

RHODIUM(I) AND PLATINUM(II) COMPLEXES WITH CHELATING BIDENTATE ISONITRILE LIGANDS

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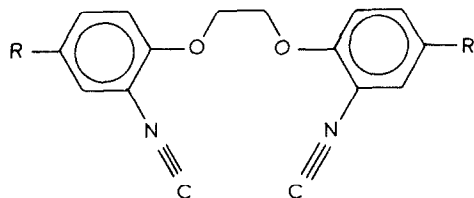
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Summary

Rhodium(I) complexes, $[\text{Rh}(\text{DiNC})_2]\text{A}$, where $\text{A}^- = \text{Cl}^-$, BF_4^- , or BPh_4^- , and $[\text{Rh}(\text{t-BuDiNC})_2]\text{A}$, where $\text{A}^- = \text{Cl}^-$, BPh_4^- , or PF_6^- , were prepared by reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with the bidentate chelating isonitrile ligands, DiNC and t-BuDiNC. The solid compounds are variously colored yellow, green, blue or violet. In dilute ($\sim 10^{-5} \text{ M}$) solutions, the compounds are yellow, but as the concentrations of the solutions are increased, the colors become green or blue. Ultraviolet-visible spectroscopic studies suggest, as found previously for monodentate isonitrile rhodium(I) complexes, that the $[\text{Rh}(\text{DiNC})_2]^+$ cation exists as a monomer in dilute solutions, but dimers, trimers, and tetramers are found at higher concentrations. For $[\text{Rh}(\text{t-BuDiNC})_2]^+$, only monomers and dimers are observed; presumably the bulky t-butyl groups prevent the formation of higher oligomers in this case. Equilibrium constants for the dimerizations of $[\text{Rh}(\text{DiNC})_2]^+$ and $[\text{Rh}(\text{t-BuDiNC})_2]^+$ were determined. When exposed to room light, blue solutions of the oligomers $[\text{Rh}(\text{DiNC})_2]_x^{x+}$ fade to the yellow color of the monomer; ^1H NMR spectra of the solutions confirm the photodissociation of the oligomers. The reaction of $[\text{Rh}(\text{DiNC})_2]^+$ with I_2 yields the binuclear $[\text{Rh}_2(\text{DiNC})_4\text{I}_2]^{2+}$ presumed to have a structure with a Rh–Rh bond and terminal I^- ligands. Under the same conditions, monodentate isonitrile complexes $[\text{Rh}(\text{CNAr})_4]^+$ yield mononuclear $[\text{Rh}(\text{CNAr})_4\text{I}_2]^+$ upon reaction with I_2 . The greater stability of the dimeric structure for DiNC may be due to the smaller steric bulk of the DiNC ligand as a consequence of its near planarity as compared with monodentate CNAr ligands in which the Ar groups may rotate. Additional evidence for dimer stabilization by DiNC is the high temperature (70°C) required for Rh–Rh bond cleavage as observed in ^1H NMR studies of $[\text{Rh}_2(\text{DiNC})_4\text{I}_2]^{2+}$. The yellow platinum(II) complex $[\text{Pt}(\text{DiNC})_2]\text{PtCl}_4$ is isolated from the reaction of $(\text{Et}_4\text{N})_2\text{PtCl}_4$ with DiNC. The reaction of K_2PtCl_4 with t-BuDiNC yields white *cis*- $\text{PtCl}_2(\text{t-BuDiNC})$. Complexes reported herein are characterized by their UV-visible, IR, and ^1H and ^{13}C NMR spectra.

Introduction

We recently reported the synthesis of multidentate ligands containing isonitrile [1–3], nitrile [1,2], and diazonium [4] donor groups. The bidentate chelating isonitrile



(DiNC, R = H,
t-BuDiNC, R = t-Bu)

ligands, DiNC and t-BuDiNC have been shown to form complexes of Cr, Mo, W, Mn and Fe [1,2]. Molecular models indicate that these ligands should chelate to a metal with the donor groups at 90° with respect to each other, as occurs in octahedral or square planar complexes. To date, all reported complexes of these ligands have octahedral or pseudo-octahedral structures; none with square planar geometries has been described. In special situations, the DiNC ligand bridges two metals as in $(\text{OC})_5\text{Cr}-\mu\text{-DiNCCr}(\text{CO})_5$ [1,2].

In the present study, we sought to synthesize square planar complexes of these ligands and compare their properties with those of related monodentate isonitrile analogs. Although many isonitrile complexes are known [5], the square planar complexes of rhodium(I) [6–11], $\text{Rh}(\text{CNR})_4^+$, and iridium(I) [7,12–14], $\text{Ir}(\text{CNR})_4^+$, have been of particular recent interest. The monomeric $\text{Rh}(\text{CNR})_4^+$ complexes are characterized by their yellow color; however, in more concentrated solutions, they associate to give blue or violet oligomers [14,15]. X-Ray diffraction studies [16,17] of three arylisonitrile complexes show them to have dimeric $\text{Rh}_2(\text{CNAr})_8^{2+}$ structures with Rh–Rh interactions. The aryl groups in these dimers are not co-planar with the Rh square plane in the solid state [16,17] and may rotate in solution; both factors may weaken the Rh–Rh interaction. In this work, we sought to prepare the analogous chelating isonitrile complex $\text{Rh}(\text{DiNC})_2^+$ where the aryl groups of the ligand are constrained to lie nearly in the rhodium square plane, which might promote association between the monomers and yield more chemistry characteristic of the oligomers.

Other bidentate isonitrile ligands such as $\text{CN}(\text{CH}_2)_x\text{NC}$ also form $\text{Rh}(\text{CN}(\text{CH}_2)_x\text{NC})_2^+$ complexes. In these compounds, where the ligands contain 6 or fewer methylene groups (i.e., $x \leq 6$) and are sterically incapable of coordinating to a single metal [18–20], the ligands bridge two metals with the NC groups coordinating to separate metal atoms in a dimeric structure $[\text{Rh}(\text{CN}(\text{CH}_2)_x\text{NC})_2]_2^{2+}$. For ligands with 7 or 8 methylene groups, chelated ligand complexes $\text{Rh}(\text{CN}(\text{CH}_2)_x\text{NC})_2^+$ are formed [20]; like other $\text{Rh}(\text{CNR})_4^+$ complexes, they oligomerize in solution through Rh–Rh interactions.

Square planar complexes of nickel(II), palladium(II), and platinum(II), $\text{M}(\text{CNR})_4^{2+}$, with monodentate isonitrile ligands have also been reported [21–23]; however, none with chelating diisonitrile ligands has been described. It was hoped

that the relatively planar DiNC ligand would also favor oligomerization of its platinum(II) square planar complexes.

Experimental

General procedures. All reactions were performed under an atmosphere of dry N_2 . Tetrahydrofuran (THF) and diethyl ether were distilled from sodium benzophenone ketyl prior to use. Dichloromethane, acetonitrile and *N,N*-dimethylformamide (DMF) were purged thoroughly with N_2 and distilled from CaH_2 . Dimethylsulfoxide (DMSO) was distilled from $CaSO_4$. All other solvents were reagent grade; they were dried over molecular sieves (4A) and purged with dry N_2 before use.

Infrared spectra were recorded on Nujol mulls between NaCl plates or on solutions in 1.0 or 0.1 mm NaCl cells using a Perkin-Elmer 281 spectrometer. Proton and ^{13}C NMR spectra were obtained on a JEOL FX-90Q Fourier transform spectrometer; chemical shifts are reported in δ values relative to tetramethylsilane (TMS). Visible spectra were recorded on either a Perkin-Elmer 320 or Cary 219 spectrophotometer in 1 cm cells. Absorption spectral data used for the determination of equilibrium constants were obtained from solutions of Ic ($5.22 \times 10^{-5} M$ to $1.10 \times 10^{-3} M$) at 602 nm and Iib ($7.79 \times 10^{-5} M$ to $5.10 \times 10^{-3} M$) at 612 nm in 0.1 M NaBPh₄/DMF at 25°C. Melting points were taken on a Thomas hot stage and are uncorrected. Conductivities were measured on approximately $10^{-4} M$

TABLE I

UV-VISIBLE ABSORPTION SPECTRA OF Rh^I AND Rh^{II} COMPLEXES^a

Rh^I complexes ^b	Monomer absorptions				Oligomer absorptions		
	$^1A_{1g} \rightarrow ^1E_u$	$^1A_{1g} \rightarrow ^3E_u$	$^1A_{1g} \rightarrow ^1A_{2u}$	$^1A_{1g} \rightarrow ^3A_{2u}$	Dimer	Trimer	Tetramer
$[Rh(DiNC)_2]^+{}^c$ (I)	357 (70.1)	415 (sh)	427 (6.08)	472 (1.07)	602 ^d (18.6)	780 ^e	960 ^e
$[Rh(t-BuDiNC)_2]^+{}^c$ (II)	361 (66.5)	413 (sh)	421 (5.23)	472 (1.15)	612 ^d (14.5)	^f	^f
$[Rh(CNPh)_4]^+{}^g$	335 (40.2)	^f	411 (5.00)	463 (0.63)	568 ^d	727 ^d	
Rh^{II} Complexes ^b	$\sigma \rightarrow \sigma^*$		$d^n \rightarrow \sigma^*$				
$[Rh_2(DiNC)_4I_2]^{2+}{}^h$	421 (10)		474 (10)				
$[Rh_2(bridge)_4I_2]^{2+}{}^i$	397 (62.0)		465 (23.2)				
$[Rh_2(CNC_4H_9)_8I_2]^{2+}{}^j$	380 ^k		448 ^k				

^a Band positions are in nm; $\epsilon \times 10^{-3}$ ($\pm 10\%$)($M^{-1} cm^{-1}$) are in parentheses. ^b Spectra are independent of the counter anion. ^c Measured in dilute ($10^{-5} < M < 10^{-4}$) DMF solutions. ^d In DMF solution; observed only at concentrations greater than $\sim 10^{-4} M$. ^e In DMF solution; observed only at concentrations greater than $10^{-3} M$. ^f Not observed. ^g From ref 19; in CH_3CN . ^h In DMF; approximate ϵ values (see text). ⁱ From ref 18, in CH_3CN ; bridge = $CN(CH_2)_3NC$. ^j From ref 33; in CH_3CN . ^k ϵ values not reported.

solutions of the complexes in DMF using an Industrial Instruments RC-16B2 conductivity bridge.

The following compounds were prepared according to published procedures: $[\text{Rh}(\text{COD})\text{Cl}]_2$ [24], $\text{K}_2(\text{PtCl}_4)$ [25], *cis*- $\text{PtCl}_2(\text{NCCH}_3)_2$ [26], DiNC [1], and *t*-BuDiNC [1]. All other chemicals were reagent grade and used without further purification.

Synthesis of complexes $[\text{Rh}(\text{DiNC})_2]\text{Cl}$ (Ia). A solution of DiNC (0.132 g, 0.501 mmol) in CH_2Cl_2 (20 ml) was added over a period of 5 min to a stirred CH_2Cl_2 solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0615 g, 0.125 mmol). The resulting deep blue suspension was stirred for an additional hour and then treated with hexanes (80 ml) to complete the precipitation of the product. The blue powder was collected on a medium frit, washed with Et_2O , and vacuum dried to yield 0.141 g (85%) of Ia. The solid rapidly absorbs water from the air causing it to become red. The water can be removed by drying in high vacuum. Anal. Found: C, 57.20; H, 3.84. $\text{C}_{32}\text{H}_{24}\text{N}_4\text{ClRhO}_4$ calcd.: C, 57.63; H, 3.63%. IR (CH_3CN): $\nu(\text{NC})$ 2200 sh, 2161 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$): δ 7.38 (m, phenyl), 4.43 ppm (br, s, CH_2CH_2). The visible spectra of this and related salts are given in Table 1. $\Lambda_{\text{M}}(\text{DMF})$: 62 $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$. Above 170°C, Ia darkens and progressively decomposes without melting when heated slowly (2°/min). Rapid heating (10°/min) results in melting in the range 229–232°C.

$[\text{Rh}(\text{DiNC})_2]\text{BF}_4$ (Ib). A CH_2Cl_2 solution (10 ml) of DiNC (0.0272 g, 0.103 mmol) was added slowly (10 min) to a stirred CH_2Cl_2 solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0127 g, 0.0258 mmol). After 1 h, the addition of NaBF_4 (0.2 g, 2 mmol) in EtOH (5 ml) produced a green precipitate. Stirring was continued another 2 h. The solvent was then removed in vacuo, and the residue was washed with pentane (20 ml) and vacuum dried briefly. The solid was then suspended in a few ml of EtOH, treated with H_2O (40 ml), and collected on a medium frit. Washing with H_2O (3×10 ml), EtOH (5 ml), and Et_2O (3×10 ml) followed by vacuum drying gave 0.030 g (85%) of Ib. It was dissolved in CH_3CN (30 ml); the resulting solution was filtered, concentrated to a small volume in vacuo, and treated slowly with excess Et_2O . The mother liquor was decanted from the solid, which was washed with Et_2O , pentane, and vacuum dried. A final yield of 0.0236 g (64%) of pure Ib was obtained. Anal. Found: C, 53.04; H, 3.49; N, 8.19. $\text{C}_{32}\text{H}_{24}\text{N}_4\text{BF}_4\text{RhO}_4$ calcd.: C, 53.51; H, 3.37; N, 7.80%. IR (CH_3CN): $\nu(\text{CN})$ 2001 sh, 2161 cm^{-1} . ^1H NMR ($\text{acetone}-d_6$): δ 7.14 (m, phenyl), 4.49 (s, CH_2CH_2), 4.35 ppm (sh, CH_2CH_2 , oligomer). $\Lambda_{\text{M}}(\text{DMF})$: 75 $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$.

$[\text{Rh}(\text{DiNC})_2]\text{BPh}_4$ (Ic). First, Ia was prepared as described above from $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0628 g, 0.127 mmol) and DiNC (0.145 g, 0.548 mmol). Metathesis with $\text{Na}[\text{BPh}_4]$ (0.0927 g, 0.271 mmol) in acetone followed by the addition of H_2O gave a green solid. It was collected on a medium frit, washed with H_2O , and vacuum dried to yield 0.238 g (98%) of pure Ic. Anal. Found: C, 70.92; H, 4.82. $\text{C}_{56}\text{H}_{44}\text{N}_4\text{BO}_4\text{Rh}$ calcd.: C, 70.75; H, 4.67%. IR (CH_3CN): $\nu(\text{CN})$ 2200 sh, 2158 cm^{-1} . ^1H NMR ($\text{DMSO}-d_6$): δ 7.32 (m, phenyl, DiNC), 6.84 (m, phenyl, BPh_4), 4.61 (s, CH_2CH_2), 4.49 ppm (sh, CH_2CH_2 , oligomer). $\Lambda_{\text{M}}(\text{DMF})$: 69 $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$. When slowly heated above 190°C, Ic becomes rust colored and progressively decomposes without melting below 300°C.

$[\text{Rh}(\text{t-BuDiNC})_2]\text{Cl} \cdot 3/2 \text{H}_2\text{O}$ (IIa $\cdot 3/2 \text{H}_2\text{O}$). A solution of *t*-BuDiNC (0.0674 g, 0.179 mmol) in benzene (100 ml) was added over a 2 h period to a stirred

benzene (100 ml) solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0220 g, 0.0446 mmol). The resulting blue suspension of **Ia** was filtered through a medium frit; the blue solid was washed with benzene (20 ml), and vacuum dried. It was then dissolved in CH_2Cl_2 (15 ml); the resulting solution was filtered, evaporated to a small volume, and treated with excess Et_2O . After decanting off the clear mother liquor, the blue solid was washed with Et_2O and vacuum dried yielding 0.0752 g (92%) of **Ia** $\cdot 3/2 \text{H}_2\text{O}$. The presence of $3/2 \text{H}_2\text{O}$ was established by integration of the ^1H NMR (CDCl_3) spectrum which showed 3 H_2O protons to eight CH_2CH_2 ligand protons. M.p. 212–214°C. Anal. Found: C, 62.78; H, 6.18; N, 6.12. $\text{C}_{48}\text{H}_{54}\text{N}_4\text{ClO}_4\text{Rh} \cdot 3/2 \text{H}_2\text{O}$ calcd.: C, 62.78; H, 6.26; N, 6.10%. IR (CH_2Cl_2): $\nu(\text{CN})$ 2153 s cm^{-1} . IR (Fluorolube mull): $\nu(\text{CN})$ 2153 s, $\delta(\text{OH}_2)$ 1635 w cm^{-1} . ^1H NMR (CDCl_3): δ 7.41 (m, phenyl), 4.59 (s, $-\text{CH}_2\text{CH}_2-$), 1.68 (s, H_2O), 1.33 ppm (s, $\text{C}(\text{CH}_3)_3$). $\Lambda_{\text{M}}(\text{DMF})$: 67 $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$.

$[\text{Rh}(\text{t-BuDiNC})_2]\text{BPh}_4 \cdot \text{CH}_3\text{CN}$ (**Iib** $\cdot \text{CH}_3\text{CN}$). To a stirred solution of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0112 g, 0.0227 mmol) in CH_2Cl_2 (30 ml) was slowly added (90 min) a solution of t-BuDiNC (0.0342 g, 0.0908 mmol) in 30 ml of CH_2Cl_2 . The yellow-green solution was stirred for an additional hour. Evaporation of the solvent gave a blue oil. It was dissolved in acetone (5 ml) and treated with an acetone solution (5 ml) of $\text{Na}[\text{BPh}_4]$ (0.071 g, 0.21 mmol). The mixture was stirred for 2 h, evaporated to dryness, washed with pentane (40 ml) and redissolved in CH_2Cl_2 (20 ml). Filtration of the solution, addition of hexane (20 ml) and slow evaporation of the solvent gave a bright yellow powder which ^1H NMR indicated to be a non-stoichiometric CH_2Cl_2 solvate of **Iib**. Recrystallization from acetonitrile by slow concentration in vacuo gave 0.0447 (81%) of **Iib** $\cdot \text{CH}_3\text{CN}$ as small red-violet needles. Anal. Found: C, 72.77; H, 6.56; N, 6.15. $\text{C}_{72}\text{H}_{76}\text{N}_4\text{BO}_4\text{Rh} \cdot \text{CH}_3\text{CN}$ calcd.: C, 73.05; H, 6.55; N, 5.76%. IR (CH_2Cl_2): $\nu(\text{CN})$ 2155 s cm^{-1} . ^1H NMR (CDCl_3): δ 7.40 (m, phenyl DiNC), 6.98 (m, phenyl BPh_4), 4.11 (s, CH_2CH_2), 1.97 (s, CH_3CN), 1.33 ppm (s, $\text{C}(\text{CH}_3)_3$). The molar conductivity Λ_{M} in DMF of solutions of 3.34×10^{-4} , 2.43×10^{-4} , and $1.40 \times 10^{-4} \text{ M}$ concentration were 36.4, 40.6, and 46.1 $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$, respectively. The violet needles became yellow at 145°C, darkened above 185°C, and progressively decomposed without melting thereafter.

$[\text{Rh}(\text{t-BuDiNC})_2]\text{PF}_6$ (**Iic**). Dark blue **Ia**, prepared from $[\text{Rh}(\text{COD})\text{Cl}]_2$ (0.0336 g, 0.0682 mmol) and t-BuDiNC (0.101 g, 0.269 mmol) in CH_2Cl_2 , was treated with a large excess of $\text{NH}_4(\text{PF}_6)$ (0.3 g, 2 mmol) in acetone (20 ml). After being stirred for an hour, the solvent was removed in vacuo, and the residue was extracted into CH_2Cl_2 . The green solution was filtered, and hexanes (30 ml) were added to precipitate a yellow powder. Slow evaporation in vacuo to $\sim 5 \text{ ml}$ completed the precipitation. The solid was filtered off, washed with ether, and vacuum dried. It was recrystallized from a minimum volume of CH_3CN layered with excess Et_2O at -20°C to yield yellow crystals. Prolonged vacuum drying at room temperature gave 0.127 g (93%) of pure **Iic** as a green powder. Anal. Found: C, 57.45; H, 5.56; N, 5.51. $\text{C}_{48}\text{H}_{56}\text{N}_4\text{F}_6\text{O}_4\text{PRh}$ calcd.: C, 57.60; H, 5.64; N, 5.60%. IR (CH_2Cl_2): $\nu(\text{CN})$ 2156 s cm^{-1} . IR (Nujol mull): $\nu(\text{CN})$ 2163 s, $\nu(\text{PF})$ 843 s cm^{-1} . ^1H NMR (CD_2Cl_2): δ 7.50 (m, phenyl), 4.47 (s, CH_2CH_2), 1.34 ppm (s, $\text{C}(\text{CH}_3)_3$). $\Lambda_{\text{M}}(\text{DMF})$: 69 $\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$.

$[\text{Rh}_2(\text{DiNC})_4\text{I}_2](\text{BF}_4)_2 \cdot 3 \text{H}_2\text{O}$ (**IIIa** $\cdot 3 \text{H}_2\text{O}$). A mixture of $[\text{Rh}(\text{DiNC})_2]\text{BF}_4$ (**Ib**) (0.0519 g, 0.0723 mmol) and I_2 (0.0093 g, 0.0366 mmol) were refluxed for 4 h in CH_2Cl_2 (20 ml). After cooling to room temperature, the solution was treated with

Et₂O (80 ml) and filtered. The red-brown precipitate was vacuum dried at room temperature overnight to give 0.0556 g (88%) of IIIa · 3 H₂O. Two integrations of the ¹H NMR spectrum yielded 5.7 and 6.4 H atoms of water per molecule. Anal. Found: C, 44.03; H, 2.79; N, 6.37; I, 14.62. C₃₂H₂₄N₄BF₄IO₄Rh · 3/2 H₂O calcd.: C, 44.07; H, 2.77; N, 6.42; I, 14.55%. IR (Nujol mull): ν(CN) 2224 sh, 2209 s cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 7.15 (m, phenyl); 4.66, 4.35 (A₂B₂ q, *J*_{AB} = 8.07 Hz, CH₂CH₂); 3.29 ppm (s, H₂O). Λ_M(DMF): 62 cm² ohm⁻¹ mol⁻¹. On heating, IIIa · 3 H₂O darkens noticeably at 145°C without melting.

[Rh₂(DiNC)₄I₂](BPh₄)₂ (IIIb). A mixture of [Rh(DiNC)₂]₂BF₄ (0.0358 g, 0.0498 mmol) and I₂ (0.113 g, 0.445 mmol) was refluxed in CH₂Cl₂ (20 ml) overnight. The solvent was evaporated, and the residue was washed with Et₂O to remove excess I₂. The remaining solid was dissolved in CH₃CN (40 ml); the resulting solution was filtered and treated with Na(BPh₄) (0.10 g, 0.3 mmol). After the solution was concentrated in vacuo, water (50 ml) was added to precipitate a flocculent precipitate. It was collected on a medium frit, washed with H₂O (40 ml), EtOH (40 ml), and Et₂O (40 ml), and vacuum dried to yield 0.0465 g (86%) of IIIb as a red-brown powder. Anal. Found: C, 61.89; H, 4.19; N, 5.19. C₅₆H₄₄N₄BO₄IRh calcd.: C, 62.41; H, 4.12; N, 5.20%. IR (Nujol mull): ν(CN) 2224 sh, 2209 m cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 7.42 (m, phenyl DiNC), 6.83 (m, phenyl BPh₄), 4.55 ppm (m, CH₂CH₂). Λ_M(DMF): 83 cm² ohm⁻¹ mol⁻¹. IIIb melts with decomposition at 192–211°C.

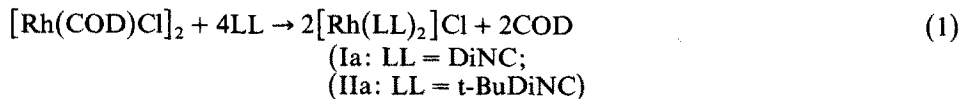
[Pt(DiNC)₂]₂PtCl₄ (IV). A solution of K₂PtCl₄ (0.304 g, 0.703 mmol) and (Et₄N)Cl · H₂O (0.5 g, 3 mmol) in water (5 ml) was evaporated to dryness. The residue was washed with EtOH (20 ml) and then dissolved in hot CH₃CN (10 ml). After filtration, the solvent was removed from the filtrate in vacuo to yield 0.396 g (90%) of dark yellow (Et₄N)₂PtCl₄. IR (Nujol mull): ν(Pt–Cl) 307 m cm⁻¹. ¹H NMR (D₂O): δ 3.25 (q, CH₂), 1.25 ppm (tt, CH₃).

The (Et₄N)₂PtCl₄ prepared above was refluxed with DiNC (0.192 g, 0.993 mmol) in CH₃CN (15 ml) for 40 min which resulted in the formation of a bright yellow suspension. The solid was filtered, washed with EtOH and Et₂O, and dried in vacuo to yield 0.256 g (73%) of IV. Anal. Found: C, 35.95; H, 2.29; N, 5.19. C₁₆H₁₂N₂Cl₂O₂Pt calcd.: C, 36.24; H, 2.28; N, 5.28%. IR (Nujol mull): ν(CN) 2268 w, sh, 2238 s cm⁻¹; ν(Pt–Cl) 305 s cm⁻¹. On heating solid IV (2°/min on hot stage), it gradually turns white (~140°C) but progressively darkens without melting above 250°C.

cis-PtCl₂(*t*-BuDiNC) (V). A mixture of K₂PtCl₄ (0.0995 g, 0.240 mmol) and *t*-BuDiNC (0.0623 g, 0.166 mmol) was refluxed in CH₃CN for 18 h. After cooling, a white precipitate was removed by filtration, and the red solution was evaporated to dryness. The residue was washed with H₂O and vacuum dried. Recrystallization from a minimum volume of CH₂Cl₂ by addition of excess Et₂O yielded 0.106 g (99%, based on ligand) of V as a cream-colored powder. Carbon analyses of this powder were 1.5% lower than required. An amber-colored impurity was removed with great difficulty by slow evaporation of a CH₂Cl₂/EtOH (1/1) solution yielding pure V as white plates (~20% yield). Anal. Found: C, 44.67; H, 4.31; N, 4.32. C₂₄H₂₈N₂Cl₂O₂Pt calcd.: C, 44.87; H, 4.39; N, 4.36%. IR (Nujol mull): ν(CN) 2238 w, 2212 m cm⁻¹; ν(Pt–Cl) 346 w, 320 w cm⁻¹. ¹H NMR (acetone-*d*₆): δ 7.4 (m, phenyl), 4.61 (s, CH₂CH₂), 1.33 ppm (s, C(CH₃)₃). ¹³C NMR (acetone-*d*₆): 130.59, 125.14, 116.42 ppm (C(3), C(5), C(6) in phenyl), 69.34 (CH₂CH₂), 35.00 (CMe₃), 31.36 ((CH₃)₃). V melts with decomposition at 263–270°C.

Results and discussion

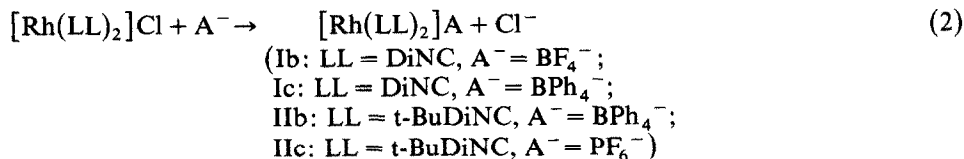
$[Rh(DiNC)_2]^+$ (I) and $[Rh(t-BuDiNC)_2]^+$ (II). *Synthesis and properties.* The square planar complexes, $[Rh(DiNC)_2]^+$ (I) and $[Rh(t-BuDiNC)_2]^+$ (II), are conveniently synthesized as their chloride salts by slow addition of the appropriate ligand to a dilute solution of the cyclooctadiene complex $[Rh(COD)Cl]_2$ (eq. 1).



Using CH_2Cl_2 solvent for the preparation of Ia and benzene for IIa, the reactions proceed rapidly at room temperature, precipitating the blue chloride salts Ia and IIa $\cdot 3/2 H_2O$. In the presence of water or moist air, solid samples of Ia rapidly become red in color. Vacuum drying (10^{-2} Torr, $25^\circ C$) overnight regenerates the blue anhydrous salt. When preparations of Ia are carried out in $CHCl_3$ or CH_3CN , Ia precipitates as a light green ($CHCl_3$) or dark green (CH_3CN) powder. Although the color of isolated solid Ia depends upon the solvent used, IR, 1H NMR and visible spectra (vide infra) of dilute solutions of differently-colored Ia samples are identical. The different colors of the solids may indicate oligomerization of the complexes and/or possibly different crystal structures incorporating solvent of crystallization. A similar behavior is observed for IIa; while IIa $\cdot 3/2 H_2O$ is blue, perhaps indicating oligomerization, a variable solvate IIa $\cdot xCH_2Cl_2$ isolated from CH_2Cl_2 solution by precipitation with hexanes is yellow; this is probably a monomeric form of the complex.

Both Ia and IIa are 1/1 electrolytes in dilute ($\sim 10^{-4} M$) DMF and are stable thermally and in air. Complex Ia is soluble in MeOH, EtOH, DMSO, DMF and CH_3CN to the extent of a few milligrams per milliliter; it is less soluble in CH_2Cl_2 , very sparingly soluble in acetone, $CHCl_3$, and water, and insoluble in Et_2O and hydrocarbons. By comparison, IIa is generally substantially more soluble in all of the above organic solvents. Solutions of both Ia and IIa decompose slowly upon exposure to UV light (vide infra).

The chloride anions of Ia and IIa may be exchanged with other anions (eq. 2).



Metathesis of Ia with $NaBF_4$ in EtOH or $NaBPh_4$ in acetone followed by precipitation with water yields Ib and Ic, respectively. These salts are only very sparingly soluble in alcohols and insoluble in water. Initially obtained as green powders, they can be carefully reprecipitated as blue powders from acetonitrile with excess Et_2O (Ib) or from acetone with excess Et_2O (Ic). Visible solution spectra (vide infra) of these dark blue compounds indicate that they exist as oligomers.

Treatment of IIa with NH_4PF_6 or $NaBPh_4$ in acetone followed by extraction into CH_2Cl_2 and precipitation with Et_2O yields IIC and IIb, as yellow to yellow-green powders containing variable amounts of CH_2Cl_2 . Yellow, green, blue or violet

needles, often containing solvent of crystallization, are obtained depending upon the solvent, counter solvent, and temperature. In general, the physical properties of IIb and IIc are similar to those of IIa apart from their insolubility in alcohols and water.

Recrystallization of IIb from CH_3CN yields $\text{IIb} \cdot \text{CH}_3\text{CN}$ as red-violet needles. An X-ray diffraction study [27] of this compound shows that it, like $[\text{Rh}_2(\text{CNPh})_8](\text{BPh}_4)_2$ [16], $[\text{Rh}_2(\text{CN-}p\text{-C}_6\text{H}_4\text{F})_8]\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ [17], and $[\text{Rh}_2(\text{CN-}p\text{-C}_6\text{H}_4\text{NO}_2)_8]\text{Cl}_2$ [17], has a dimeric structure with two square planar $\text{Rh}(\text{t-BuDiNC})_2^+$ units face-to-face to each other. However, unlike the other $[\text{Rh}_2(\text{CNAr})_8]^{2+}$ complexes, the Rh atoms in $\text{IIb} \cdot \text{CH}_3\text{CN}$ are not directly over each other but are shifted such that the angle between the Rh–Rh vector and the normal to the least squares plane at the Rh atom is 22.7° . This shift gives a Rh–Rh distance of $3.384(2)$ Å as compared with 3.133 Å for the normal between the planes. The shift places the Rh atom almost directly above an isonitrile carbon atom of the other $\text{Rh}(\text{t-BuDiNC})_2^+$ group. The weak Rh–Rh interaction, even as compared with those (3.19 to 3.25 Å) in the $[\text{Rh}_2(\text{CNAr})_8]^{2+}$ complexes, suggests that interactions other than Rh–Rh bonding may contribute to the stability of the $[\text{Rh}(\text{t-BuDiNC})_2]_2^{2+}$ dimer. A possible contributor is π – π interaction between the π -systems of the t-BuDiNC ligands in the two halves of the molecule. Such interactions appear to be of importance in the crystallization of anthracene with bis(difluoroborondimethylglyoximate)nickel(II), $\text{Ni}(\text{dmgBF}_2)_2$, and related systems [28].

UV-visible spectra and photolysis of $[\text{Rh}(\text{DiNC})_2]^+$ (I) and $[\text{Rh}(\text{t-BuDiNC})_2]^+$ (II). The visible absorption spectra (Table 1) of freshly prepared, pale yellow, dilute ($\sim 10^{-5}$ M) solutions of Ia–Ic and IIa–IIc are typical of $[\text{Rh}(\text{CNR})_4]^+$ complexes [16,29]. The band maxima and extinction coefficients are not affected by the anions used in this study. The band assignments in Table 1 are made by analogy to those reported for $[\text{Rh}(\text{CNPh})_4]^+$ [15,16,29]. As observed for $\text{Rh}(\text{CNPh})_4^+$, when solutions of Ia–Ic and IIa–IIc are made increasingly concentrated, they become green and then blue, as a result of oligomerization of the square planar cations. At concentrations of $\sim 10^{-4}$ M, the visible spectra of Ia–Ic in DMF or CH_3CN and IIa–IIc in DMF, CH_3CN , or CH_2Cl_2 exhibit a broad band at ~ 600 nm. A plot of A_{602} (Ic) or A_{612} (IIb) vs. $(A_{472})^2$ (DMF solutions) yields a straight line, indicating that these lower energy bands arise from dimers of I and II according to equilibrium 3.



These bands are analogous to the 568 nm band of $[\text{Rh}_2(\text{CNPh})_8]^{2+}$ [15,16] in acetonitrile solution. In more concentrated ($> 10^{-3}$ M) DMF solutions of Ib and Ic, additional bands appear at ~ 760 nm and ~ 960 nm. By analogy to the $[\text{Rh}(\text{CNPh})_4]^+$ system, we assign these to the trimer (~ 760 nm) and tetramer (~ 960 nm) of I. Even in very concentrated solutions of IIa–IIc, the dimer is the only oligomer observed. Presumably the bulky t-Bu groups reduce the tendency of $[\text{Rh}(\text{t-BuDiNC})_2]^+$ to give higher oligomers. It has been observed previously that the $\text{Rh}(\text{CNR})_4^+$ complex with 2,4,6-tri-*t*-butylphenyl isocyanide ligands shows no evidence of oligomer formation; this behavior was also attributed to the bulkiness of the ligand [30].

Equilibrium constants for the formation of the dimers (eq. 3) and extinction coefficients (Table 1) of the dimers of I and II in DMF solution were obtained from equation 4 where $[Rh]$ is the total rhodium concentration, A_D is the absorbance of

$$\frac{[Rh]}{(A_D)^{1/2}} = \frac{2(A_D)^{1/2}}{\epsilon_D} + \frac{1}{(\epsilon_D K)^{1/2}} \quad (4)$$

the dimer and ϵ_D is the corresponding molar extinction coefficient. Equilibrium constants (eq. 3) for both I and II are larger than that reported for the dimerization of the monodentate complex $[Rh(CNPh)_4]^+$ (K 35 M^{-1}) [16] in acetonitrile solution. The higher equilibrium constant for the formation of dimers I and II as compared with $Rh(CNPh)_4^+$ may be explained by considering the nearly planar structures of the DiNC and *t*-BuDiNC ligands which would provide less steric repulsion than the monodentate CNPh ligands between halves of the dimer. The differences in equilibrium constants might, however, also be due to the different solvents used or to an electronic effect of the *ortho*-alkoxy group in the chelating ligands.

Solutions of Ia–Ic only slowly reach equilibrium when protected from light. We found it necessary to warm DMF solutions to 50–60°C for several hours and then store them at room temperature overnight to obtain true equilibrium concentrations. Prior to such treatment the A_{602} measurements indicated much higher concentrations of the dimer and higher oligomers than found at equilibrium. One likely explanation is that salts of $[Rh(DiNC)_4]^+$ are oligomeric in the solid state, dissolving initially to yield higher concentrations of oligomers which subsequently dissociate to the monomer. This explanation is consistent with the deep blue colors of salts of Ia–Ic in the solid state.

Blue solutions (10^{-4} M) of Ia–Ic in DMF, DMSO, acetonitrile, and acetone, while stable in the dark for days, fade to a yellow color on exposure to light. This phenomenon is also observed in more concentrated solutions. A deep blue, saturated ($\sim 10^{-3}$ M , DMF) solution of Ib faded to light blue-green during the ten minutes required to scan the UV-visible spectrum, corresponding to the loss of trimer (~ 760 nm) and tetramer (~ 960 nm) bands and a large decrease in the dimer (602 nm) band. While some of this change is due to photodecomposition, photodissociation of the oligomers to the monomer has been observed. The A_{602} band of a thermally equilibrated 6.77×10^{-4} M DMF solution of Ic was originally recorded at 0.95. After several minutes exposure to the tungsten light of the spectrophotometer, the value fell to 0.88. Storage of the sample in the dark for 0.5 h returned the value to 0.92. Another 0.5 h in the dark brought the value to 0.93. The cycle could be repeated several times, demonstrating photodissociation of the dimer to the monomer on exposure to light and slow return to equilibrium in the dark. The detection of photo-generated monomers is possible because of their slow rate of reassociation; perhaps solvent coordination to the monomers prevents rapid reassociation. Photodecomposition to unidentified products competes with this process, resulting in slightly lower absorbance values with each cycle. Photodissociation is most noticeable with freshly prepared, nonequilibrated solutions of Ic. While repetitively scanning at 10 minute intervals the visible spectrum of a freshly prepared solution of Ic (2.15×10^{-4} M , DMF), we observed that over a period of 3 h the dimer band at 602 nm steadily decreased in intensity while that of the monomer at 472 nm increased. Photodissociation of $Ir(CNCH_3)_4^+$ under similar conditions has been reported

[13,14] but this is the first example of photodissociation in the rhodium system.

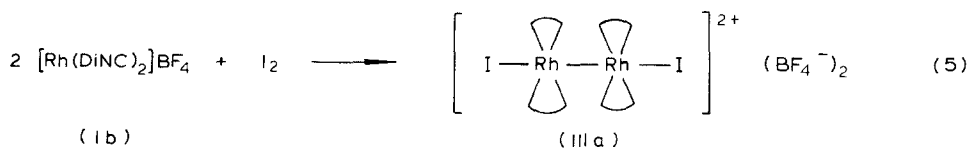
Solutions of IIa–IIc, in DMF, acetonitrile, or acetone are less intensely colored than Ia–Ic at the same concentration since $[\text{Rh}(\text{t-BuDiNC})_2]^+$ is less extensively oligomerized than $[\text{Rh}(\text{DiNC})_2]^+$, as noted above. Equilibria between the monomers and dimers were established rapidly on dilution and no photodissociation was observed. These solutions, as well as those in CH_2Cl_2 and CHCl_3 , fade to yellow upon overnight exposure to room light. However, all absorptions in the solution spectra decrease in intensity indicating that photodecomposition is occurring.

NMR and IR spectra of $[\text{Rh}(\text{DiNC})_2]^+$ (I) and $[\text{Rh}(\text{t-BuDiNC})_2]^+$ (II). Like the visible spectra, the ^1H NMR spectra (see Experimental) of Ia–Ic and IIa–IIc are dependent upon concentration and exposure to light. Spectra of pale yellow dilute solutions show the simple bands expected for the monomeric cations. In more concentrated green or blue solutions, signals due to the oligomers are observed: an additional phenyl multiplet 0.2 ppm downfield of the monomer and a broad featureless shoulder upfield of the CH_2CH_2 singlet for the monomers. In addition to these features, solutions of IIa–IIc in acetone- d_6 show 3 lines of unequal intensity slightly upfield of the t-butyl singlet of the monomer. All signals assigned to the oligomers diminish in relative intensity upon dilution of the solutions. The observation of separate signals for the monomer and oligomers indicates that the rates of association and dissociation are slow on the NMR time scale at ambient temperature. Further evidence of the slow rates of association and dissociation are the variable rates at which solid I and II complexes dissolve and reach equilibrium colors of the solutions. Qualitatively, it appears that coordinating solvents such as DMSO reduce the rate of oligomer formation from the monomers.

As expected, signals arising from the oligomers of I in DMSO- d_6 vanish upon *in situ* photolysis to give a yellow solution of the monomer. The same loss of oligomer signals occurs when the sample is heated in the probe at 70°C overnight. Upon cooling the sample to the ambient probe temperature, the solution remains yellow, and there is also no NMR evidence for the reformation of oligomers, presumably because coordination of the monomer by the DMSO solvent retards the rate of oligomerization.

Infrared spectra (see Experimental) of CH_3CN or CH_2Cl_2 solutions of Ia–Ic and IIa–IIc in the $\nu(\text{C}\equiv\text{N})$ region all show a single medium-to-strong band at approximately 2158 cm^{-1} ; in complexes Ia–Ic, a shoulder at about 2200 cm^{-1} is also observed. For D_{4h} local symmetry, only one $\nu(\text{C}\equiv\text{N})$ infrared absorption is expected; however, the A_{1g} or B_{1g} mode is also sometimes observed [7]. The position of the principal band is approximately 30 cm^{-1} higher in the complexes than in the free DiNC (2128 s , CHCl_3) and t-BuDiNC (2126 s , CHCl_3) ligands [1], which suggests that the ligands serve primarily as σ -donors. Solutions containing oligomers of I or II give IR solution spectra no different than those with only monomers.

Synthesis and characterization of $[\text{Rh}_2(\text{DiNC})_4\text{I}_2]^{2+}$ (III). Reaction of Ib with excess I_2 in refluxing CH_2Cl_2 for 4 h yields the dimer $[\text{Rh}_2(\text{DiNC})_4\text{I}_2](\text{BF}_4)_2$ (IIIa)



as a microcrystalline red-brown product, according to the equation 5. The stoichiometry of the reaction was confirmed by noting the quantitative conversion (by IR) of I to III using 1/2 mole of I_2 per mole of Ib. Use of an excess of I_2 under the reaction conditions does not give other products. Metathesis of IIIa with $NaBPh_4$ in CH_3CN gives $[Rh_2(DiNC)_4I_2](BPh_4)_2$ (IIIb) as a rust-colored powder.

The structure of the cation in III is presumably analogous to that of $[Rh_2(CN-p-C_6H_4CH_3)_8I_2]^{2+}$, whose structure has been established by an X-ray diffraction study [31] to have a Rh–Rh bond with terminal iodo ligands as shown in eq. 3.

Solid IIIa and IIIb are stable to air and moisture and show no decomposition for months when stored at room temperature and protected from light. Both IIIa and IIIb are more soluble than Ib and Ic, but even so they are still only slightly soluble in polar solvents such as DMSO, DMF, and CH_3CN . When finely dispersed in a mull or dissolved in solution IIIa, IIIb are quite light sensitive. Mulls exposed to room light become green in several hours and a $\nu(C\equiv N)$ absorption at 2156 cm^{-1} , typical of $[Rh(DiNC)_2]^+$, appears in the spectrum. Yellow-orange, dilute solutions ($\sim 10^{-4}\text{ M}$) rapidly become green and then yellow on exposure to room light; these yellow solutions have visible spectra characteristic of I. These observations suggest that photolysis of IIIa, IIIb liberates I_2 and $[Rh(DiNC)_2]^{2+}$, which subsequently dissociates to the yellow $[Rh(DiNC)_2]^+$ monomer.

Although arylisonitrile complexes, $[Rh(CNAr)_4]^+$, are reported [9,32] to react at room temperature with I_2 to give monomeric rhodium(III) complexes $[Rh(CNAr)_4I_2]^+$, only dimeric rhodium(II) complexes (III), were isolated under these conditions with $[Rh(DiNC)_2]^+$. The formation of $[Rh_2(DiNC)_4I_2]^{2+}$ rather than $[Rh(DiNC)_4I_2]^+$ suggests that the dimeric structure is more stable for the DiNC complex than for monodentate isonitrile complexes. The near planarity of the DiNC ligand, which provides less steric repulsion than monodentate CNAr ligands between halves of the dimer, may be responsible for this unusual stability of the

TABLE 2
INFRARED ABSORPTIONS OF Rh^I , Rh^{II} , AND Rh^{III} ISONITRILE COMPLEXES

Compound	$\nu(C\equiv N)$ (cm^{-1})
<i>Rh^I</i>	
$[Rh(DiNC)_2]^+{}^a$	2201 w,sh; 2156 s
$[Rh(CN-p-C_6H_4OMe)_4]^+{}^b$	2200 w; 2150 s
$[Rh_2(\text{bridge})_4]^{2+}{}^c$	2172 s
$[Rh(CNC_6H_{11})_4]^+{}^d$	2170
<i>Rh^{II}</i>	
$[Rh_2(DiNC)_4I_2]^{2+}{}^a$	2224 w,sh; 2209 s
$[Rh_2(CN-p-C_6H_4CH_3)_8I_2]^{2+}{}^e$	2194
$[Rh_2(\text{bridge})_4I_2]^{2+}{}^c$	2227 s
$[Rh_2(CNC_6H_{11})_8I_2]^{2+}{}^d$	2214
<i>Rh^{III}</i>	
$[Rh(CN-p-C_6H_4OMe)_4I_2]^+{}^f$	2246 vw, 2222 vs
$[Rh(CNC_6H_{11})_4I_2]^+{}^d$	2239

^a Nujol mull. ^b From ref 7; KBr. ^c From ref 18; KBr; bridge = $CN(CH_2)_3NC$. ^d From ref 33; in acetone.

^e From ref 31. ^f From ref 9; KBr.

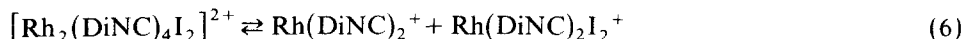
$[\text{Rh}_2(\text{DiNC})_4\text{I}_2]^{2+}$ complex. Prolonged refluxing (1 week) of Ib with excess I_2 in CH_3CN gives a brown solid with two $\nu(\text{C}\equiv\text{N})$ bands (Nujol mull) of roughly equal intensity at 2209 (for IIIa) and 2224 cm^{-1} . The latter frequency is very similar to that for the rhodium(II) complex $[\text{Rh}(\text{CN}-p\text{-C}_6\text{H}_4\text{OMe})_4\text{I}_2]^+$ (Table 2), which may indicate the presence of $[\text{Rh}(\text{DiNC})_2\text{I}_2]^+$; however, attempts to isolate it were unsuccessful.

The reaction of Ib with one equivalent of Br_2 in CH_2Cl_2 , followed by metathesis with NaBPh_4 , yields an extremely photosensitive yellow powder, which rapidly decomposes in room light to give $[\text{Rh}(\text{DiNC})_2]^+$ which was identified by its infrared spectrum. The position (2214 cm^{-1}) of the $\nu(\text{C}\equiv\text{N})$ absorption suggests that the yellow powder is $[\text{Rh}_2(\text{DiNC})_4\text{Br}_2]^{2+}$, the bromo analog of III, which we could not isolate as the pure compound. The reaction of Ib with 2 equivalents of Br_2 at room temperature did not give any evidence for a rhodium(III) complex.

Ib is resistant to oxidative-addition by other reagents. No reaction occurred with acetyl chloride or Ph_3SnCl in refluxing CH_2Cl_2 or with CH_3I in refluxing THF. Reductions of Ib were also unsuccessful inasmuch as there was no reaction with NaBH_4 in EtOH, and Ia decomposed to unidentified products with Na amalgam.

Infrared spectra (Table 2) of IIIa, IIIb show one strong and one weak $\nu(\text{C}\equiv\text{N})$ band. The strong absorption is about 50 cm^{-1} higher than that of I. Such increases in $\nu(\text{C}\equiv\text{N})$ frequencies are commonly observed when the metal is oxidized. Dilute solutions of IIIa or IIIb in DMF show two visible absorption maxima (Table 1), which are similar to those of other rhodium(II) dimers previously reported. The electronic transitions in Table 1 are assigned following those made for $[\text{Rh}_2(\text{bridge})_4\text{I}_2]^{2+}$ [18]. Reproducible extinction coefficients for IIIa or IIIb could not be determined as significant photodecomposition to I occurred during the recording of the spectrum.

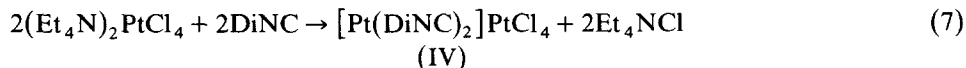
The ^1H NMR spectrum of IIIb confirms the 2/1 ratio of DiNC to $[\text{BPh}_4]^-$. The spectrum of the more soluble $[\text{BF}_4]^-$ salt IIIa shows an A_2B_2 quartet for the ethylene protons of the DiNC ligand. The two types of ethylene protons presumably arise from the different environments on opposite sides of the Rh square plane; on one side is the I^- ligand, while $\text{Rh}(\text{DiNC})_2$ is on the other. The A_2B_2 quartet coalesces to a broad singlet upon heating in the probe to 70°C ; upon cooling to ambient probe temperature ($\sim 35^\circ\text{C}$), the spectrum returns to the A_2B_2 quartet. A possible explanation



tion for the equalization of the protons is the disproportionation reaction, shown in eq. 6, which is known [31] to occur rapidly for $[\text{Rh}_2(\text{CN}-p\text{-C}_6\text{H}_4\text{CH}_3)_8\text{I}_2]^{2+}$. For the cyclohexylisonitrile complex dimer $[\text{Rh}_2(\text{CNC}_6\text{H}_{11})_8\text{I}_2]^{2+}$, the equilibrium of the type in eq. 4 is so rapid that only an averaged C_6H_{11} ^1H NMR spectrum is observed (presumably at ambient temperature) for the mixture of the 3 complexes [33]. The need to go to 70°C to make the protons equivalent in $[\text{Rh}_2(\text{DiNC})_4\text{I}_2]^{2+}$ suggests that disproportionation is slower in this instance, perhaps because of the greater stability of the dimeric complexes of DiNC as compared with those of monomeric isonitriles.

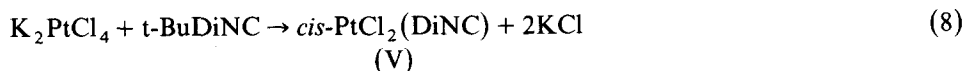
$[\text{Pt}(\text{DiNC})_2]\text{PtCl}_4$ (IV) and $\text{PtCl}_2(t\text{-BuDiNC})$ (V). The reaction of $(\text{Et}_4\text{N})_2\text{PtCl}_4$ with DiNC in refluxing CH_3CN gives the bright yellow powder $[\text{Pt}(\text{DiNC})_2]\text{PtCl}_4$, IV, in 73% yield (eq. 7). The compound is stable to air, light, and storage at room

temperature for long periods. Like the related monodentate aryl isonitrile complexes $[\text{Pt}(\text{CNAr})_4]\text{PtCl}_4$ [5,23], IV is insoluble in all common solvents. Its infrared spectrum (Nujol mull) exhibits a strong $\nu(\text{C}\equiv\text{N})$ absorption at 2238 cm^{-1} with a



weak shoulder at 2268 cm^{-1} . A $\nu(\text{Pt}-\text{Cl})$ band is observed at 305 cm^{-1} for the PtCl_4^{2-} anion, as found in the related $[\text{Pt}(\text{CNAr})_4]\text{PtCl}_4$ complexes [23]. The yellow color of IV is intermediate between the deep blue of $[\text{Pt}(\text{CN-}p\text{-C}_6\text{H}_4\text{Me})_4]\text{PtCl}_4$ with Pt-Pt interactions and the red of unassociated $[\text{Pt}(\text{CN-}p\text{-C}_6\text{H}_4\text{OMe})_4]\text{PtCl}_4$ [23]. The mass spectrum of IV at 140°C shows a peak corresponding to $\text{PtCl}_2(\text{DiNC})^+$ suggesting that $\text{PtCl}_2(\text{DiNC})$ may be formed upon heating IV, a reaction that is known to occur with the $[\text{Pt}(\text{CNAr})_4]\text{PtCl}_4$ complexes [23].

Refluxing K_2PtCl_4 and *t*-BuDiNC in CH_3CN yields white plates of $\text{PtCl}_2(\text{t-BuDiNC})$ (V, eq. 8.). The low solubility of K_2PtCl_4 is evidently important for this reaction, because slow addition of *t*-BuDiNC to $(\text{Et}_4\text{N})_2\text{PtCl}_4$ generates a dark



amber, possibly polymeric, species. In the preparation according to eq. 8 some amber by-product is also formed, although in small quantities. Solid V is stable upon storage in air and light at room temperature. Two $\nu(\text{C}\equiv\text{N})$ and two $\nu(\text{Pt}-\text{Cl})$ absorptions are observed in IR spectra of the compound as expected for the *cis* geometry. The ^1H NMR spectrum (see Experimental) is as expected for V. The low solubility of the complex gave only a marginally acceptable ^{13}C NMR spectrum; the isonitrile carbon and the phenyl carbon attached to the nitrogen were not observed, possibly due to quadrupolar broadening by the nitrogen.

Attempts to prepare the *cis*- $\text{PtCl}_2(\text{LL})$ complexes by reaction of *cis*- $\text{PtCl}_2(\text{NCMe})_2$ with DiNC or *t*-BuDiNC in MeCN or CH_2Cl_2 give only uncharacterized products containing an IR absorption at 1550 cm^{-1} , possibly due to a polymeric isonitrile species with a $\nu(\text{N}\equiv\text{C}\langle)$ vibration; this absorption increases in intensity when 2 additional equivalents are added to the solution. Also this band is observed when *t*-BuDiNC is added to $\text{PtCl}_2(\text{t-BuDiNC})$ suggesting that the complex catalyzes the polymerization of the diisonitrile ligand.

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