

Preliminary communication

CLEAVAGE OF TETRAARSENIC TRISULFIDE BY NICKEL MOIETIES

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(Received October 17th, 1983)

Summary

Tetraarsenic trisulfide undergoes cleavage in the presence of triphos-nickel moieties (triphos = 1,1,1-tris(diphenylphosphinomethylethane) to give good yields of compounds containing the cyclic triarsenic unit.

It has been recently found that the tetraphosphorus chalcogenides P_4S_3 and P_4Se_3 react with various transition metal moieties to yield compounds which contain either the intact cage molecule [1] or fragments of formula P_3X_3 [2], P_2X ($X = S, Se$) [3] or P_3 [4]. In particular, tetraphosphorus trisulfide and tetraphosphorus triselenide react with triphos-cobalt and -nickel moieties (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) to give complexes of formulae [(triphos)Co(P_2X)] BF_4 ($X = S, Se$) [3] and [(triphos)Ni(P_3)] BF_4 ; both the cobalt and nickel compounds contain a three-membered cyclic unit trihapto bonded to the metal. The formation of the homoatomic cyclotriphosphorus ring in the nickel derivatives [4], and of the heteroatomic diphosphorus sulfide and diphosphorus selenide units in the cobalt complexes [3] is evidence for variation in the nature of the cleavage of the cage molecules upon changes in the metal atom.

We have begun a study of the reactivity of tetraarsenic trisulfide, which has the same geometry as P_4S_3 and P_4Se_3 , toward triphos-cobalt and -nickel moieties in order to ascertain whether a change in the nature of the pnictogen atom affects the reactivity of the cage molecule.

The dicationic complex [(triphos)Ni(As_3)Ni(triphos)](BF_4) $_2$ is obtained from the reaction of equimolar amounts of tetraarsenic trisulfide, nickel tetrafluoroborate and triphos in a 1/2 ethanol/tetrahydrofuran mixture in an inert atmosphere for two days at room temperature. The monocationic compound [(triphos)Ni(As_3)Ni(triphos)] BF_4 is obtained by refluxing the above reagents together overnight. Both compounds are obtained in a 70% yield. The two compounds which have the homocyclic triarsenic group trihapto bonded to two triphos-nickel units have been characterized by comparing their elemental anal-

yses and physical properties with those of the authentic samples [5]. The formation of these triple-decker complexes provides the first example of cleavage of the As_4S_3 molecule by transition metal complexes. Moreover it should be noted that tetraarsenic trisulfide, which is the origin of the homocyclic As_3 ring in the reaction with the triphos-nickel moiety, undergoes a similar cleavage to that of the tetraphosphorus trisulfide and tetraphosphorus triselenide molecules. Such behaviour of P_4S_3 , P_4Se_3 and As_4S_3 suggests that in the reaction the differences in atomic sizes and orbital energies between phosphorus and arsenic or sulfur and selenium are overridden by other factors, probably related to orbital symmetry requirements.

It may be noted in this connection that although the mechanism of cleavage of the pnictogen chalcogenides is not yet understood, some hint may be provided by the fact that the highest peaks in the mass spectra of P_4S_3 , P_4Se_3 and As_4S_3 are respectively due to P_3S^+ , P_3Se^+ and As_3S^+ species [6], from which the triatomic fragments might originate. This unprecedented cleavage of the As_4S_3 cage molecule provides a high yield, one-step route to the triple-decker sandwich complexes $[(\text{triphos})\text{Ni}(\text{As}_3)\text{Ni}(\text{triphos})](\text{BF}_4)_2$ and $[(\text{triphos})\text{Ni}(\text{As}_3)\text{Ni}(\text{triphos})]\text{BF}_4$ in particular the use of As_4S_3 avoids synthesis and handling of the unstable light sensitive yellow arsenic, which has been previously used to obtain the two nickel derivatives [5].

References

- 1 M. Di Vaira, M. Peruzzini and P. Stoppioni, *Inorg. Chem.*, **22** (1983) 2196; M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Organomet. Chem.*, **258** (1983) 373.
- 2 M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Chem. Soc. Chem. Commun.*, (1983) 903.
- 3 M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Chem. Soc. Chem. Commun.*, (1982) 894; M. Di Vaira, M. Peruzzini and P. Stoppioni, *J. Chem. Soc.*, in press.
- 4 M. Di Vaira, L. Sacconi and P. Stoppioni, *J. Organomet. Chem.*, **250** (1983) 183.
- 5 M. Di Vaira, S. Midollini and L. Sacconi, *J. Amer. Chem. Soc.*, **101** (1979) 1757.
- 6 G.J. Penney and G.M. Sheldrick, *J. Chem. Soc.*, (1971) 243 and unpublished results of this laboratory.