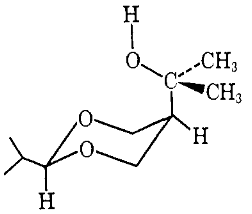
formation, which is stabilized by *inter*molecular hydrogen bonding in concentrated solution, to the predominantly "OH-inside" conformation, more stable on steric grounds, in dilute solution where association plays no part.[8]

That **1c** exists largely with the OH over the ring and yet forms an intramolecular hydrogen bond only to a slight extent must mean that the predominant conformation in dilute solution is **3** rather than **4**. Since $\Delta\bar{\nu}$ is 51–68 cm^{-1} (depending on the choice of reference for free OH; see Table I), pointing to a moderately strong hydrogen bond,[1b] there must be a strong opposing force to keep the population of the hydrogen-bonded conformation so low. We see this force in a combination of eclipsing and dipolar interactions: in **4** there is both H–O–C_α–C_5 and partial O–C_α–C_5–C_4, Me–C_α–C_5–C_4, and Me–C_α–C_5–H eclipsing, as well as a repulsion of the near-parallel dipoles of C_α–O–H and of the ring oxygen which is *not* hydrogen bonded.



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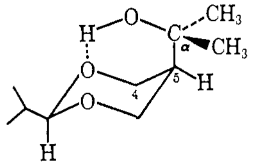

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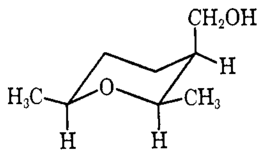
In order to sort out the two factors, we synthesized[9] 3-hydroxymethyltetrahydropyran (**5**) and its *r*-2,*cis*-**6**-dimethyl homologs (**6, 7**). In these compounds, dipolar factors are absent, since there is only one ring oxygen which would be involved in the intramolecular hydrogen bond, if any; eclipsing factors, however, are similar to those in **1a**. Compound **5** did not display an intramolecular hydrogen bond; this may well be due to its being very predominantly in the equatorial conformation (analogous to **7**, minus the Me groups). There was, however, a clear indication of a strong intramolecular hydrogen bond in **6** (Table I). The difference between **6** and **1a** supports the hypothesis that unfavorable dipole interactions do inhibit hydrogen bonding in **1a**.[10]

Nevertheless we believe that eclipsing forces make a strong contribution to the absence of hydrogen bonding in **1a**, **1b**, and **5** and its weakness in **1c**. Three lines of evidence lead to this conclusion. First, the axial



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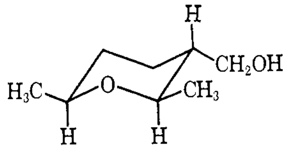

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conformation of **5** should be destabilized *vis-à-vis* the equatorial by *less* than 1.65 kcal/mol, the corresponding value in cyclohexylcarbinol,[11] even in the absence of hydrogen bonding. The hydrogen bond should overcome this energy disadvantage sufficiently to produce a palpable amount of the bonded conformation, unless there are other factors interfering with the hydrogen bond. Secondly, it has been calculated[3a,10] that dipolar factors alone do not suffice to explain the complete absence of bonding in **1a** and **1b**. Thirdly, and most significantly, the intensity ratio of the bonded and unbonded OH stretching frequencies in **6**, *ca.* 1:1, is nearly the same as in the acyclic analog 3-methoxypropanol (**8**), $CH_3OCH_2CH_2CH_2OH$.[12] Hydrogen-bond formation in **8** requires conformational "freezing" about the four bonds shown; in contrast, formation of an intramolecular hydrogen bond in **6** involves conformational rigidity about two bonds only (C_5–C_α and C_α–O). Thus, in the absence of opposing factors, **6** should show a much more populous hydrogen-bonded conformation than **8**. That this prediction is not borne out by experiment suggests bond eclipsing as a factor complicating hydrogen bonding in **6**. Model considerations show that **8**, in contrast, can form an intramolecular hydrogen bond in a nearly perfectly staggered, cyclohexane-like conformation.

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(8) The large observed shift is not just due to a change in magnetic anisotropy of the medium. That change may be gauged by the change in carbinol methyl shift in **2c** upon dilution (71.2 to 68.7 Hz) and a similar shift of about 3 Hz in the isopropyl methyl shift in both **1c** and **2c**.

(9) Reduction of 3-formyl-5,6-dihydro-2H-pyran (C. W. Smith, Ed., "Acrolein," Wiley, New York, N. Y., 1962, p 149) with lithium aluminum hydride followed by hydrogenation over Pt gave **5**, identical in ir and nmr spectra with an authentic sample (J. Falbe and F. Korte, *Chem. Ber.*, **97**, 1104 (1964)); Sadtler spectra 1074 (nmr) and 28058 (ir). Dimerization of crotonaldehyde (F. E. Bader, *Helv. Chim. Acta*, **28**, 225 (1953); A. Losse, *Chem. Ber.*, **100**, 1266 (1967)) followed by crystallization at −78° from pentane gave 2,6-dimethyl-3-formyl-5,6-dihydro-2H-pyran, presumed to be the *cis* isomer. $LiAlH_4$ reduction and hydrogenation over 5% Pd on charcoal gave a mixture of *ca.* 44% of **6** and 56% of **7** which was separated by preparative glpc.

(10) Professor Laszlo has kindly informed us (personal communication, April 9, 1970; see also ref 3a) that calculation of dipole interactions gives an amount of repulsive energy insufficient to account for the observed phenomena. Underestimation of intramolecular dipolar interactions by calculations based on Coulomb's law seems to be typical; for a similar situation with regard to the "rabbit-ear effect," see E. L. Eliel, *Kem. Tidskr.*, **81** (6/7), 22 (1969).

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Insertion Reactions Involving Isocyanide Ligands in Platinum Alkyl and Aryl Complexes

Sir:

We wish to report recent studies involving reactions of methyl isocyanide with platinum(II) alkyl and aryl compounds.

When 1 mol of methyl isocyanide is added to a slurry of *trans*-$[(C_6H_5)_3P]_2Pt(R)X$ [for (R)X = $(CH_3)I$, $(C_6H_5)Cl$, $(C_6H_5)Br$, or $(C_6H_5)I$] in benzene, an immediate change in color from white to yellow is observed. From these reactions a product is obtained which on crystallization at 25° gives white or pale yellow crystals of a 1:1 adduct $[(C_6H_5)_3P]_2Pt(R)X\cdot CNCH_3$. These compounds are soluble in chloroform and dichloromethane, but not soluble in hydrocarbon solvents. They can be formulated as five-coordinate platinum complexes, or, more likely, as the ionic four-coordinate platinum complexes, *trans*-$[(C_6H_5)_3P]_2Pt(CNCH_3)R^+X^-$.

Table I. Isocyanide Platinum(II) Complexes

Compound[a]	Yield, %	Mp, °C	$\nu(C\equiv N)$, cm^{-1}	$\nu(C=N)$, cm^{-1} [b]	Nmr data, ppm[c]
$[(C_6H_5)_3P]_2Pt(C_6H_5)I \cdot CH_3NC$	84	220–230[d]	2220		$Pt-C_6H_5$, 6.50; $Pt-CNCH_3$, 2.63 (J_{Pt-CH_3} = 12 Hz)
$[(C_6H_5)_3P]_2Pt[C(C_6H_5)=NCH_3]I$	35	236–238		1597 (sh), 1585	$Pt-C_6H_5$, 6.97; $Pt-C(=NCH_3)-$, 3.27 (J_{Pt-CH_3} = 14 Hz)
$[(C_6H_5)_3P]_2Pt(C_6H_5)Br \cdot CH_3NC$	90	235–237	2220		$Pt-C_6H_5$, 6.45; $Pt-CNCH_3$, 2.68 (J_{Pt-CH_3} = 12 Hz)
$[(C_6H_5)_3P]_2Pt[C(C_6H_5)=NCH_3]Br$	80	241–243		1597 (sh), 1585	$Pt-C(C_6H_5)=$, 6.97; $Pt-C(=NCH_3)-$, 3.20 (J_{Pt-CH_3} = 14 Hz)
$[(C_6H_5)_3P]_2Pt(C_6H_5)Cl \cdot CH_3NC$	87	234–236	2215		$Pt-C_6H_5$, 6.47; $Pt-CNCH_3$, 2.72 (J_{Pt-CH_3} = 12 Hz)
$[(C_6H_5)_3P]_2Pt[C(C_6H_5)=NCH_3]Cl$	86	240–242		1595 (sh), 1585	$Pt-C(C_6H_5)=$, 6.86; $Pt-C(=NCH_3)-$, 3.17 (J_{Pt-CH_3} = 14 Hz)
$[(C_6H_5)_3P]_2Pt(CH_3)I \cdot CH_3NC$	83	230–235[d]	2220		$Pt-CNCH_3$, 2.67[e]
$[(C_6H_5)_3P]_2Pt[C(CH_3)=NCH_3]I$	32	193–194		1620	$Pt-C(CH_3)=$, 1.47 (J_{Pt-CH_3} = 30 Hz); $Pt-C(=NCH_3)-$, 3.08 (J_{Pt-CH_3} = 13 Hz)
$[(C_6H_5)_3P](CH_3NC)Pt(C_6H_5)_2$	95	175–177 dec	2195		$Pt-CNCH_3$, 2.60 (J_{Pt-CH_3} = 12 Hz); $Pt-C_6H_5$ (trans P), 6.34; $Pt-C_6H_5$ (cis P), 6.90
$[(C_6H_5)_3P](CH_3NC)Pt(CH_3)_2$	93	159–161	2195		$Pt-CNCH_3$, 2.72 (J_{Pt-CH_3} = 12 Hz); $Pt-CH_3$ (trans P), 0.34 (J_{P-CH_3} = 18 Hz, J_{Pt-CH_3} = 70 Hz); $Pt-CH_3$ (cis P), 0.81 (J_{P-CH_3} = 15 Hz, J_{Pt-CH_3} = 73 Hz)
$[(C_6H_5)_3P]_2Pt[C(C_6H_5)=NCH_3]Br \cdot CH_3NC$	84	223–224	2225	1597 (sh), 1585	$Pt-CNCH_3$, 2.79 (J_{Pt-CH_3} = 11 Hz); $Pt-C(=NCH_3)-$, 3.13 (J_{Pt-CH_3} = 12 Hz); $Pt-C(C_6H_5)=$, 6.97
$[(C_6H_5)_3P]_2Pt(C_6F_5)Br \cdot CH_3NC$			2240		$Pt-CNCH_3$, 2.84 (J_{Pt-CH_3} = 12 Hz)
$[(C_6H_5)_3P]_2Pt(C_6F_5)CN$	83	305–308	2135		

[a] Satisfactory analyses have been obtained for all compounds. [b] As Nujol mulls. [c] In $CDCl_3$ solution with TMS internal standard. [d] These two compounds melted in the range 90–100° giving off a gas, resolidified near 120°, and then remelted as reported above. [e] No platinum coupling visible, as the spectrum of this compound was extremely broadened.

If suspensions of these complexes in benzene are refluxed for a short time a further reaction ensues, involving alkyl or aryl migration to the coordinated isocyanide; in good yield, the products $[(C_6H_5)_3P]_2Pt(CR=NCH_3)X$ are obtained. Interestingly, these products can then react with further methyl isocyanide to give 1:1 adducts, $[(C_6H_5)_3P]_2Pt(CR=NCH_3)X \cdot CH_3NC$.

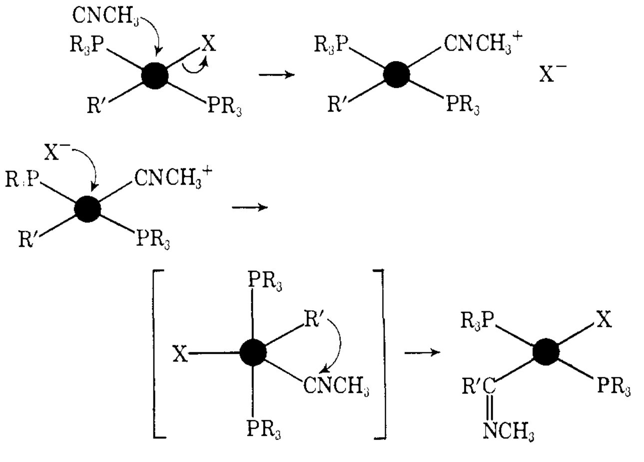

Figure 1. Proposed mechanism of isocyanide insertion into the platinum–carbon bond.

In contrast to the above reactions, the reaction of $[(C_6H_5)_3P]_2Pt(C_6F_5)Br$ and methyl isocyanide at 25° gave a very weak 1:1 adduct, which can be identified by infrared and nmr measurements, but which rapidly loses isocyanide as a solid or in solution. If this reaction is refluxed one obtains an unexpected product, $[(C_6H_5)_3P]_2Pt(C_6F_5)CN$. Failure to insert the isocyanide is in accord with the observation that insertions into metal–pentafluorophenyl or metal–perfluoroalkyl bonds are not known to occur.[1] This reaction, the dealkylation of alkyl isocyanides, is worthy of further consideration, however.

In the reaction of *cis*-$[(C_6H_5)_3P]_2PtR_2$ (R = CH_3, C_6H_5) the only product isolated is *cis*-$[(C_6H_5)_3P](CH_3NC)PtR_2$; there is no evidence that an intermediate 1:1 adduct occurs. We have not yet observed rearrangement of these complexes with alkyl or aryl migration, albeit under mild conditions.

Compounds and some of their appropriate data, are listed in Table I.

Apart from two recent reports[2,3] on insertion reactions of isocyanides into palladium–[2] and nickel–[2,3] alkyl bonds, such reactions have not been reported. These reactions are to be anticipated, however, as carbonyl insertion reactions are well known,[4] and since isocyanide and carbonyl ligand groups are in many ways analogous. The interesting carbonylation of $[(C_2H_5)_3P]_2Pt(CH_3)Cl$ to give $[(C_2H_5)_3P]_2Pt(COCH_3)Cl$ under somewhat more severe conditions (90°, 50 atm) is analogous to the reactions reported here.[5] However, unlike the previous work on isocyanide insertions[2,3] and also the carbonylation work,[5] it is possible to follow this reaction through an isolable intermediate, a 1:1 adduct of the square-planar organoplatinum com-

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plex and methyl isocyanide. This intermediate then rearranges on heating to the inserted product. The structure of the intermediate is open to some consideration. A five-coordinate complex, such as proposed in the carbonylation reaction,[5] is possible, since the starting platinum complex is formally coordinately unsaturated. The solubility in chloroform and the molecular weight values (osmometric in chloroform) are in accord with this. On the other hand, there are few known five-coordinate platinum(II) complexes, if one excludes those well-known complexes of polydentate phosphines and arsines, and no analogous complexes of the general formula $(phos)_2Pt(L)RX$ with other ligands. Failure to observe an intermediate, $[(C_6H_5)_3P]_2PtR_2 \cdot CNCH_3$, in the reaction of $[(C_6H_5)_3P]_2PtR_2$ and methyl isocyanide lends indirect support also. We feel that a more likely structure is an ionic complex, *trans*-$(R_3P)_2Pt(CNCH_3)R'^+X^-$.[6] Conductivity data in dichloromethane indicate their formulation as 1:1 electrolytes.[7] It is possible, of course, that solid-state and solution structures will be different, the latter depending also on the nature of the solvent. Additional work, including possibly a crystal structure determination, is needed to clarify this situation.

Assuming an ionic structure for this intermediate, one can then visualize the resultant rearrangement to proceed by halide ion attack at the metal, displacing the alkyl or aryl group to the coordinated isocyanide; perhaps *via* a five-coordinated intermediate (Figure 1).

In this work no evidence was obtained which suggested that aggregation of isocyanides to oligomeric or polymeric structures occurred even if excess isocyanide was present. Such reactions appeared rather favorable in the nickel isocyanide work.[3] We did observe, however, that a second isocyanide did react with the insertion product $[(C_6H_5)_3P]_2Pt(CR{=}NCH_3)Br$ to give $[(C_6H_5)_3P]_2Pt(CR{=}NCH_3)Br \cdot CH_3NC$, which could presumably be an early precursor to such oligomers.

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(6) The methyl groups bound to phosphorus in the analogous compound $[(C_6H_5)_2(CH_3)P]_2(C_6H_5)I \cdot MeNC$ are split into a triplet in the nmr, indicating a trans arrangement of the phosphines.

(7) At ~5 × 10^{-4} *M* concentrations, Λ_M [cm^2/(ohm mol)] (25°) is 54, 57, and 56 for $[(C_6H_5)_3P]_2Pt(CNCH_3)C_6H_5{}^+I^-$, $[(C_6H_5)_3P]_2Pt(CNCH_3)C_6H_5{}^+Cl^-$, and $[(C_6H_5)_3P]_2Pt(CNCH_3)CH_3{}^+I^-$. The Λ_M value for 5 × 10^{-4} *M* concentrations of $(C_4H_9)_4N^+I^-$ and $(C_2H_5)_4N^+ClO_4{}^-$ in dichloromethane is ~72 cm^2/(ohm mol).

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Characterization of Pentaaquomonoamminecobalt(III)

Sir:

The enormous decrease in reactivity brought about by replacing H_2O in $Co(H_2O)_6{}^{3+}$ completely by NH_3 is a matter of interest. A systematic study of the reactions of the entire series of the aquoammine complexes can be expected to help in understanding this particular problem in chemical reactivity. Such a study has, until now, not been possible because the ions at the aquo end of the series are poorly characterized. We have been investigating these ions, and in the course of this work have characterized the species $CoNH_3(H_2O)_5{}^{3+}$, which has not hitherto been described. This report deals with the preparation of this new species and with some of its properties.

The species $CoNH_3(H_2O)_5{}^{3+}$ was first encountered in separating, by means of a cation-exchange resin, the products obtained from treating "$KCo(NH_3)_2(CO_3)_2$"[1] with 1 *M* $HClO_4$. However, the yields of the new species obtained by this method proved to be small and erratic. A slight change in the procedure has led to success in the three preparative attempts which have been made with the modified procedure.

The method described by Mori, *et al.*, is followed up to the point at which ammonium carbonate is to be added to convert the carbonatocobalt(III) complex to a carbonatodiammine. Our modification consists in adding solid ammonium chloride instead of ammonium carbonate, 1 mol for each mole of cobalt. The product from this step is obtained in solid form by following the Mori procedure, and this solid is the starting material for the operations which are to be described.

The solid material (10 g) is dissolved in 100 ml of cold 1 *M* $HClO_4$. A solution of $Hg(ClO_4)_2$ is added until the color of the cobalt species changes from blue to violet (this step removes Cl^- from the Co(III) complex). The resulting solution is charged onto a column of Dowex 50X2 100–200 mesh cation-exchange resin, kept at 0°. The column is first eluted with cold 0.5 *M* $HClO_4$ to remove Hg(II) and Co(II) and then with cold 2 *M* $HClO_4$. At this stage a broad violet band moves down the column. From its ion-exchange behavior, and the chemistry of the treatment needed to convert it, we take the band to be comprised of a condensed form of the monoammine complex. The corresponding diammine species is eluted less rapidly and it would tend to concentrate in the trailing part of the band. Thus only the leading 80% or so of the violet band was collected.

Analyses for Co(III), Co(T) (total cobalt), and NH_3 were made on the violet solution eluted, with the results for three separate preparations being as follows: (1) 2.52 × 10^{-3}, 2.47 × 10^{-3}, 2.51 × 10^{-3} (2) 1.10 × 10^{-3}, 1.09 × 10^{-3}, 1.10 × 10^{-3} *M;* (3) 1.00 × 10^{-3}, 9.91 × 10^{-4}, 1.04 × 10^{-3} *M.*

The methods of analysis applied to the violet material and to the monoammine were as follows. For Co(III), the solution was added to excess Fe^{2+} and Fe^{2+} was titrated with $Cr_2O_7{}^{2-}$, using sodium diphenylaminesulfonate as indicator[2] (the monoammine, its precursor, and the diammine and its precursor all react rapidly enough with Fe^{2+} to make this method of analysis feasible). For Co(T), thiocyanate[3] was used to develop the color of Co^{2+} after decomposing the Co(III) with NaOH and then acidifying with HCl. For NH_3, am-

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