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On the Isolation of Trimethylphosphine as a Silver Iodide Complex

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According to Mann and Wells,[1] trimethylphosphine is most conveniently isolated as its silver iodide complex. No analysis or yield was given in their paper, but the white complex obtained was assumed to be $[(AgIMe_3P)_4]$ by analogy with the known complexes with higher aliphatic tertiary phosphines.[2] In a recent paper, however, Evans, Goggin, Goodfellow and Smith [3] reported that they were not able to obtain any compound with a 1:1 silver iodide to trimethylphosphine ratio using the method of Mann and Wells. The compound which they obtained showed variable composition approximating a silver iodide to trimethylphosphine ratio of 1:0.3. Their results prompt us to report here of our findings using the method of Mann and Wells for the isolation of trimethylphosphine.

The details of the synthesis of trimethylphosphine and of the silver iodide complex used in our laboratory are given in a previous paper.[4] When the crude silver iodide complex is washed with saturated aqueous potassium iodide and then water and finally dried *in vacuo* over $CaCl_2$, the pure 1:1 complex is obtained. Analyses, melting points and yields of three independent preparations are listed in Table 1. Thus the claim of Evans *et al.*[3] that "it does not seem possible to produce the stoichiometric $[AgIPMe_3]$ in this way" cannot be substantiated.

The problem concerning the value of n in $[(AgIMe_3P)_n]$ rests to be solved. As

Table 1. Analyses, melting points, and yields of trimethylphosphine silver iodide.

	Analyses C	H	I	m.p.,°C[a]	Yield, %[b]
Calc. for C_3H_9AgIP	11.59	2.92	40.83		
prep. I	11.52	3.00	41.00	137–140	44
prep. II	11.51	2.80	40.94	140–142	40
prep. III	11.42	2.73	41.14	133–142	30

[a] In closed capillary tubes. [b] Based on PCl_3.

Table 2. Molecular weight of trimethylphosphine silver iodide.

Weight of compound, g	Weight of benzene, g	ΔT	Molecular weight, found	Calc. for $[(AgIMe_3P)_4]$
0.2424	18.62	0.051	1310	1243.6
0.2247	17.11	0.053	1260	

shown by Jensen and Dahl,[5] trimethylphosphine forms Ni(II) complexes which differ in composition from those formed by triethylphosphine and higher aliphatic phosphines. *A priori*, therefore, the same structures for the trimethylphosphine and the triethylphosphine silver iodide complexes can not be assumed. The molecular weight of the trimethylphosphine complex was determined cryoscopically in benzene. The agreement between the measured molecular weight (Table 2) and the calculated molecular weight for a tetrameric compound is satisfactory, as the uncertainty in the measured values is approximately 10 % because of the rather low solubility in benzene. Several other solvents (acetophenone, bromoform, ethylene bromide) were tried, but in cases where the compound was more soluble than in benzene, extensive decomposition or dissociation occurred.

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Note on the Crystal Structure of $Cu(N_3)_2$

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Recently the crystal structure of $Cu(N_3)_2$ has been determined,[1,2] by means of single crystal X-ray methods. The structure can be visualized as being built up of almost planar chain molecules, running parallel to the *b*-axis. These chains are coupled to form double chains, which in their turn are joined together by azide groups lying in planes perpendicular to the *b*-axis. Although the two investigations gave identical pictures of the structure within the limits of experimental error, we thought it worth while to combine the intensity data from both determinations and to refine the structure further, in the hopes that still more accurate atomic parameters might be obtained.

In order to be able to compare the two sets of data, they were first refined separately on the same computer. The magnitudes of the temperature factors computed were, however, found to differ for the two reflexion materials, which meant that there were discrepancies especially between reflexions with high sin θ-values. In order to make the two sets of data comparable, the ratio between the structure factors for the same reflexion in the two reflexion materials was plotted as a function of sin θ/λ. This plot was used to obtain the reflexions which were present in only one of the two reflexion materials on the same basis as the average value of the observed structure factors for the reflexions present in both sets of data. The reflexions which were present in only one reflexion material (R.S.) were among the weakest ones.

The final refinement, based on the combined reflexion material, was performed in two different ways:

A. All reflexions were given equal weight and the refinement was based on 408 observed independent reflexions. The *R*-value obtained was 0.062 and the standard deviations were a little lower than for the original sets of data.

B. The average values of the reflexions observed in both reflexion materials were given double weight compared with those observed in only one of the reflexion materials. This was achieved by giving the computer the average values twice and the single values once. The *R*-value thus obtained was 0.055.

In both cases all atoms were refined anisotropically. There was no statistical difference between the atomic positions determined by the two different methods, although method B might be supposed to yield the more accurate parameters. The results given in the tables are therefore those of method B. Since the standard deviations must, however, be based on the independent reflexions, the values of the