-}Me_2C_6H_3$; (**8c**), R = $2,4,6\text{-}Bu^t_3C_6H_2$] were also obtained from the appropriate isocyanide complexes; perchlorate complexes were obtained using sodium perchlorate. A similar type of cationic complex has been prepared by the reaction of $[PtCl_4]^{2-}$ with methyl isocyanide.[9] Since this preparative method is limited to only methyl isocyanide, the present reaction serves as a useful preparative method.

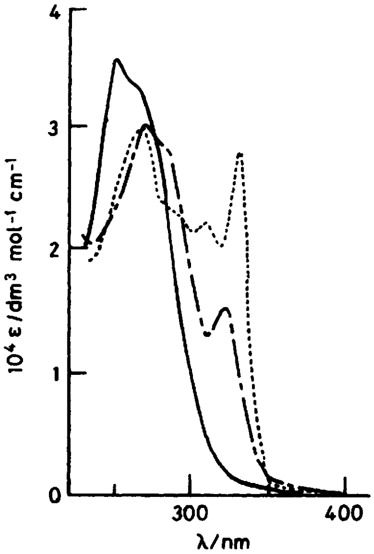


Figure 3. Electronic spectra of $2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC$ complexes in CH_2Cl_2: $[PtCl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_2]$ (**1a**) (———); $[Pt_2Cl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4]$ (**2a**) (- - - -); $[Pt_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6][PF_6]_2$ (**8a**) (- — - —)

Table 2. Electronic absorption spectral data

Complex	Solvent	$\lambda_{max.}$/nm	ε*/dm³ mol⁻¹ cm⁻¹
(**2a**)	CH_2Cl_2	324	15 320
	MeCN	323	13 350
	CCl_4	327	11 820
(**2b**)	CH_2Cl_2	315 (sh)	7 440
	MeCN	318	8 320
(**2c**)	CH_2Cl_2	333	10 160
(**8a**)	CH_2Cl_2	332	28 130
(**8b**)	CH_2Cl_2	315	21 230
$[Pt_2(2,6\text{-}Me_2C_6H_3\text{-}NC)_6][ClO_4]_2$	CH_2Cl_2	315	19 680

* Absorption coefficient per metal atom.

The proton n.m.r. spectrum of (**8b**) at room temperature showed only one singlet. At −50 °C, this resonance is split into two: (**8b**) is therefore fluxional. Similar behaviour has been observed for $[Pd_2(MeNC)_6]^{2+}$.[9] The proton n.m.r. spectrum of (**8a**) showed the presence of two kinds of isocyanide ligands in different environments (equatorial and axial; see Experimental section). Complex (**8a**) is rigid and (**8b**) fluxional, depending on the bulkiness of the isocyanide ligands. Intermolecular exchange was observed in a system containing (**8b**) and 2,6-xylyl isocyanide, but not for (**8a**) and 6-methyl-2,4-di-t-butylphenyl isocyanide, again due to the steric bulkiness of the ligands.

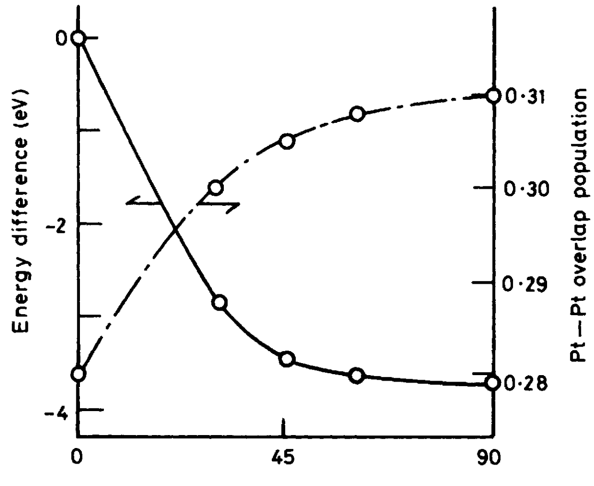
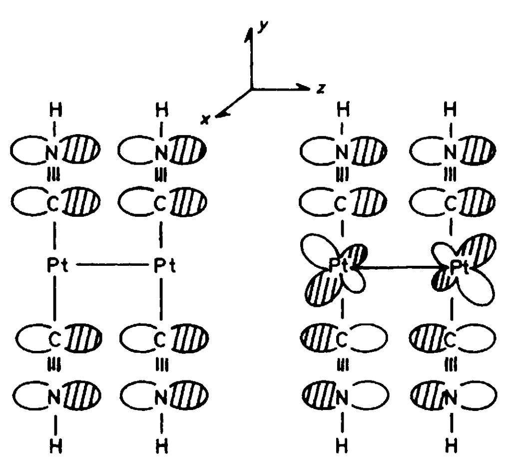


Figure 4. Plot of dihedral angle (θ) against total energy difference (planar/bent) and Pt–Pt overlap population in $[Pt_2Cl_2(HNC)_4]$



(II) **(III)**

The electronic spectra of the binuclear complexes are listed in Table 2 and the spectra of (**2a**) and (**8a**), together with that of (**1a**), are depicted in Figure 3. The binuclear complexes exhibit intense electronic absorptions around 320 nm. For example, (**8a**) has $\lambda_{max.}$ = 332 nm (ε = 28 130 dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2, the molar absorption coefficients of these complexes range from *ca.* 28 000 [for (**8a**)] to *ca.* 7 000 dm^3 mol^{-1} cm^{-1} [for (**2b**)]. There was essentially no dependence of $\lambda_{max.}$ on solvent, and also relatively little intensity dependence on solvent for (**2a**). From these results and the similarity of the absorption bands to those assigned to σ–σ* excitation in $[MM'(MeNC)_4]^{2+}$ (M = M′ = Pd; M = Pd, M′ = Pt),[6b,10] we can assign the intense absorptions near 320 nm to σ–σ* excitation, consistent with a transition from the highest occupied molecular orbital (σ) to the σ* orbital above the lowest unoccupied molecular orbital (π*).

Photochemical reaction of (**2a**) in CCl_4 led to cleavage of the Pt–Pt bond to give (**1a**), equation (5).

$$[Pt_2Cl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4] \xrightarrow[CCl_4]{h\nu} [PtCl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_2] \quad (5)$$

The potential energy of a dimer, $[Pt_2Cl_2(HNC)_4]$, was calculated as a function of dihedral angles (θ) between the two $PtClC_2$ planes, using extended Hückel molecular orbital calculations. Plots of the total energy difference between the planar (θ = 0) and bent geometries and the Pt–Pt overlap population against the dihedral angle are shown in Figure 4. With increasing θ, the energy difference compared with the planar structure increased and became virtually constant for θ ⩾ 45°; the Pt–Pt overlap population also increased, suggesting increasing stability of the geometry with a large dihedral angle. Since the stabilities of molecules having geometries with dihedral angles > *ca.* 45° were estimated to be almost the same, steric requirements and crystal packing forces may reflect the geometry of the binuclear complexes. The perpendicular geometry was estimated to be more stable by 3.7 eV than the planar one with θ = 0. The filled antibonding molecular orbitals shown in diagrams (**II**) and (**III**) are mainly responsible for instability of the planar geometry.

Experimental

Materials.—Acetonitrile was purified by distillation from calcium hydride. $[NBu^n_4][ClO_4]$, as supporting electrolyte, was used as purchased. Isocyanides[11] and $[PtCl_2(RNC)_2]$[12] were prepared according to literature methods, some with modification.

Apparatus.—Electronic and i.r. spectra were recorded on Hitachi 330 and JASCO 442 spectrometers, respectively. Hydrogen-1 n.m.r. spectra were recorded on a JEOL FX100 instrument. Potentiostatic electrolyses with coulometry and polarography were carried out using a HUSO 956B potentiostat and a HUSO 321 potential scanning unit. The electrolytic cell consisted of a conventional three-electrode system: a mercury pool electrode (*ca.* 12 cm^2) or Pt plate electrode (*ca.* 12 cm^2) as a working electrode, a Pt wire as a counter electrode, and an $Ag/AgNO_3$–$[NBu^n_4][ClO_4]$/MeCN reference electrode, whose electrode potential was 328 ± 3 mV *versus* a saturated calomel electrode (s.c.e.). All potentials are *versus* an aqueous s.c.e.

Electrochemical Reactions—*cis*-Dichlorobis(aryl isocyanide)-platinum(II) (*ca.* 0.4 mmol) was dissolved or suspended in 0.1 mol dm^{-3} $[NBu^n_4][ClO_4]$–MeCN (30 cm^3). The solution was deaerated by bubbling with nitrogen, and the reaction monitored by the polarograms using a conventional dropping mercury electrode. After passage of the appropriate amount of charge at constant potential, the solution was separated by decantation and the solvent removed under reduced pressure. The residue was extracted with benzene or CH_2Cl_2. Removal of the solvent to *ca.* 3 cm^3 and additon of hexane to the solution gave the complex. $[Pt_2Cl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4]$ (**2a**). I.r. (Nujol): 2 142 cm^{-1} (C≡N). ^{1}H N.m.r. ($CDCl_3$): δ 1.19 (4-Bu^t), 1.53 (2-Bu^t), 2.56 (6-Me), *ca.* 7.1 (aromatic protons) (Found: C, 57.0, H, 7.05; N, 3.90. Calc. for $C_{68}H_{96}Cl_2N_4Pt_2$: C, 57.1; H, 6.75; N, 3.90%). $[Pt_2Cl_2(2,4,6\text{-}Bu^t_3C_6H_2NC)_4]$ (**2c**). I.r. (Nujol): 2 165, 2 136 cm^{-1} (C≡N). ^{1}H N.m.r. ($CDCl_3$): δ 1.34 (2-, 6-Bu^t), 1.59 (4-Bu^t), *ca.* 7.8 (aromatic protons) (Found: C, 59.4; H, 7.65, N, 3.50. Calc. for $C_{76}H_{116}Cl_2N_4Pt_2$: C, 59.0; H, 7.55; N, 3.60%).

Preparation of $[Pt_2Cl_2(2,6\text{-}Me_2C_6H_3NC)_4]$ (**2b**).—A mixture of $[Hg\{Pt_3(2,6\text{-}Me_2C_6H_3NC)_6\}_2]$ (0.19 mg, 0.065 mmol) and $[PtCl_2(2,6\text{-}Me_2C_6H_3NC)_2]$ (0.20 g, 0.38 mmol) was stirred in CH_2Cl_2 (20 cm^3) at room temperature. After 2 h, the solution was filtered and the solvent was removed to *ca.* 5 cm^3; addition of hexane (10 cm^3) to the residue gave (**2b**) (0.33 g, 88%). I.r. (Nujol): 2 142 cm^{-1} (C≡N), ^{1}H N.m.r. ($CDCl_3$): δ 2.55 (2,6-Me$_2$), *ca.* 7.2 (aromatic protons) (Found: C, 43.75; H, 3.85; N, 5.80. Calc. for $C_{36}H_{36}Cl_2N_4Pt_2$: C, 43.85; H, 3.70; N, 5.65%).

Preparation of $[Pt_3(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_3NC)_6]\cdot 0.5C_6H_6$ (**4a**) *using a Mercury Electrode.*—*cis*-$[PtCl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}$

$MeC_6H_2NC)_2$] (0.23 g, 0.32 mmol) was dissolved in 0.1 mol dm^{-3} $NaClO_4$–MeCN (30 cm^3). After *ca.* 2.1 F of charge was passed at −1.70 V, the solvent was removed. The residue was extracted with benzene and the yellow-green solution reduced to *ca.* 3 cm^3; hexane (10 cm^3) was added to the solution to give yellow-green solids. I.r. (Nujol): 2 160 (C≡N), 1 718 cm^{-1} (C=N). Electronic spectrum (CH_2Cl_2): $\lambda_{max.}$ 845, 624, 366, 329 nm. Disagreement between the found and calculated analysis values is probably due to partial loss of Hg from $[Hg\{Pt_3(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6\}_2]$ (**3a**). Crude (**3a**) was chromatographed on deactivated alumina (containing 10% H_2O), using benzene as an eluant. Removal of the solvent and crystallization of the residue from benzene–hexane gave brown-yellow crystals of (**4a**) in 86% yield. I.r. (Nujol): 2 108, 2 088 (C≡N), 1 720 cm^{-1} (C=N). ^{1}H N.m.r. ($CDCl_3$): δ 1.00 (s, 4-Bu^t, terminal isocyanide), 1.15 (s, 4-Bu^t, bridging) 1.41 (s, 2-Bu^t, terminal isocyanide), 1.56 (s, 2-Bu^t, bridging isocyanide), 2.30 (s, 6-Me, terminal isocyanide), 2.59 (s, 6-Me, bridging isocyanide), *ca.* 7.0 (aromatic protons) (Found: C, 59.7; H, 7.35; N, 4.20. Calc. for $C_{99}H_{141}N_6Pt_3$: C, 59.45; H, 7.10; N, 4.20%). A similar procedure was employed using Pt electrodes.

Preparation of $[Pt_2(RNC)_6][PF_6]_2$.—A solution of $[Pt_2Cl_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4]$ (0.1 g, 0.073 mmol), $2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC$ (0.04 g, 0.17 mmol), and $[NH_4][PF_6]$ (0.04 g, 0.21 mmol) in acetone (20 cm^3) was stirred for 30 min at room temperature. The solvent was removed and the residue extracted with CH_2Cl_2. The solvent was removed from this yellow solution and the residue recrystallized from C_6H_6–hexane to give $[Pt_2(2,4\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_6][PF_6]_2\cdot3C_6H_6$ (**8a**) (0.1 g, 70%). I.r. (Nujol): 2 179 cm^{-1} (C≡N). ^{1}H N.m.r. ($CDCl_3$): δ 1.30 (eq., 2-Bu^t), 1.55 (eq., 4-Bu^t), 1.36 (ax., 2-Bu^t), 1.55 (ax., 4-Bu^t), 2.47 (eq., 6-Me), 2.55 (ax., 6-Me), and *ca.* 7.2 (aromatic protons) (Found: C, 60.3; H, 6.95; N, 3.65. Calc. for $C_{114}H_{156}F_{12}N_6P_2Pt_2$: C, 60.6; H, 6.70; N, 3.60%). $[Pt_2(2,6\text{-}Me_2C_6H_3NC)_6][PF_6]_2$ (**8b**) (yield 85%). I.r. (Nujol): 2 205, 2 176 cm^{-1} (C≡N). ^{1}H N.m.r. ($CDCl_3$): δ 2.53 (2,6-Me$_2$), *ca.* 7.2 (aromatic protons) (Found: C, 44.35; H, 3.65; N, 5.65. Calc. for $C_{54}H_{54}F_{12}N_6P_2Pt_2$: C, 44.2; H, 3.70; N, 5.7%).

$[Pt_2(2,6\text{-}Me_2C_6H_3NC)_6][ClO_4]_2$ was prepared similarly (yield 93%) using $NaClO_4$. I.r. (Nujol): 2 170 cm^{-1} (C≡N). ^{1}H N.m.r. ($CDCl_3$): δ 2.56 (2,6-Me$_2$), *ca.* 7.2 (aromatic protons) (Found: C, 47.05; H, 4.00; N, 6.15. Calc. for $C_{54}H_{54}Cl_2N_6O_8Pt_2$: C, 47.15; H, 3.95; N, 6.10%).

Appendix

The parameters used in the extended Hückel molecular orbital calculations were taken from ref. 13. The Pt–Pt, Pt–C, and Pt–Cl distances were set to 2.56, 2.38, and 1.95 Å, respectively, and to the experimental values in $[Pt_2Cl_2(2,6\text{-}Bu^t_2\text{-}6\text{-}MeC_6H_2NC)_4]$.[5] All C–N and N–H distances were set to 1.17 and 1.01 Å, respectively. The Cl–Pt–C and C–Pt–Pt angles were set to 90°, and the Pt–Pt–Cl and C–Pt–C bond angles were idealized to be linear.

Acknowledgements

We wish to thank the Ministry of Education, Science and Culture for a grant-in-aid for scientific research (to Y. Y. and K. T.), in particular for the purchase of the electrochemical instrument.

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Received 6*th August* 1986; *Paper* 6/1620