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TRICARBONYLNICKEL COMPLEXES OF TETRAARSENIC AND TETRAPHOSPHORUS HEXAMETHYLIMIDES

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This is a report of the preparation and some of the properties of the complexes formed in the reaction of nickel tetracarbonyl with the bird-cage molecule, tetraarsenic hexamethylimide[1], $As_4(NCH_3)_6$, and with its phosphorus analog[2], $P_4(NCH_3)_6$. This investigation was inspired by a preceding study[3,4] which showed that phosphorus trioxide, P_4O_6—another tetrahedral bird-cage molecule—behaves as a nonchelating tetradentate ligand in its reactions with transition-metal carbonyls.

EXPERIMENTAL

General

$As_4(NCH_3)_6$ and $P_4(NCH_3)_6$ were prepared according to the respective procedures[1,2] given by their discoverers. Nickel tetracarbonyl was purchased from the Mathieson Company. All handling and mixing of reagents were carried out in a dry box flushed with carefully dried nitrogen; and the evolution of carbon monoxide was measured with a burette-type gasometer.

The ^{31}P and ^{1}H nuclear-magnetic-resonance (NMR) measurements were carried out at 40.5 and 60.0 Mc on Varian HR 100 and A56–60 spectrometers, with the chemical shifts being referenced with respect to 85% phosphoric acid and tetramethylsilane, respectively. Temperature measurements were made on the A56–60 unit which becomes unreliable below −40°. The infrared spectra were measured on KBr pellets with a Beckman IR-4 spectrometer.

As,As′,As″,As‴-Tetrakis(tricarbonylnickel)tetraarsenic hexamethylimide

Finely ground tetraarsenic hexamethylimide (5.99 g, 12.6 mmoles) was treated with an excess of nickel tetracarbonyl (15 g, 88 mmoles) without a solvent at 25°. Gentle evolution of carbon monoxide accompanied the dissolution of the arsenic compound. The rate of the reaction was observed to diminish after about a half hour, at which time the mixture is entirely liquid, and to accelerate again when crystals of the product began to precipitate. After 3 h, the product was repeatedly crushed and washed three times, each time with 10 ml of cold dry pentane, giving a yield of 12.8 g (97%).

The resulting compound, $As_4(NCH_3)_6 \cdot 4\,Ni(CO)_3$, is insoluble in the common solvents. The originally clear crystals exhibit a greenish-gray color upon standing at room temperature and decompose rapidly when heated at temperatures around 130° to give a nickel mirror on the container walls. (Found: C, 19.42; H, 1.92;

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N, 8.07; Ni, 21.11. $C_{18}H_{18}As_4N_6Ni_4O_{12}$ calcd.: C, 20.69; H, 1.74; N, 8.04; Ni, 22.48%.)

P,P',P'',P'''-Tetrakis(tricarbonylnickel)tetraphosphorus hexamethylimide

A 1.0 g portion (5 mmoles of nickel tetracarbonyl was added to a solution of 307 mg (1.03 mmoles) of tetraphosphorus hexamethylimide in 0.5 ml chloroform. Upon completion of CO evolution (*i.e. ca.* 5 min at 22°), the insoluble reaction product was crushed and washed three times, each time with 10 ml of cold dry pentane, to give a yield of 840 mg (97%).(Found: C, 24.54; H, 2.38; N, 9.78; Ni, 25.60; P, 14.86. $C_{18}H_{18}N_6Ni_4O_{12}P_4$ calcd.: C, 24.88; H, 2.09; N, 9.67; Ni, 27.02; P, 14.25%.)

RESULTS AND INTERPRETATION

Reaction of the arsenic compound

At room temperature, tetraarsenic hexamethylimide is found to react smoothly with nickel tetracarbonyl, either without solvent or in dry benzene or chloroform solution. When four moles or more of $Ni(CO)_4$ per mole of $As_4(NCH_3)_6$ are present, four equivalents of carbon monoxide are produced as expected, and an insoluble crystalline white product is formed. As shown in Fig. 1, the rate of the reaction slows down when *ca.* 2 moles of CO is evolved per $As_4(NCH_3)_6$. However, this is followed by an increase in rate concomitant with the initial observation of precipitation. The reaction again slows down and comes to a standstill when the CO evolution approaches 4 moles per $As_4(NCH_3)_6$. The first part of the curves of the type of Fig. 1 are reproducible but the time before the second hump appears is quite variable as would be expected for a phenomenon linked to the formation of the precipitate.

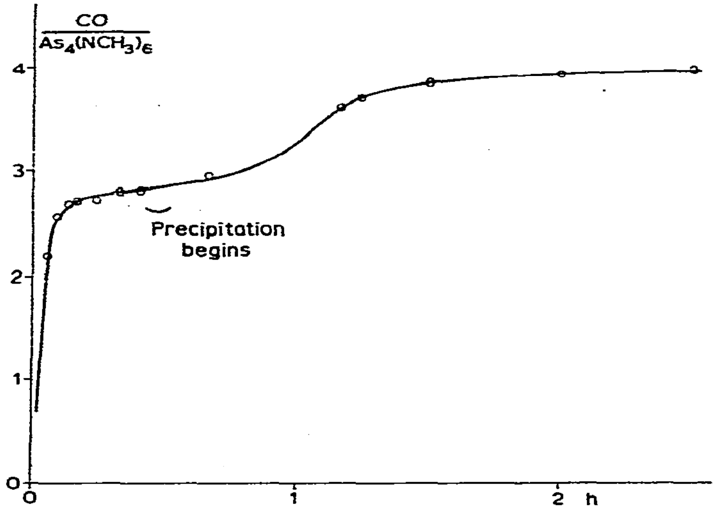

Fig. 1. Rate of evolution of carbon monoxide with time when tetraarsenic hexamethylimide is reacted with eight equivalents of nickel tetracarbonyl without a solvent at 25°.

The ^1H spectra of the methylimido group, as measured on various reaction mixtures, show fine structure only when the samples are cooled below the normal probe temperature of 38°, as shown in Fig. 2. These spectra indicate that the molecules rapidly exchange parts either inter- or intramolecularly and such data have been used to obtain an optimum temperature at which to make NMR observations which will lead to the greatest amount of structural information. This temperature was found to

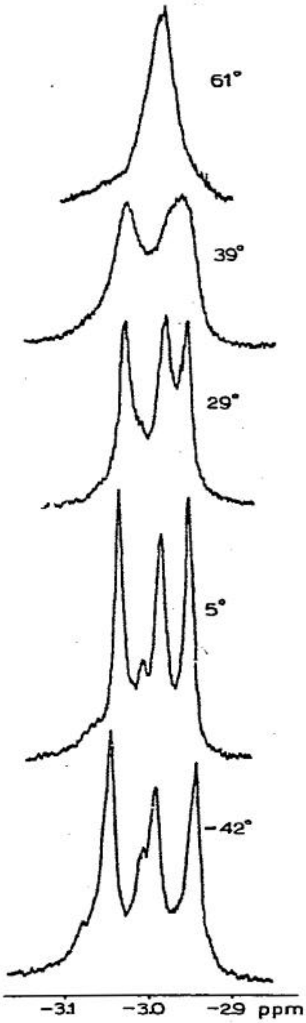

Fig. 2. Proton NMR patterns at various temperatures of a chloroform solution of $As_4(NCH_3)_6 \cdot jNi(CO)_3$ complexes, with the solution being one molar in total $As_4(NCH_3)_6$ and an $Ni(CO)_3/As_4N(CH_3)_6$ mole ratio of *ca.* 0.83.

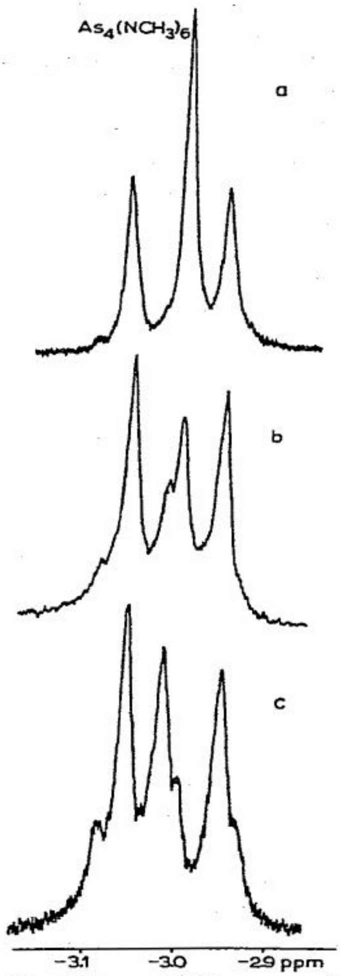

Fig. 3. Proton NMR spectra obtained at −40° on chloroform solutions of $As_4(NCH_3)_6 \cdot jNi(CO)_3$ where the solution is one molar in total $As_4(NCH_3)_6$ and there are increasing amounts of nickel carbonyl. Spectra a, b, and c correspond respectively to $Ni(CO)_3/As_4(NCH_3)_6$ mole ratios of *ca.* 0.69, 0.83, and 1.4, as calculated from the amount of reagents used or from the carbon-monoxide evolution. Values of 0.61, 0.85, and 1.3, respectively, were estimated from the relative peak areas in the NMR spectra.

be *ca.* −40°, with line broadening being observed at both higher and lower temperatures. In Fig. 3, ^1H spectra obtained at −40° are presented for a series of reagent mixtures having increasing amounts of nickel tetracarbonyl with respect to the tetraarsenic hexamethylimide. Analysis of the spectra of Fig. 3 shows the successive maximization of a doublet exhibiting a 1:1 peak-area ratio, followed by a triplet pattern with a 1:4:1 peak-area ratio, while the original resonance due to uncoordinated $As_4(NCH_3)_6$ is seen to decrease continuously.

These observations are compatible with a stepwise coordination of one and then two tricarbonylnickel groups on the arsenic atoms of the bird-cage molecule, resulting in differentiation of the methylimido groups. With the coordination of one tricarbonylnickel group, three methylimido groups must bridge between a nickel-substituted and an uncoordinated arsenic in the tetrahedral bird cage; whereas, the remaining three link pairs of uncoordinated arsenic atoms—thus leading to the 1:1 doublet. When two tricarbonylnickel groups are coordinated by the molecule, there is one methylimido bridge connecting the pair of uncoordinated arsenic atoms, while four such bridges link a coordinated with an uncoordinated arsenic and the remaining bridge links the pair of uncoordinated arsenic atoms—thus the 1:4:1 triplet. Coordination of tricarbonylnickel groups by the nitrogen atoms or, alternatively, a breaking up of the cage structure would result in larger shift changes for the methyl groups bonded to the nitrogen atoms, as well as different peak-area ratios. When the reagent mixture contains more nickel tetracarbonyl than corresponds to spectrum c of Figure 3, precipitation results and makes it more difficult to obtain clean NMR spectra.

The NMR patterns presented in Fig. 2 show the temperature variation for a given composition. Similar effects were seen for other compositions. The splitting and subsequent sharpening of the spectra when going from 61 to −40° is attributed to a fast redistribution of tricarbonylnickel groups around the $As_4(NCH_3)_6$ central core(s). The broadening of the individual resonances observed below −40° may be due to the well-known viscosity effect or alternatively to the "freezing" of individual conformations. At room temperature, the average lifetime of the individual species with respect to exchange as determined from the NMR spectra[5], was found to be *ca.* 0.2 sec in a $1M$ chloroform solution. For $j=0$ to 4 in the general formula $As_4(NCH_3)_6 \cdot jNi(CO)_3$, there are six chemically nontrivial exchange-pair reactions in which the tetra-coordinated compound ($j=4$) does not occur as the reagent or product and three additional such reactions in which it is a product. Because of this complicated system of reactions, it is not surprising that estimations of the exchange rate from the various peaks and combinations of peaks give lifetimes for exchange at a given temperature which differ considerably. Because of this, we were unable to make a proper estimate of the average activation energy of the exchange processes.

Reaction of the phosphorus compound

The reaction of neat tetraphosphorus hexamethylimide with an excess of nickel tetracarbonyl seems to follow the same general pattern as was observed in the case of the arsenic compound. This reaction terminates with the precipitation of insoluble $P_4(NCH_3)_6 \cdot 4\,Ni(CO)_3$ upon evolution of four moles of carbon monoxide per mole of the $P_4(NCH_3)_6$ bird-cage molecule. However, the reaction is faster than with the $As_4(NCH_3)_6$ so that the two steps seen in the previous case (Fig. 1) could not be distinguished. The ^{31}P NMR spectra of solutions containing increasing amounts of nickel tetracarbonyl showed successive maximization of three patterns, each consisting of two broad peaks with area ratios of 1 : 3, 1 : 1, and 3 : 1, respectively. These resonances were assigned to increasing coordination of the phosphorus atoms, *i.e.* stepwise increase from $j = 1$ to $j = 3$ in the formula $P_4(NCH_3)_6 \cdot jNi(CO)_3$, according to the rationale already reported in the study of the P_4O_6/BH_3 system[6] and the $P_4(NCH_3)_6/BH_3$ system[7] of complexes. Again the completely coordinated molecule ($j = 4$) is insoluble so that its spectrum is not readily observed by NMR. The chemical shifts of these complexes have been reported in a preliminary note[7]. The proton NMR spectra of the methylimido groups is highly complex and presumably of higher order, as expected from the manifold PNCH and PNP couplings to be found for the partially coordinated but structurally unaltered bird-cage molecules.

When some $P_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ is suspended in a chloroform solution of $P_4(NCH_3)_6$, it dissolves very slowly with the simultaneous appearance of the NMR peaks attributed to the $P_4(NCH_3)_6 \cdot Ni(CO)_3$ molecule, proving that exchange of tricarbonylnickel groups occurs under these conditions. It is interesting to note that in contradistinction to the situation found in the $P_4O_6/Ni(CO)_4$ family of complexes, no gel-point phenomena[4] were encountered as the Ni/P ratio was varied so that there appears to be little if any linking of two $P_4(NCH_3)_6$ bird-cage structures by means of dicarbonylnickel bridges.

Structure of the crystalline species

In addition to the evidence garnered from NMR and carbon-monoxide evolution, the following additional proof was obtained to show that the basic bird-cage structure of the $As_4(NCH_3)_6$ molecule is retained during the coordination process. A suspension in chloroform of the $As_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ complex, which is insoluble in the common nonreactive solvents, was combined with a chloroform solution of triphenylphosphine resulting in the stripping away of all four tricarbonylnickel groups per $As_4(NCH_3)_6$ by this stronger complexing agent. This was observed by noting that the single resonance peak at -300 ppm due to the $As_4(NCH_3)_6$ bird-cage molecule reappeared in the low-temperature ^1H NMR spectrum. At the same time, in the ^{31}P spectrum, the $(C_6H_5)_3PNi(CO)_3$ resonance at -31.5 ppm was seen to replace that of uncoordinated triphenylphosphine at $+5.8$ ppm.

The infrared spectra of both the $As_4(NCH_3)_6$ and $P_4(NCH_3)_6$ complexes are very close to that of the respective uncoordinated molecule except for the appearance of strong $\nu(CO)$ stretching frequencies at 2065 and 1990 cm^{-1}. The complex $P_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ was found* by X-ray study to be microcrystalline and to yield a good powder photograph. It was found that the unit cell is primitive and cubic with $a = 11.89$ Å. Our observed density of 1.716 g/cc agrees well with the value of 1.717 calculated on the assumption that there are two molecules in the unit cell. Although the number of systematic absences to be observed in a powder pattern is limited, it was concluded that the most probable space group is P4.32. In this space group, the required molecular symmetry is 23, probably with the nickel atoms lying on the threefold axes. The symmetry of the molecule is thus lower than the isoelectro-

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* These X-ray diffraction data were obtained in the Monsanto Zurich laboratories by P. J. WHEATLEY and J. J. DALY on a sample prepared independently, without knowledge of the work described herein, by L. MAIER.

nic one in which oxygen atoms replace the methylimido groups[8]. A spacial model sustains this conclusion since it indicates that steric repulsion between the methyl and carbonyl groups must be considerable.

The $As_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ molecule also reflects lessened symmetry since it does not crystallize in the cubic system as does P_4O_6. The observed density of $As_4(NCH_3)_6$ of 1.94 g/cc checks with the calculated value of 2.03 obtained by indexing the powder pattern as orthorhombic with $a=8.57$, $b=12.08$, and $c=8.25$ Å.

DISCUSSION

Previous work[4] has shown that the rate of evolution of carbon monoxide from nickel tetracarbonyl is greatly reduced when the final one or two tricarbonylnickel groups coordinate with the tetradentate bird-cage ligand. However, as exemplified by Fig. 1, there is an upsurge in the rate of CO evolution upon formation of the $As_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ precipitate. This upsurge may involve a "catalytic" effect in which the $As_4(NCH_3)_6 \cdot 3\ Ni(CO)_3$ molecule is affixed to the crystal lattice conjointly with its conversion to the $As_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ structure which, perhaps for reasons of symmetry, is energetically more favored in the crystalline form than in solution

The cubic crystal structure of the $P_4(NCH_3)_6 \cdot 4\ Ni(CO)_3$ complex gives strong evidence for complexing of the nickels by the phosphorus but not the nitrogen atoms since there seems to be no other way to achieve the required molecular symmetry. Likewise such coordination of the nickel by the nitrogens would lead to very different ^{31}P spectra. Thus for example, with a single tricarbonylnickel group on the bird cage, nitrogen coordination ought to lead to a relatively closely spaced 1:1 doublet near the resonance of the $P_4(NCH_3)_6$ molecule instead of the observed 1:3 doublet. The presence of positional isomers for the cases where two through four tricarbonylnickel groups were substituted on nitrogen atoms would be expected to give considerably more complicated NMR spectra than observed. This last argument also applies to the ^1H spectra of the $As_4(NCH_3)_6$ complexes. Further support for the coordination of the nickels by the arsenic rather than by the nitrogen atoms is the small range of shifts (± 1 ppm from that of the uncoordinated structure) seen in Fig. 3.

The single resonance making up the ^1H NMR spectrum of the $As_4(NCH_3)_6$ molecule is sharp over a range of dilutions (1:1 to 1:10) and temperatures (+40° to −40°), a fact that indicates there is rapid inversion at the nitrogen atoms, which are expected to exhibit bond angles[9] (*ca.* 108°) commensurate with the presence of an unshared pair of electrons. Since the ^{31}P spectrum of the $P_4(NCH_3)_6$ molecule also exhibits only a single line (broadened soewhat by coupling with the hydrogen atoms) and the ^1H spectrum is symmetrical[10], rapid inversion at the nitrogen is also believed to occur, as previously postulated[10].

SUMMARY

Both tetraarsenic and tetraphosphorus hexamethylimide react with nickel tetracarbonyl to form complexes in which from one to four tricarbonylnickel groups coordinate with the arsenic or phosphorus atoms. The totally coordinated species are crystalline and insoluble in all common solvents whereas the other complexes

have only been investigated in solution. Evidence is presented to show that complexing does not destroy the bird-cage structure and that it is the arsenic or phosphorus rather than the nitrogen which is donating an unshared pair of electrons to form bonds with the tricarbonylnickel groups.

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