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NEW ISOCYANIDE COMPLEXES OF PLATINUM(II)

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SUMMARY

New platinum compounds, of formula $[Pt(CNR)_4][PtCl_4]$ and *cis*-$Pt(CNR)_2Cl_2$, with R = cyclohexyl, *p*-tolyl, and *p*-anisyl, have been prepared and characterized. Reaction with stannous chloride yields *trans*-$[(RNC)_2Pt(SnCl_3)_2]$ and reaction with methanol gives the "carbene" complexes *cis*-$[(RNH{-}C{-}OCH_3)(RNC)PtCl_2]$.

As part of our activity in the field of isocyanide complexes[1], we have prepared some platinum(II) isocyanide complexes and examined their behaviour with tin(II) chloride[2] to give insertion products, and with methanol to give a methoxy(alkylamino)carbene complex[3].

RESULTS AND DISCUSSION

The complexes $[Pt(CNR)_4][PtCl_4]$ were prepared in good yields from aqueous potassium tetrachloroplatinate(II) and the appropriate ligand. The compounds are blue and insoluble in organic solvents (R = phenyl[4], *p*-tolyl) or red and soluble in common organic solvents (R = *p*-anisyl, cyclohexyl). The difference between the two types is probably due to the existence in the blue compounds of a strong metal–metal interaction which is permitted because the organic group bonded to the isocyanide function is fairly flat, as with phenyl or *p*-tolyl groups. Such a platinum–platinum interaction is not possible, when the organic group has bigger steric requirements, as with the derivatives of cyclohexyl or of *p*-anisyl isocyanide: the salts containing these ligands are nearly red, the colour of the $[PtCl_4]^{2-}$ anion. An unstable red form of $[Pt(p\text{-}CH_3C_6H_4NC)_4][PtCl_4]$ and an unstable blue form of $[Pt(p\text{-}CH_3OC_6H_4NC)_4][PtCl_4]$ were observed, but, in both cases only the more stable form was actually isolated. A similar type of metal–metal interaction has previously been observed in other platinum(II)[5], rhodium(I)[6], and iridium(I)[7,8] complexes, but not in the case of the isocyanide complexes of palladium(II)[9,10]; with palladium, $[Pd(CNR)_4][PdCl_4]$ compounds have not been obtained. Palladium, platinum, rhodium, and iridium have nearly the same atomic radius; therefore, the absence of palladium(II) isocyanide complexes involving a metal–metal interaction and the presence of rhodium(I) complexes in which such metal–metal interaction occurs is probably due to the difference in the formal oxidation state of the two square-planar complexes: the element in the lower oxidation state has a more

TABLE 1

COMPOUNDS OBTAINED AND ANALYTICAL DATA

No.	Compound and colour	M.p. (°C)	Analyses, found (calcd.) (%)			
			C	H	N	Mol.wt.[a]
(I)	$[Pt(CNC_7H_7)_4][PtCl_4]$ blue	144			5.82 (5.60)	Insol. (1000)
(II)	*cis*-$Pt(CNC_7H_7)_2Cl_2$ yellow	170–172	38.93 (38.40)	2.58 (2.80)	5.54 (5.60)	640 (500)
(III)	*trans*-$Pt(CNC_7H_7)_2(SnCl_3)_2$[b] dirty yellow	292 dec. ca. 250	21.91 (21.8)	1.47 (1.60)	2.95 (3.2)	Insol. (879)
(IV)	*cis*-$Pt(CNC_7H_7O)(C_9H_{11}NO)Cl_2$ yellow	158	38.04 (38.34)	3.22 (3.38)	5.33 (5.26)	880 532
(V)	$[Pt(CNC_7H_7O)_4][PtCl_4]$[c] brick-red	152				Insol. (1064)
(VI)	*cis*-$Pt(CNC_7H_7O)_2Cl_2$[d] yellow	122				
(VII)	*trans*-$Pt(CNC_7H_7O)_2(SnCl_3)_2$ orange-yellow	305 dec. ca. 250	21.34 (21.07)	1.37 (1.54)	3.09 (3.08)	Insol.
(VIII)	$[Pt(CNC_6H_{11})_4][PtCl_4]$[e] orange-red	121	34.84 (34.71)	4.82 (4.55)	5.88 (5.78)	
(IX)	*cis*-$Pt(CNC_6H_{11})_2Cl_2$ ivory-white	126	34.81 (34.71)	4.66 (4.55)	5.75 (5.78)	590 (484)
(X)	*trans*-$Pt(CNC_6H_{11})_2(SnCl_3)_2$ yellow	247 (dec.)	19.45 (19.66)	2.48 (2.55)	3.37 (3.25)	944 (863)
(XI)	*cis*-$Pt(CNC_6H_{11})(C_8H_{15}NO)Cl_2$ white	105–115 (dec.)	35.06 (34.88)	5.27 (5.04)	5.42 (5.42)	652 (516)

[a] Osmometrically in chloroform at 37°. [b] Pt found 22.5, calcd. 22.2%; Cl found 24.35, calcd. 24.2%. [c] Pt found 36.0, calcd. 36.7%. [d] Pt found 37.0, calcd. 36.7%. [e] Λ 65 $cm^2 \cdot mole^{-1} \cdot ohm^{-1}$ in nitromethane, 0.001 *M*.

extended d_{z^2} orbital and is, therefore, in the required condition for a metal–metal interaction. The existence of a metal–metal bond has been suggested[11] for the black form of $[Pd(CNR)_2]_n$ complexes[12]: in these compounds the electron density at the metal atom is certainly higher than in a corresponding square-planar complex.

The infrared spectra of the ionic complexes showed the required single and strong Pt–Cl stretching frequency in the range 303–307 cm^{-1}, at a lower value than that generally found for $[PtCl_4]^{2-}$ derivatives (320 cm^{-1})[13]. The lowering may arise from the large size of the counter ion or from some other solid state interaction. In view of this observation, it is doubtful whether a clear-cut correlation between ν(Pt–Cl) and steric or electronic effects of the substituents will be possible.

The isocyanide stretching frequency was observed at 2205–2270 cm^{-1}, and not always as singlets, probably because of solid state splitting. Reliable solution spectra could not be obtained because of the easy isomerization to *cis*-$Pt(CNR)_2Cl_2$ compounds. The ν(CN) frequency is in all cases considerably larger than in the free ligand. The shift, $\Delta\nu$, observed is of the same order of magnitude and has the same sign as that recorded for aluminum[14] or boron[15] complexes, so that any significant contribution of π-back-donation to the Pt–C bond is excluded: π-back-donation would shift ν(CN) towards lower wavenumbers[1b].

All the $[Pt(CNR)_4][PtCl_4]$ compounds prepared were transformed into their

TABLE 2

SPECTRAL DATA

Compound	Infrared spectrum[a]			NMR spectrum[b]
	ν(CN)		ν(M–Cl)	
	Nujol	$CHCl_3$		
(I)	2248 s		303 s	Insol.
	2205 m			
(II)	2254 s		334	7.6
	2216 s		315	2.44–2.84 pseudoquartet
(III)	2201 s		336 vs br	Insol.
(IV)	2207 s		328 m	2.2–3.1 [8 H]
			294 m	5.40 [3 H] br[c]
		2204 vs		7.65 [6 H] br
				8.28 [1 H][d]
(V)	2205 s, br		307 m	
(VI)	2228 m, sh		338 m	
	2198 s		319 s	
(VII)	2210 s		346 vs br	
(VIII)	2270 s		305 s	ca. 6 [1 H]
	2212 m			ca. 7.1 and 8.4 [10 H]
		2252 s		
		2219 s		
(IX)	2255 s		339 s	5.9 br [1 H][c]
	2230 s		318 s	ca. 7.12 and 8.48 [10 H]
		2251 s		
		2222 vs		
(X)	2237 s		333 vs	ca. 6 [1 H]
			323 sh	ca. 8.0 and 8.46 [10 H]
		2226 s		
(XI)	2215 s		325 m	5.63 [3 H]
			291 m	ca. 6.05 [2 H]
		2218 vs		ca. 7.22 and 7.50 [21 H]

[a] Perkin–Elmer 621 instrument. [b] Perkin–Elmer R-10 instrument at 60 Mc, 33°, $CDCl_3$ solution, τ values in ppm. [c] Some splitting is present. [d] Disappears on treatment with trifluoroacetic acid.

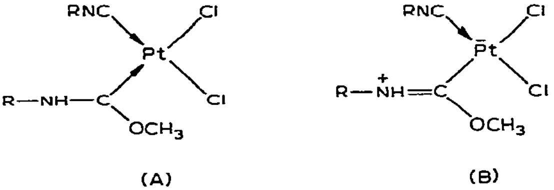
soluble *cis*-$Pt(CNR)_2Cl_2$ isomers on refluxing their chloroform solutions. The *cis* structure was assigned because all the compounds show two Pt–Cl and two CN stretching vibrations in the IR spectrum; the former vibration is scarcely affected by change in the isocyanide ligand (less than 5 cm^{-1}) while the position of the latter vibrations allows the same conclusion as above about π-bonding.

The reaction of *cis*-$Pt(CNR)_2Cl_2$ with anhydrous tin(II) chloride was carried out in chloroform; even with a 1/1 Sn/Pt ratio no monosubstituted compound was obtained, but only the yellow, high-melting, stable $(RNC)_2Pt(SnCl_3)_2$ compounds; use of excess of $SnCl_2 \cdot 2H_2O$ in acetone led to displacement of all the isocyanide molecules. A *trans* configuration was assigned to the tin-containing complexes because only one C–N stretching band was observed both in the solid state and in solution. A *trans* configuration was previously[10] found for the similar $[(C_6H_5NC)_2$-

PdX_2] and [(p-$CH_3C_6H_4NC)_2PdX_2$] compounds[9] when X was a bulky group, such as bromide or iodide. Again, the position of ν(CN) suggests the absence of significant amounts of π-back-donation, but some of d_π–p_π bonding must be present in the Pt–Sn bonds. The values for the ν_s(Sn–Cl) and ν_{as}(Sn–Cl) are found at 333 and 323 cm^{-1} for $(C_6H_{11}NC)_2Pt(SnCl_3)_2$ and are merged into a broad band at about 340 cm^{-1}. All the values are markedly higher than those in either [Ph_4As][$SnCl_3$] (289 and 252 cm^{-1}) or [Ph_4As][Cl_3SnBCl_3] (284 and 252 cm^{-1})[16] in which only σ-bonding is possible.

The $\Delta\nu$(CN) show that cyclohexyl isocyanide is the most electron-donating toward the metal, and consequently has the highest *trans*-influence, as measured by the position of ν(Pt–Cl) in these compounds.

The reaction of *cis*-$Pt(CNR)_2Cl_2$ with methanol gave *cis*-[(RNH–C–OCH_3)-(RNC)$PtCl_2$] (R = p-tolyl, cyclohexyl). The corresponding palladium complexes do not react appreciably at room temperature with the alcohol used as a solvent for their preparation[10], but do react under reflux[17]. Two limiting structures, (A) and (B), can be written for the compounds obtained:



The infrared spectra show the required single CN stretching frequency, two ν(Pt–Cl), ν(N–H) at ca. 3200 and a strong band in the region 1500–1600 cm^{-1}. Molecular weight determinations suggest that the compounds are associated in chloroform solution, probably through hydrogen bonding. All the data suggest that the compounds should be considered as a "carbene" complex, but with a contribution of the ylide form (B)[3]. The ν(N–H) is lower by 200–300 cm^{-1} than ν(N–H) reported for $Cr(CO)_5C(R'NH)Me$ compounds[18], and the NMR resonance due to the CH_3O group is displaced to lower field than in chromium carbene complexes. The shift to lower wavelength of ν(Pt–Cl) on going from the starting material to the carbene complex suggest that this ligand has a rather high *trans*-effect.

Further work is in progress.

EXPERIMENTAL

Evaporation was carried out under reduced pressure. Platinum analysis was carried out by ashing the sample with the aid of fuming nitric acid; tin was removed by twice mixing the ashes with ammonium chloride and subliming it away.

Preparation of the compounds

Tetrakis(p-tolyl isocyanide)platinum(II) tetrachloroplatinate(II), (I). The appropriate quantity of ligand was added with a stirring to a saturated aqueous solution of K_2PtCl_4. A red precipitate formed immediately, and turned blue soon afterwards. The precipitate was filtered and washed with water, methanol, ether, benzene, and ether again.

Compounds (V) and (VIII) were obtained similarly, but were washed only with water, and ether.

cis-Bis(p-tolyl isocyanide)dichloroplatinum(II), (II). A chloroform (30 ml) suspension of (I) (1.0 g) was refluxed. After 4 h a yellow solution was formed. Addition of diethyl ether to the concentrated solution afforded (II) as yellow crystals.

Compounds (VI) and (IX) were obtained similarly.

trans-Bis(p-tolyl isocyanide)bis(trichlorostannyl)platinum(II), (III). A suspension of anhydrous tin(II) chloride (0.380 g) in a solution of (II) (1.0 g) in absolute chloroform was stirred 4 days. The yellowish compound (0.380 g) was filtered and washed liberally with chloroform and with diethyl ether. Treatment of the mother liquor with additional tin(II) chloride (0.38 g) gave more (III).

Compound VIII was prepared similarly.

trans-Bis(cyclohexyl isocyanide)bis(trichlorostannyl)platinum(II), (X). A solution of compound (IX) (0.500 g) in absolute chloroform (40 ml) was stirred for 4 h with anhydrous tin(II) chloride (0.380 g). The yellow solution was concentrated to small volume and the product (0.75 g) was isolated by addition of diethyl ether. It was crystallized from chloroform/ether.

cis-[Methoxy(p-tolylamino)carbene](p-tolyl isocyanide)dichloroplatinum(II), (IV). Compound (II) (500 mg) was dissolved in absolute chloroform (20 ml) and methanol (8 ml) was added. After 3 days the solution was evaporated to dryness and the residue was crystallized from methylene chloride/diethyl ether to yield the yellow compound (0.155 g).

cis-[Methoxy(cyclohexylamino)carbene](cyclohexyl isocyanide)dichloroplatinum(II), (XI). Compound (X) (0.484 g) was suspended in methanol and allowed to stand 3 days. The infrared spectrum of the solid recovered from the suspension revealed that no reaction had occurred. So, the mixture was refluxed overnight. The solution was then evaporated to dryness and treatment of the residue with petroleum ether gave a white crystalline solid, (XI). It was very soluble in common organic solvents.

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