Contribution from the School of Molecular Sciences,
University of Sussex, Brighton, BN1 9QJ, United Kingdom

Eletronic Effects in the Reactions of Coordinated Isonitriles; Bis-carbene Complexes of Platinum(II) and Palladium(II)*

J. Chatt, R.L. Richards* and G.H.D. Royston

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The reactions of complexes of the type cis-[$PtCl_2(RNC)(PR'_3)$] *(R =* p-$CH_3OC_6H_4$, C_6H_5 *or* p-$NO_2C_6H_4$; PR'_3 *=* PPh_3, $PEtPh_2$, PEt_2Ph *or* PEt_3*) with ethanol have been investigated. Reaction of the coordinated isonitrile with ethanol to give an ethoxy-carbene ligand is quickest for R=* p-$NO_2C_6H_4$ *and slowest for R=* p-$MeOC_6H_4$ *consistent with nucleophilic attack at isonitrile carbon by ethanol. Variation of* PR'_3 *has little effect on the reaction rate. The derived carbene complexes are characterised together with the bis-carbene complexes* cis-[$MCl_2\{C(OEt)NH$p-$NO_2C_6H_4\}_2$] *(M = Pt or Pd) obtained by reaction of the* cis-[MCl_2(p-$NO_2C_6H_4NC)_2$] *compounds with ethanol.*

Introduction

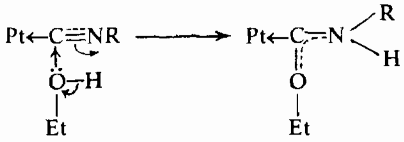
In order to throw light on the factors involved in the activation of coordinated isonitrile towards attack by such nucleophilic reagents as alcohols and amines[1] we have prepared a series of complexes of the type *cis*-[$PtCl(RNC)(PR'_3)$] (R = *p*-$MeOC_6H_4$, C_6H_5 or *p*-$NO_2C_6H_4$; PR'_3 = PPh_3, $PEtPh_2$, PEt_2Ph, PEt_3) and compared the reactivity of the RNC ligand towards ethanol. Ethanol was chosen because its relative weakness as a nucleophile makes it a selective reagent towards sites which might have varying electrophilic character.

When reaction occurred, the RNC ligand was converted into the $\{C(NHR)OEt\}$ ligand and the times required for reaction with boiling ethanol to reach completion are shown in Table I. These data, while at best qualitative, nevertheless show that variation of the PR'_3 ligand has a relatively small effect on the reaction rate, but when the RNC ligand carries the electron withdrawing *p*-$NO_2C_6H_4$ group the reaction rate is most rapid, whereas the electron-releasing *p*-$CH_3OC_6H_4$ group greatly slows the reaction rate.

Table I. Reaction times for formation of the complexes *cis*-[$PtCl_2\{C(RNH)OEt\}PR_3$].

RNC	PR'_3	Reaction time (h)
PhNC	PEt_3	6
PhNC	PEt_2Ph	6
PhNC	$PEtPh_2$	12
PhNC	PPh_3	18
p-$CH_3OC_6H_4NC$	PEt_3	only 50% after 48 h
p-$NO_2C_6H_4NC$	PPh_3	1

Thus the reactivity of coordinated isonitrile is enhanced by withdrawal of electron density from the isonitrile carbon atom, consistent with the rate determining step of the reaction being nucleophilic attack at carbon as in (a).



(a)

The CNPh bond angle of only 165.5° in *cis*-[$PtCl_2(PhNC)(PEt_3)$] led to an earlier suggestion[1] that electrophilic attack at nitrogen might occur. However, subsequent X-ray studies[2] indicate that such non-linearity is not a general feature of the Pt—C—N—R system, therefore nucleophilic attack as suggested above and by other workers[3,4] is much more likely.

Physical data for the carbene complexes thus obtained and the parent isonitrile compounds, where new, are shown in Table II. N.m.r. and m.wt. data for carbene complexes are precluded by their low solubility and configurations are therefore assigned by analogy with similar compounds.[1]

The complexes *cis*-[$MCl_2(RNC)_2$] or the isomeric [$M(RNC)_4$][MCl_4] (M = Pt or Pd) compounds[5] show a similar variation in reactivity depending upon R. When R = *p*-NO_2Ph, both isonitrile ligands react to give bis-carbene complexes whereas when R = *p*-$OMeC_6H_4$ no reaction occurs with ethanol. When R = C_6H_5 only one isonitrile ligand reacts. At this stage it is not clear whether kinetic or thermodynamic factors determine the nature of the final product in these cases. Data for these compounds are also in Table II. All the compounds prepared in this study are white or cream.

We have thus shown that the mechanism of the conversion of an isonitrile ligand into a carbene ligand

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(*) Discussed by R.L. Richards at the Chemical Society Symposium on Reactions of Coordinated Ligands, Leeds, 1971.

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(3) F. Bonati and A. Minghetti, *Synthesis in Inorganic and Metal-organic Chem.*, *1*, 299 (1971).
(4) H.C. Clark and L.E. Manzer, *Inorg. Chem.*, *11*, 503 (1972).
(5) L. Malatesta and F. Bonati, « *Isocyanide complexes of metals* », Wiley-Interscience, London, 1969, p. 167.

Table II. Isonitrile and carbene complexes of platinum(II) and palladium(II)

				Analyses ^{a}		
Complex	M.p.	yield %	C	H	N	ν(X-Y)
cis-$[PtCl_2(PhNC)(PPh_3)]$	248-255	85	47.9(47.6)	3.2(3.2)	2.5(2.2)	2200 ^{b}
cis-$[PtCl_2(p\text{-}NO_2C_6H_4NC)(PPh_3)]$	230-232	65	44.5(44.4)	2.8(2.8)	4.1(4.1)	2200 ^{b}
cis-$[PtCl_2(p\text{-}CH_3OC_6H_4NC)(PEt_3)]$	187-189	80	32.5(32.5)	4.3(4.3)	2.7(2.7)	2205 ^{b}
cis-$[PtCl_2\{C(OEt)(NHPh)\}(PEt_2Ph)]$	191-192	30	39.5(39.3)	4.7(4.5)	2.4(2.4)	31503115,3050 ^{c}
cis-$[PtCl_2\{C(OEt)(NHPh)\}(PPh_3)]$	209-214	30	47.8(47.9)	3.9(3.9)	2.2(2.1)	3180 br ^{c}
cis-$[PtCl_2\{C(OEt)(NHpOMePh)\}(PEt_3)]$	172-175	65	34.5(34.1)	5.1(5.0)	2.5(2.5)	3165,3120,3040 ^{c}
cis-$[PtCl_2\{C(OEt)(NHpNO_2Ph)\}(PPh_3)]$	212-214	50	44.6(44.9)	3.5(3.5)	4.0(3.9)	3190,3060 ^{c}
cis-$[PtCl_2\{C(OEt)(NHp\text{-}NO_2Ph)\}_2]$	191-193	35	33.0(33.0)	3.4(3.1)	8.1(8.6)	3280,3195 ^{c} 316,283 ^{d}
cis-$[PtCl_2\{C(OEt)(NHPh)\}(PhNC)]$	182-184	15	37.3(37.1)	3.6(3.1)	5.0(5.4)	3205 ^{c} 2185 ^{b}
cis-$[PdCl_2\{C(OEt)(NHp\text{-}NO_2Ph)\}_2]$	167-169	40	38.4(38.2)	3.7(3.6)	9.9(9.9)	3260,3175 ^{c}

^{a} Calculated values in parentheses. ^{b} (X—Y) = (N≡C). ^{c} (X—Y) = (N—H). ^{d} (X—Y) = (metal-Cl). br = broad.

involves nucleophilic attack at the relatively electron deficient[6] isonitrile carbon and it follows that the reactivity of coordinated isonitrile will be enhanced by electron withdrawing substituents. However, the failure to obtain such a reaction with isonitrile complexes of rhodium and iridium[7] indicates the crucial importance of other as yet uninvestigated effects involved in the activation of coordinated isonitriles.

Experimental Section

Reactions of the complexes cis-$[PtCl_2(RNC)(PR'_3)]$ with ethanol. The complexes *cis*-$[PtCl_2(RNC)(PR'_3)]$, prepared by published methods[1] and carefully purified before use were heated in dry, distilled ethanol under reflux and the progress of the reaction was monitored at intervals by taking aliquots from the solution, removing solvent and measuring the ir. spectrum of the resulting solid. Reaction was adjudged complete when no (N≡C) stretching band could be observed.

Preparation of cis-$[MCl_2\{C(OEt)(NHp\text{-}NO_2C_6H_4)\}_2]$ (M = Pt or Pd). The compounds *cis*-$[MCl_2(p\text{-}NO_2C_6H_4NC)_2]$ or $[M(p\text{-}NO_2PhNC)_4][MCl_4]$ (M = Pt or Pd) (2 g) were heated in ethanol (50 ml) at 60° for 12 h. The resultant brown solid was dissolved in hot chloroform (100 ml) and the solution treated with charcoal then filtered. After concentrating the solution *in vacuo* the white *product* was precipitated with ether (Yield 0.68 g).

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