Lewis Acid Controlled Tautomerization of a Metallated Cyclenphosphorane

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The species HcyclenPMo(CO)$_5$ (**2**), which contains a trigonal bipyramidal phosphorus with a P $\cdots$ N transannular interaction, reacts with HBF$_4$ or Me$_3$OBF$_4$ and leads to formation of phosphoranide (R$_4$P:$^-$) adducts, whereas reaction of (**2**) with THF·BH$_3$ (THF = tetrahydrofuran) yields the unexpected phosphine adduct H(BH$_3$)cyclenP-Mo(CO)$_5$ (**5**), the *X*-ray structure of which reveals an unprecedented conformation of the cyclenP ring.

The constraint of the twelve-membered ring in cyclenphosphorane (cyclenPH, **1a**) is known to stabilize the pentacoordinate trigonal bipyramidal (tbp) geometry around phosphorus to such an extent that the 'open' phosphine tautomer (**1b**) is not observed in solution.[1] This has led to a variety of unusual reactions and products, most often featuring the tbp phosphorus.[2] We recently succeeded in isolating the open form of cyclenPH *via* reaction with Mo(CO)$_6$, which yielded HcyclenPMo(CO)$_5$ (**2**) (Scheme 1).[3] However, the *X*-ray crystal structure of this product revealed that the tautomer is not really open, but contains an essentially tbp phosphorus atom featuring a P $\cdots$ N transannular interaction [P $\cdots$ N(H) = 2.36 Å]. Subsequent treatment of (**2**) with HBF$_4$ resulted in [H$_2$cyclenPMo(CO)$_5$]BF$_4$ (**3a**), a species in which both axial nitrogens are protonated. In this case, the constraint of the cyclen ring appears to favour the pentacoordinate phosphorus rather than the alternative R$_2$NH$_2$$^+$ ammonium salt formation (**4a**). However, the reactions of (**2**) with Lewis acids turn out to be remarkably acid dependent, and we herein report its reaction with THF·BH$_3$ (THF = tetrahydrofuran) which leads to an entirely different product with a reduced phosphorus co-ordination number and a new cyclenP ring conformation.

Treatment of (**2**) with THF·BH$_3$ in a 1:1 molar ratio in hexane yields a white precipitate (**5**), soluble in toluene, THF, and chloroform. The ^{31}P{^{1}H} n.m.r. spectrum of (**5**) shows one peak at δ 154 p.p.m., which is 40 p.p.m. downfield of (**2**) (δ 116 p.p.m.) and 119 p.p.m. downfield of (**3**) (δ 35 p.p.m.). This chemical shift indicates a four-, rather than a five-co-ordinate phosphorus. The ^{13}C{^{1}H} n.m.r. and i.r. spectra indicate that the Mo(CO)$_5$ unit has remained intact, while the observed two-bond P–Mo–C coupling shows that the phosphorus is still bound to the metal.[†] These data suggest that the

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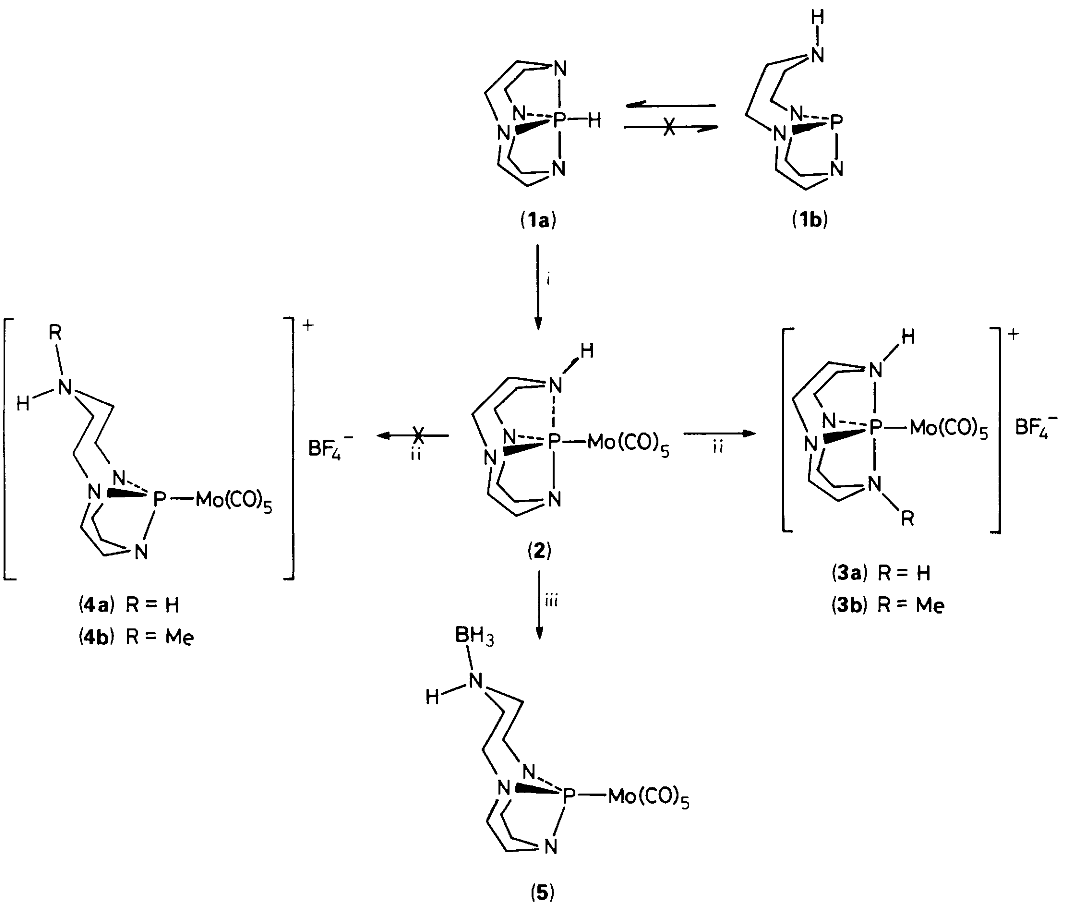
[†] In a nitrogen atmosphere (with all solvents dried, distilled, and deoxygenated), a stirred solution of (**2**) (250 mg, 0.573 mmol) in hexanes at 0 °C was treated dropwise with 1.0 M THF·BH$_3$ (Aldrich, 0.57 ml, 0.57 mmol). The reaction mixture was allowed to warm to ambient temperature and the mixture was stirred for 8 h. The resulting precipitate was filtered, washed with hexanes, and pumped dry to yield (**5**) as a white, air-stable solid (201 mg, 79%), m.p. 180—182 °C (decomp.). Spectroscopic data for (**5**): n.m.r. (CDCl$_3$), ^{31}P{^{1}H}, δ 154 p.p.m.; ^{13}C{^{1}H}, δ 41.5 (d, CH$_2$, $^2J_{PC}$ 10 Hz), 47.7 (d, CH$_2$, $^2J_{PC}$ 6 Hz), 50.7 (s, CH$_2$), 52.1 (d, CH$_2$, $^2J_{PC}$ 5 Hz), 204.7 (d, CO, $^2J_{PC}$ 12 Hz), 208.7 (d, CO, $^2J_{PC}$ 32 Hz); ^{11}B{^{1}H}, δ −15.3 p.p.m.; ^{1}H, δ 4.17 (br., NH, 1H), 2.6—3.6 (complicated m, CH, 16H), 0.8—2.2 (v br., BH). I.r. ν_{CO} (CHCl$_3$, cm^{-1}), 1935 (vs), 2060 (w).



Scheme 1. *Reagents and conditions*: i, $Mo(CO)_6$, toluene, reflux; ii, HBF_4 or $Me_3O^+BF_4^-$, hexanes; iii, THF·BF_3, hexanes.

product formed is $H(BH_3)cyclenPMo(CO)_5$, resulting from rupture of the P · · · N transannular interaction and formation of an $R_2HN \rightarrow BH_3$ linkage. This structure was confirmed by *X*-ray crystallography and is illustrated in Figure 1, along with selected bond distances and angles.‡

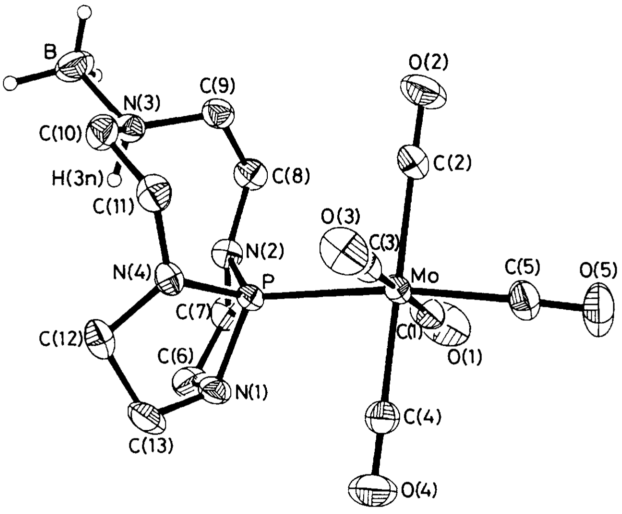


Figure 1. Computer generated drawing of $H(BH_3)cyclenPMo(CO)_5$ (**5**). Thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity except for those attached to B and N(3). Selected bond lengths (Å) and angles (°): Mo–P 2.483(1), P–N(1) 1.711(2), P–N(2) 1.707(2), P–N(4) 1.690(2); Mo–P–N(1) 117.8(1), Mo–P–N(2) 120.2(1), N(1)–P–N(2) 93.1(1), Mo–P–N(4) 117.2(1), N(1)–P–N(4) 94.9(1), N(2)–P–N(4) 108.7(1).

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‡ *Crystal data for* (**5**): crystals were grown by liquid diffusion of hexanes into a solution of (**5**) in THF. $C_{13}H_{20}BN_4O_5PMo$, $M = 450.1$, $a = 7.7312(11)$, $b = 9.2146(10)$, $c = 14.032(3)$ Å, $\alpha = 95.57(1)$, $\beta = 92.024(1)$, $\gamma = 106.18(1)°$, $U = 953.4(3)$ Å, triclinic, space group $P\bar{1}$, $Z = 4$ and $D_c = 1.57$ g cm^{-3}, $\mu = 7.81$ cm^{-1}. A total of 2732 reflections were collected at 299 K on a Nicolet R3m/V diffractometer in the 2θ range 3.00—45.00°. Data were corrected for decay and Lorentz polarization effects, but not for absorption. The structure was solved by direct methods using SHELXTL-PLUS (G. M. Sheldrick, Structure Determination Software Programs, Nicolet Instrument Corp., U.S.A., 1988) and subsequent difference Fourier methods. The structure was first solved in the $P1$ space group with two independent molecules, and then translated to fit $P\bar{1}$ with one independent molecule. Final full-matrix least-squares refinement (SHELXTL-PLUS) using 2287 observed reflections with $I > 3.0\,\sigma(I)$ converged to $R = 0.022$ and $R_w = 0.036$. All non-hydrogen atoms were refined anisotropically. Hydrogens attached to N and B were located on difference maps. Hydrogen atoms were included in the refinement with fixed isotropic thermal parameters and geometrical constraints for CH_2 protons. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

The effect of decreasing the phosphorus co-ordination from an approximate tbp to a distorted tetrahedron results in significant changes in the cyclenP ring. First of all, considering the eight-membered ring containing P and N(3), the conformation has changed from a boat–boat form in (**2**), to a boat–chair form in (**5**), *via* rotation about the four (C–C and C–N) bonds connected to C(9) and C(10). This conformation is unique for the cyclenP unit. Secondly, the P–N(1) bond has decreased by about 0.10 Å, and is now about equal to the other P–N bond lengths. Finally, the N_3P unit has tilted 'up', with the sum of the Mo–P–N(2), Mo–P–N(4), and N(2)–P–N(4) angles being 346.1 (2)° in (**5**), compared to 359 (2)° in (**2**).

The structure of (**5**) is unusual since it represents the first example of the completely open form of the cyclenP ring, outside of a few bidentate complexes of (**1b**) (which co-ordinate the phosphine and amine ends of this open form).[2] Even more significant is the fact that previous attempts to isolate the open tautomer by reaction of cyclenPH with diborane were completely unsuccessful, and led only to cyclenPH$(BH_3)_2$ (**6**), a pentaco-ordinate phosphorus species in which both axial nitrogens of (**1a**) are co-ordinated to borane groups.[4] The reasons for the different products obtained in the reactions of (**2**) with HBF_4 and THF·BH_3 are unclear, since previous evidence has shown that the cyclen ring usually prefers the tbp geometry about phosphorus;[2] furthermore, the existence of (**6**) proves that the axial nitrogens in this geometry are basic enough to complex borane. There seem to be no steric reasons for preference of the open form with BH_3 since treatment of (**2**) with $Me_3O^+BF_4^-$ appears to yield a species with a pentaco-ordinate phosphorus (^{31}P δ 40 p.p.m.); this product is most likely [H(Me)cyclenPMo$(CO)_5$]BF_4 (**3b**), the methylated analogue of (**2**), rather than (**4b**). Several reasons could account for the different products. The observed structure of (**5**) might be an intermediate in the formation of a pentaco-ordinate species. Alternatively, the tbp geometry may not be stable with one axial nitrogen protonated and the other co-ordinated to borane. Another possibility is that the Mo$(CO)_5$ moiety may alter the stability of the products. Work is currently underway in our laboratory to yield further insight into these possibilities.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Robert A. Welch Foundation, and SMU (Seed Grant) for generous financial support. We also thank Mr. Harold S. Isom for assistance in the preparation of cyclen.

Received, 5th July 1989; Com. 9/02857I

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