lyzing the compound in vacuum. To confirm the origin of this ligand, the complex was synthesized as above except using ^{14}C-ethylene glycol as solvent. The product, processed as described previously,[2] was found to contain 1.06 ^{14}C per formula weight of the compound.

On treatment with dry HCl in ether, $[Ir^{I}Cl(CO)(Ph_3P)_2]$ is rapidly and quantitatively converted to $[Ir^{III}HCl_2(CO)(Ph_3P)_2]$. (*Anal.* Calcd. for $IrCl_2P_2C_{37}H_{31}O$: Ir, 23.5; Cl, 8.7; P, 7.6; C, 54.4; H, 3.8; O, 2.0. Found: Ir, 23.1; Cl, 8.5; P, 7.6; C, 54.7; H, 4.7; O, 2.4.) $[IrBr(CO)(Ph_3P)_2]$ (prepared as described for the chloride) behaves similarly with HBr. An analogous reaction, with $[PtHCl(Et_3P)_2]$, has been mentioned before,[3] but the product was unstable and not sufficiently characterized. This noteworthy reaction is being tested on other (low valent) transition metal complexes with the view to synthesizing new types of hydrides, including paramagnetic ones.

$[IrHCl_2(CO)(Ph_3P)_2]$ was detected (but not obtained pure) in some of the experiments leading to $[IrCl(CO)(Ph_3P)_2]$, notably when the reactants were refluxed in diethylene or triethylene glycols for longer periods than indicated above. With triphenylarsine, on the other hand, the corresponding compound (Table I) was obtained by heating the reactants in ethylene glycol to 170°.

According to their X-ray diffraction patterns, the carbonyl hydrides (Table I) are isomorphous with each other. The same is true for $[IrX(CO)(Ph_3P)_2]$ which are isomorphous also with $[RhCl(CO)(Ph_3P)_2]$.[4,5] For the latter, a *trans* configuration has been suggested on the basis of dipole moment, 3.15 *D*.[4] Preliminary measurements on $[IrCl(CO)(Ph_3P)_2]$ gave $\mu = 3.9$ *D*, which, altogether, indicates *trans* structures for the iridium compounds.

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NYSTATIN. II. THE STEREOCHEMISTRY OF MYCOSAMINE[1]

Sir:

Mycosamine, the amino-sugar moiety obtained by the hydrolysis of several of the polyene antifungal antibiotics including nystatin,[2] amphotericin B[2] and pimaricin,[3] has been shown to be a 3-amino-3,6-dideoxy-D-aldohexose.[1] Degradative studies as well as the preparation of certain new derivatives[4] have indicated that the stereochemistry of mycosamine is that of D-mannose. Confirmatory evidence for this configurational assignment has now been obtained by the following synthesis of mycosamine derivatives.

Methyl 3-amino-3-deoxy-α-D-mannopyranoside was synthesized from glucose by the ingenious method of Baer and Fischer[5] and converted with acetic anhydride in methanol to methyl 3-acetamido-3-deoxy-α-D-mannopyranoside (I, m.p. 242.5–243.5°, $[\alpha]^{23}D$ +17° (*c*, 1.1 in water); calcd. for $C_9H_{17}O_6N$: C, 45.95; H, 7.29; N, 5.95; OCH_3, 13.19. Found: C, 45.94; H, 7.22; N, 5.93; OCH_3, 13.48). Tosylation of the primary hydroxyl group at C_6 with 1.1 equivalents of tosyl chloride in pyridine and subsequent acetylation with acetic anhydride yielded an amorphous product which was converted in good yield, by heating with sodium iodide in acetone, to the crystalline methyl 2,4-diacetyl-3-acetamido-6-iodo-3,6-dideoxy-α-D-mannopyranoside (II, m.p. 196.5–197.5°, $[\alpha]^{22}D$ +22° (*c*, 1.0 in ethanol); calcd. for $C_{13}H_{20}O_7NI$: C, 36.38; H, 4.70; N, 3.26; I, 29.57; OCH_3, 7.23. Found: C, 36.18; H, 4.82; N, 3.28; I, 29.59; OCH_3, 7.40).

Reductive dehalogenation of II with hydrogen and Raney nickel yielded methyl 2,4-diacetyl-3-acetamido-3,6-dideoxy-α-D-mannopyranoside (III, m.p. 139–141°, $[\alpha]^{23}D$ +31 ± 2° (*c* 1.0 in ethanol): calcd. for $C_{13}H_{21}O_7N$: C, 51.48; H, 6.98; N, 4.62; OCH_3, 10.23. Found: C, 51.42; H, 6.79; N, 4.32; OCH_3, 10.36).

The properties of this compound, including the infrared spectrum, proved to be identical with those of methyl 2,4,N-triacetylmycosaminide (m.p. 140–141°, $[\alpha]^{23}D$ +33 ± 2° (*c*, 1.0 in ethanol); calcd. for $C_{13}H_{21}O_7N$: C, 51.48; H, 6.98; N, 4.62; OCH_3, 10.23. Found: C, 51.32; H, 6.86; N, 4.46; OCH_3, 10.44) prepared from the known methyl-N-acetylmycosaminide[1] by acetylation with acetic anhydride in pyridine.

O-Deacetylation of synthetic III with sodium methoxide in methanol afforded methyl 3-acetamido-3,6-dideoxy-α-D-mannopyranoside (m.p. 168–170°, $[\alpha]^{23}D$ +45 ±2° (*c*, 1.1 in ethanol); calcd. for $C_9H_{17}O_5N$: OCH_3, 14.15. Found: OCH_3, 14.51) identical in every respect with methyl-N-acetylmycosaminide (m.p. 168–170°, $[\alpha]^{23}D$ +47° (*c*, 0.9 in ethanol) prepared from mycosamine.[1]

In view of the incontestable evidence adduced by Baer and Fischer[5] for the stereochemistry of their synthetic product, and of the unequivocal nature of the above conversion to the 6-deoxy product, the assignment of the D-mannose configuration to mycosamine is secure. The synthetic route also furnishes proof that the methyl mycosaminide derivatives are the α-anomers. It furthermore follows that the 2-acetamido-2,5-dideoxypentose obtained from N-acetyl-mycosamine by periodate oxidation[1] is 2-acetamido-2,5-dideoxy-D-arabinose.

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