In the first-row oxometal(IV) porphyrins, MO(Por),[14] the reactivity toward organic substrates increases in the series TiO(Por) ≈ VO(Por) ≪ CrO(Por) < MnO(Por) < FeO(Por). Examples of the latter two species have yet to be obtained in a pure state. In moving along this series, the increasing number of d electrons cause an increasing repulsion of the p electron pairs at the terminal oxo group, thus destabilizing and activating the oxygen atom. The instability of the manganese systems is not due to the central metal alone since very stable, red, diamagnetic nitridomanganese(V) porphyrins have been isolated, e.g., MnN(TTP) and MnN(OEP).[25] However, the paramagnetic oxochromium(V) porphyrins appear to be very reactive.[6]

Acknowledgment. We thank Dr. J. J. Veith for the mass spectra and Professor J. T. Groves for communication of his results prior to publication. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Registry No. CrO(TPP), 78833-34-8; CrO(OEP), 79919-63-4; Cr(OH)(TTP), 33519-59-4; Cr(OH)(OEP), 50733-41-0; $PhCH_2OH$, 100-51-6.

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Preparation of a Spirocyclic Phosphorane with a P^V–P^V Bond

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Received July 27, 1981

In recent years there has been much interest in compounds containing a phosphorus–phosphorus bond with highly coordinated phosphorus atoms in these laboratories[1,2] and in others.[3] A primary thrust of the work in these laboratories has been to demonstrate that compounds with P^V–P^V bonds are stable. In fact, it was shown that when the two phosphorus atoms belong to cyclenphosphorane, such a compound could be isolated.[3] In this study it has been shown that a compound containing P^V–P^V bond can be prepared, where one phosphorus atom does not belong to a cyclic ring system and where the phosphorus atoms have coordination numbers of 5 and 4.

Experimental Section

Materials and General Procedures. The starting materials $[(C_6H_5N)CH_3NCO]_2PCl$[4] and $NaP(O)(OC_2H_5)_2$[5] were prepared according to published methods. Dry nitrogen was used to prevent the effects of moist air. All solvents were dried and purified by conventional methods and handled under a dry nitrogen atmosphere.

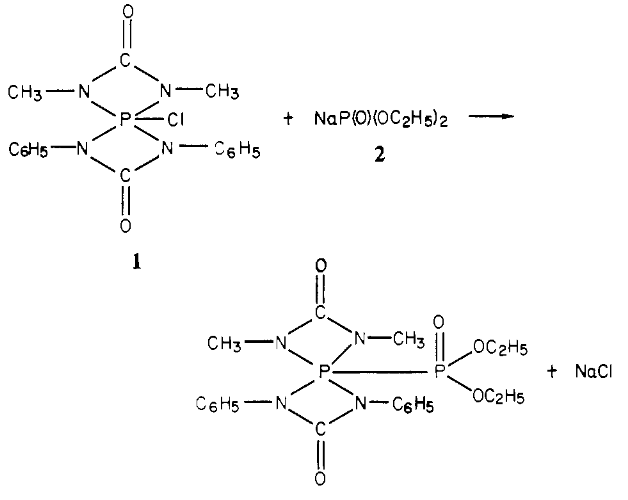
Preparation of 1,3-Dimethyl-5,7-diphenyl-4-(diethoxyphosphinyl)-1,3,5,7-tetraaza-4λ^5-phosphaspiro[3.3]heptane-2,6-dione (3). A solution of 1.32 g (8.2 mmol) of $(C_2H_5O)_2P(O)Na$ in 30 mL of benzene was added dropwise to a stirred solution of 3 g (8.2 mmol) of $[O{=}C(NCH_3)NC_6H_5]_2PCl$ in 100 mL of benzene. The reaction was conducted in a 250-mL two-necked flask, which was equipped with a reflux condenser, dropping funnel, and provision for the ingress and egress of dry nitrogen. After the addition was complete, the reaction mixture was refluxed for 4 h. Filtration of NaCl and removal of solvent afforded an oily residue, which was purified by recrystallization from THF to produce a white powder in 42% yield (1.64 g).

Anal. Calcd for $C_{20}H_{26}N_4O_5P_2$: C, 51.7; H, 5.6; N, 12.0; P, 13.5. Found: C, 51.7; H, 5.7; N, 11.8; P, 13.5. IR data (Nujol): 1780 s, 1610 w, 1510 s, 1485 s, 1395 w, 1365 s, 1350 sh, 1320 w, 1270 s, 1250 w, 1165 w, 1100 w, 1030 s, 930 w, 800 w, 780 w, 715 w, 660 w cm^{-1}. The mass spectrum exhibited a molecular ion (*m/e* 464, 1% relative intensity) and peaks corresponding to the following: $C_9H_{10}N_2O_2P_2$ (240, 7%); $C_7H_5N_2OP_2$ (195, 100%); C_7H_5NO (119, 87%); C_7H_5N (91, 54%). ^1H NMR (CH_2Cl_2): δ 1.21 (CH_3–CH_2O); 2.6 (CH_3–N); 4.21 (CH_2); 7.46 (C_6H_5). ^{31}P NMR (CH_2Cl_2): $\delta(P_O)$ 12.0; $\delta(P_N)$ −80.9; $J_{P_O-P_N}$ = 708.7 Hz.

Spectroscopic Measurements. The infrared spectrum of compound 3 was recorded as a Nujol mull by a Perkin-Elmer 735 B spectrophotometer with NaCl plates. Its mass spectrum was recorded by a Varian CH5 instrument operating at an ionizing voltage of 70 eV. ^1H and ^{31}P NMR spectra were recorded on a Bruker WH-90 instrument at spectrometer frequencies of 60 and 36.43 MHz, respectively. ^1H and ^{31}P chemical shifts (negative direction upfield) were measured with respect to internal Me_4Si and external 85% H_3PO_4, respectively.

Results and Discussion

The reaction of the spirocyclic compound **1** with $NaP(O)(OC_2H_5)_2$ (**2**) in benzene as solvent results in a phosphorus–phosphorus-bonded product, the plausible structure for which is **3**. On the basis of an X-ray analysis[4] it was shown that the chlorine atom in **1** is in an equatorial position of a trigonal-bipyramidal configuration together with two nitrogen atoms. The same structure is adopted for **3** with the exocyclic phosphorus in an equatorial position. A proof for the P–P bond is given by the ^{31}P NMR. The spin–spin coupling constant between the two phosphorus atoms falls in the range[2] of directly bonded phosphorus atoms ($^1J_{PP}$ = 708.9 Hz). It is inconceivable for J_{PP} to be over 700 without P–P direct bonding. For comparison so far coupling constants with directly bonded phosphorus atoms of coordination numbers 5 and 4 are not known. In $Me_3P{\rightarrow}PF_5$ a $^1J_{PP}$ of 715 Hz was found.[6] The stability of **3** is surprising: it can be transferred into the gas phase to get a good mass spectrum. The mass



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spectrum exhibited the parent with 1% relative intensity. The peak with the highest intensity was detected at *m/e* 195 with a composition of $C_7H_5OP_2N_2$. An isomeric structure where the oxygen atom migrates into the P–P bond can be excluded because the spin–spin coupling of $^2J_{POP}$ should be 10 times smaller.

Acknowledgment. The authors are grateful to Deutsche Forschungsgemeinschaft for financial support.

Registry No. **1**, 80049-55-4; **2**, 2303-76-6; **3**, 80049-56-5.

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First Example of Coordination of the Thionitro Group in a Cobalt Complex. Synthesis and Characterization of $Co(NSO)Cl_2[P(OPh)_3]_2$

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Received February 26, 1981

Although the conversion of a coordinated nitrosyl ligand to a nitro species by molecular oxygen in cobalt nitrosyl complexes is well-known,[1-4] no complex having a coordinated thionitro group (as an N donor) has yet been reported. We report here for the first time the synthesis of a thionitro complex $Co(NSO)Cl_2[P(OPh)_3]_2$.

Experimental Section

All the reagents used were analytical or chemical pure grade. All the solvents were dried and thoroughly degassed before use. Carbon, hydrogen, and nitrogen were analyzed by the Microanalytical Laboratory of Indian Institute of Technology, Kanpur, India. The analyses for chloride and cobalt were carried out by standard methods.[5]

For the phosphorus estimation the sample was decomposed with sodium peroxide, sugar, and sodium nitrate in the ratio 20:1:3 in a Parr-Bomb crucible, and the mass was extracted with water. A few milliliters of concentrated sulfuric acid was added to the water extract which was then heated until SO_3 fumes were evolved. It was diluted with water and filtered if necessary. Phosphorus in this solution was estimated as phosphorus ammonium molybdate.

The infrared spectra were recorded as CsI pellets with a Perkin-Elmer model 580 infrared grating spectrophotometer in the range 4000–250 cm^{-1}. Conductivity measurements were carried out on an Elico conductivity meter type CM-80 using millimolar solutions in nitrobenzene. Magnetic measurements were made with a Gouy balance at room temperature.

A green solution of $(NSCl)_3$[6] (0.08 g) in tetrahydrofuran (15 mL) was slowly added with stirring over about 15 min to a solution of $CoH[P(OPh)_3]_4$[7] (0.40 g) in tetrahydrofuran (20 mL) at 30 °C under pure and dry argon. The stirring was continued for about 30 min more when the solution turned dark green. It was concentrated to 10 mL at room temperature under reduced pressure and filtered under an argon atmosphere. On addition of degassed petroleum ether to the filtrate, a green complex precipitated out. The solid was washed with water and dried in air whereby its color changed from green to yellowish green. The yellowish green complex $Co(NSO)Cl_2[P(OPh)_3]_2$ (I) (mp 118 °C) thus obtained was analyzed (yield, 0.107 g; 43%).

Anal. Calcd for $Co(NSO)Cl_2[P(OPh)_3]_2$: C, 53.4; H, 3.7; N, 1.7; P, 7.6; Co, 7.1; S, 3.9; Cl, 8.8. Found: C, 53.5; H, 3.8; N, 1.6; P, 7.7; Co, 7.0; S, 4.1; Cl, 9.0.

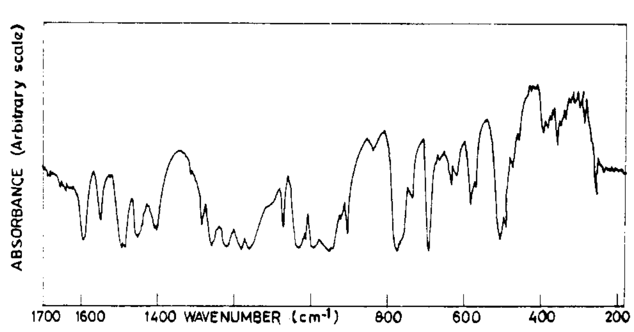

Figure 1. Infrared spectrum of $Co(NSO)Cl_2[P(OPh)_3]_2$.

The solution obtained in the above washings was concentrated on a waterbath to about 10 mL. On cooling, bright yellow needles of S_4N_4 were separated out.

Results and Discussion

Dichlorothionitrobis(triphenyl phosphito)cobalt(III) is a yellowish green, diamagnetic solid that dissolves in dichloromethane, chloroform, and benzene and is insoluble in ether. The compound is reasonably stable in air but is best stored under an inert atmosphere. Its molecular weight was found to be 772. Its conductivity data (6 Ω^{-1} cm^2 mol^{-1}) rules out the ionic character of the compound.

Its IR spectrum in CsI exhibited absorption bands at 1540 and 990 cm^{-1} besides the characteristic bands of triphenylphosphite. The band at 1540 cm^{-1} is assigned to ν(NO) since the band due to ν(NS) should not appear at such a high wave number (e.g., the NS triple bond of NSF absorbs at only 1372 cm^{-1}). The peak at 990 cm^{-1} is asigned to ν(NS).

The IR spectrum of the green solution obtained after the addition of $(NSCl)_3$ to $CoH[P(OPh)_3]_4$ exhibited a band at 1130 cm^{-1} together with weak bands at 1540 and 990 cm^{-1}. The 1130-cm^{-1} band is assigned to ν(NS).[8] This band disappears on exposing the solution to oxygen or air. It has been concluded that the green solution is a mixture of thionitrosyl and thionitro complexes, which on further exposure to air or oxygen were converted to pure thionitro complex. Presumably, first a five-coordinated air-sensitive intermediate thionitrosyl complex $Co(NS)Cl_2[P(OPh)_3]_2$ (ν(NS) = 1130 cm^{-1}) was formed which in the presence of air or oxygen was oxidized to a thionitro complex:

$$CoH[P(OPh)_3]_4 + (NSCl)_3 \xrightarrow[-2P(OPh)_3]{THF/30\ ^\circ C} Co(NS)Cl_2[P(OPh)_3]_2 + H^+ + Cl^- + 2NS$$

$$2NS \rightarrow {}^1/_2S_4N_4$$

$$Co(NS)Cl_2[P(OPh)_3]_2 + {}^1/_2O_2 \rightarrow \underset{I}{Co(NSO)Cl_2[P(OPh)_3]_2}$$

In transition-metal thionitrosyl complexes the thionitrosyl group is generally coordinated through the nitrogen atom of the NS group.[8] This has been supported by the fact that in the thionitrosyl group ($N^{\delta-}$–$S^{\delta+}$) the nitrogen end is negatively charged and the sulfur end is positively charged.[9] Therefore, it is presumed that in the cobalt thionitrosyl complex $Co(NS)Cl_2[P(OPh)_3]_2$ the thionitrosyl group is coordinated

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