of about 5.5, rather than 7, because of reaction of Mg^{2+} with ATP releasing protons from the terminal phosphate group. The spectra compared by Epp, *et al.*, therefore, represented lyophilization products from a pH 7 ATP solution and a pH 5.5 Mg^{2+}–ATP solution. In fact, their Mg^{2+}–ATP spectrum is very similar to our pH 5.3 Mg^{2+}–ATP spectrum.

Since titration curves show that the adenine moiety in an Na_2ATP solution is completely deprotonated at just about pH 5.5, one might suppose that comparison of their two spectra is still valid with respect to the point under discussion. This would be true for aqueous solution spectra but not for spectra of their lyophilization products. The effective pH near the adenine moiety and its pK undoubtedly change significantly during the freeze-drying process because of temperature and ionic strength changes, as shown by the fact that there is a weak 1695 cm.$^{-1}$ band even in our pH 5.9 ATP spectrum.

Our results are not at all in disagreement with those of Khalil and Brown. Solid-state spectra, such as ours, can suggest reaction of Mg^{2+} with the ATP adenine moiety even if such reaction does not occur in solution. The act of freeze-drying itself probably forces the Mg^{2+} ion in the dry powder to lie so close to an adenine moiety (not necessarily in the same molecule as the phosphate to which the Mg^{2+} binds) that the Mg^{2+} has an even greater electrostatic effect on the adenine moiety than in solution. Thus, in the crystal the Mg^{2+} charge produces an increase in the intensity of the 1695 cm.$^{-1}$ vibration (as suggested by Epp, *et al.*) which, though small, is larger than the intensity decrease (obtained in D_2O by Khalil and Brown) resulting from increased ionization of the adenine proton. The over-all effect, however, is considerably less than that reported by Epp, *et al.*, and seems much too small to be considered as indication of actual coordination of Mg^{2+} by the adenine moiety.

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## Structure of Some Platinum– and Palladium–Carbon σ-Bonded Complexes

Sir:

Some unusual complexes of dicyclopentadiene with platinum(II) or palladium(II) have been formulated by Chatt[1] as chloro-bridged dimers (2a) containing both a platinum(II)– or palladium(II)–carbon σ-bond and a π-coordinate bond from the remaining olefin ligand to the metal. The usually labile σ-bonded platinum(II) or palladium(II) complexes gain their stability from the olefin ligand, which affords large crystal field splitting.[2]

The reaction of dicyclopentadienedichloroplatinum or -palladium (1, M = Pt or Pd) with methanol,[1] or the direct reaction of dicyclopentadiene with sodium chloroplatinate or palladate in methanol,[3] produces the σ-bonded complex 2a. Although the type of metal–ligand linkage was described by Chatt,[2] and some of the many structural problems surrounding the isomerism in the organic ligand have been recognized,[4] the stereoisomerism associated with the organic moiety has not been established.
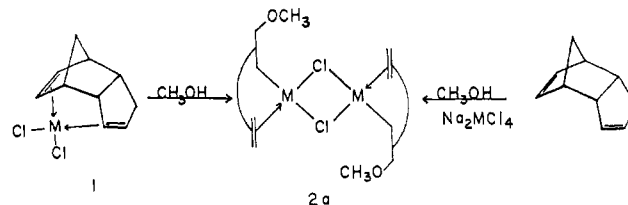
The two unequivalent double bonds in dicyclopentadiene present two different sites for the methoxy metalation. Moreover, the addition may occur *cis*, with the addends either *endo* or *exo*, or the reaction may proceed by a *trans* addition, with the metal either *exo* or *endo*. The relationship of the remaining double bond to the addends (*i.e.*, whether the remaining double bond is positioned closer to the metal or methoxy addend) doubles the number of possible isomers. Finally, rearrangement often occurs in ionic additions to *endo*-dicyclopentadiene to provide products containing the *exo*-dicyclopentadiene skeleton.[5] The 5,6-double bond (norbornene bond) is known to be much more reactive than the 2,3-double bond with respect to ionic additions. Thus, if only oxymetalation of the 5,6-double bond is considered, there are sixteen *dl*-pairs possible for an individual organic portion only.

This addition is somewhat analogous to the oxymercuration reaction of dicyclopentadiene in which *cis–exo* addition takes place at the 5,6-double bond without rearrangement.[6,7] Complexation with an *exo*-platinum or -palladium, however, would not be expected since intramolecular coordination with the remaining double bond would be impossible.

We have now established the structure of the organic ligand and the configuration associated with its bonding to the metal accordingly. Reduction of the complex 2 (M = Pt or Pd) by hydrogen or with sodium borohydride afforded only octahydro-*exo*-5-methoxy-4,7-*endo*-methanoindene (3), as established by comparison with an authentic sample.[7] Thus, the position on the ring and the *exo* arrangement of the methoxy group in the complex (2b) was established, but this provides no information as to the configuration of the metal, *exo* or *endo*.

The complexes 2b were too insoluble in solvents which would not react with them, so that suitable n.m.r. spectra could not be obtained. The *endo* position of the metal was confirmed by the n.m.r. spectrum of its

(1) J. Chatt, L. M. Vallarino, and L. M. Venanzi, *J. Chem. Soc.*, 2496, 3413 (1957).

(2) (a) J. Chatt and B. L. Shaw, *ibid.*, 705, 4020 (1959); (b) G. Calvin and G. E. Coats, *ibid.*, 2008 (1960); (c) J. R. Doyle, J. H. Hutchinson, N. C. Baenziger, and L. W. Tresselt, *J. Am. Chem. Soc.*, 83, 2768

(1961); (d) C. R. Kistner, J. H. Hutchinson, J. R. Doyle, and J. C. Storlie, *Inorg. Chem.*, 2, 1255 (1963).

(3) K. A. Hoffman and J. V. Narbutt, *Ber.*, 41, 1625 (1908).

(4) R. B. King, *Inorg. Chem.*, 2, 528 (1963).

(5) See, for example, S. J. Cristol, W. K. Seifert, D. W. Johnson, and J. B. Juvale, *J. Am. Chem. Soc.*, 84, 3918 (1962); S. J. Cristol, L. K. Gaston, and D. W. Johnson, *Tetrahedron Letters*, 185 (1963), and references therein.

(6) T. G. Traylor and A. W. Baker, *J. Am. Chem. Soc.*, 85, 2746 (1963).

(7) J. K. Stille and S. C. Stinson, *Tetrahedron*, 1387 (1964).

pyridine derivative **4** (M = Pt or Pd). Reaction of **2b** with pyridine under conditions employed for the formation of the corresponding toluidine derivatives[1] produced **4**.[8] Chloro-bridged dimers such as **2** are readily split by amines, without alteration of the remainder of the complex, to give derivatives of this type.[1] The important signal in the n.m.r. spectrum was a poorly resolved doublet at τ 6.25, which may be assigned to the proton, H_X, on the carbon bearing the methoxy group. The observed coupling constant, $J_{AX} = 2$ c.p.s. (width at half-height = 3 c.p.s.), is that expected for a 120° dihedral angle[9] and is consistent with the coupling, $J_{AX'}$ exhibited by the saturated ether **3**. The coupling constant J_{BX} for **3** is 6.8 c.p.s.[7]
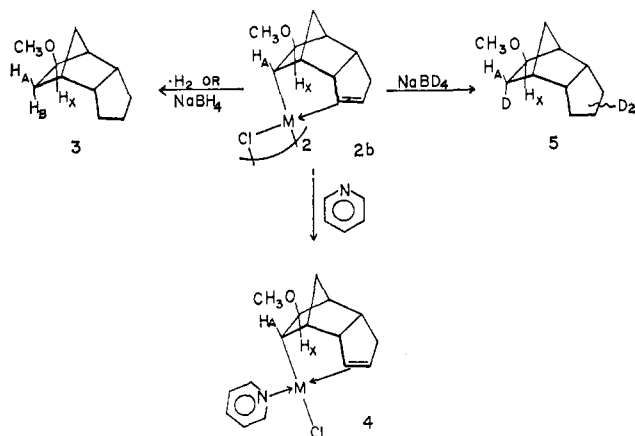
Reduction of **2** (M = Pt or Pd) with sodium borodeuteride provided the saturated deuterated methyl ether **5** by a stereospecific *cis* replacement of platinum with deuterium. The *endo* configuration of the deuterium was determined by the H_X doublet at τ 6.55, $J_{AX} = 2.3$ c.p.s.

The position of the 2,3-double bond in relation to the methoxy or metal point of attachment has not been determined by this sequence, but models show that a double bond on the metal side of the molecule affords the best angle and distance for efficacious coordination. Complex **2** has therefore been pictured as such.

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(8) Satisfactory analytical data have been obtained for all compounds described herein.

(9) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).

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1,4-Dihydropyridine

Sir:

Several N-alkyl- and N-aryl-substituted dihydropyridines are known, but none of the five isomeric unsubstituted dihydropyridines has ever been reported.[1-3] We wish to report the preparation of 1,4-dihydropyridine.

(1) F. Bohlman, *Chem. Ber.*, **85**, 390 (1952).

(2) R. A. Barnes in "Pyridine and Derivatives," Vol. I., E. Klingsberg, Ed., Interscience Publishers Inc., New York, N. Y., 1960, p. 77.

1-Trimethylsilyl-1,4-dihydropyridine[4,5] [I, b.p. 57° (6.7 mm.), n^{25} 1.4389, d^{25} 0.89, mol. wt. 153 (mass spectroscopy] on treatment with methanol yielded methoxytrimethylsilane and 1,4-dihydropyridine.
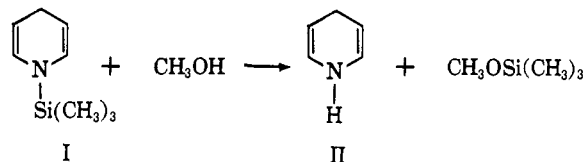
Five milliliters of I was treated with 1.25 ml. of methanol containing 0.1% KOH, and the product was immediately separated into fractions by vacuum transfer at −20 to 30°. The distillate was collected in liquid-nitrogen-cooled traps, approximately 3 cc. of methoxytrimethylsilane, 0.2 cc. of methanol (excess), 0.1 cc. of hexamethyldisiloxane, 0.1 cc. of pyridine, and 0.5 cc. of 1,4-dihydropyridine (II) being collected. A solid residue of approximately 2 cc. was not distillable. The dihydropyridine was a colorless slightly viscous liquid which v.p.c. analysis showed to contain about 5% impurities, mainly methanol and pyridine. None of the dihydropyridine passed through the v.p.c. column. A 20% solution in deuteriobenzene was used for infrared and n.m.r. spectra and a cyclohexane solution was used for ultraviolet spectra. In these solutions, when excluded from air, the dihydropyridine was stable for several days but the neat material solidified and turned orange in a few minutes to hours at room temperature. A second preparation, half the size of the first and made in ethyl ether, reacted in a manner identical with the first preparation and furnished material for C, H, and N analyses.[6] Efforts to measure the refractive index and boiling point of the material were unsuccessful due to its rapid solidification.

The ultraviolet and infrared spectra were in good agreement with those of other dihydropyridines.[3] Compound I has an ultraviolet maximum at 288 mμ (ϵ 1309) and compound II has a maximum at 278 mμ (ϵ 2500). The principal infrared absorptions were (in cm.$^{-1}$) at 3060 (=CH), 2965 (CH₃), 2820 (CH₂), and 1675 (C=C); for II (in C₆D₆) the absorptions were at 3450 (NH), 3060, 2820, and 1680.

The proton magnetic spectra of I and II were recorded with a Varian A-60 spectrometer. Measurements were made on solutions containing 10–15% of the compounds in deuteriobenzene. Shifts were measured relative to the residual protons of deuteriobenzene. These have been converted to shifts relative to tetramethylsilane by noting that the residual protons of deuteriobenzene appear 429 c.p.s. (δ = 7.15 p.p.m.) downfield from tetramethylsilane. The results are summarized in Table I, together with data reported for three closely related compounds.

The spin–spin splitting patterns of the protons of I agree with those reported for the analogous protons of compound IV. The spin–spin splitting patterns of the protons of II indicate strong coupling between the N–H

(3) E. M. Kosower and T. S. Sorensen, *J. Org. Chem.*, **27**, 3764 (1962).

(4) Formed by the palladium-catalyzed addition of trimethylsilane to pyridine. Details of the preparation and further reactions of this compound and related isomers will appear in a future paper.

(5) *Anal.* Calcd. for C₈H₁₅NSi: C, 62.8; H, 9.8; N, 9.15; Si, 18.2. Found: C, 62.8; H, 9.8; N, 9.1; Si, 18.1.

(6) *Anal.* Calcd. for C₅H₇N: C, 74.1; H, 8.6; N, 17.3. Found: C, 73.3; H, 8.4; N, 16.7.