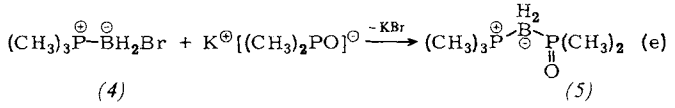
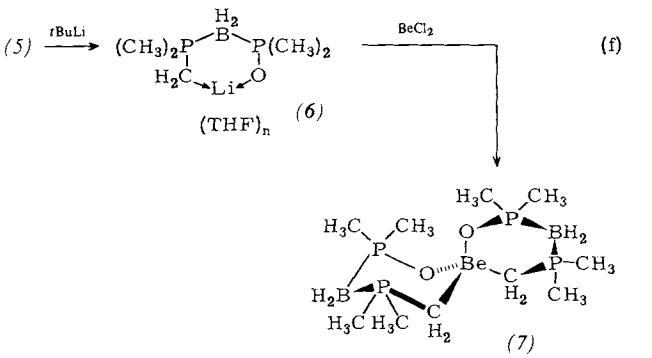
Hydrolysis of *(2)* or *(3)* with water or alkali hydroxide affords only small amounts of an oxide *(5)*, whereas reaction (e) of the readily accessible[5] bromine analog of *(1)* with the potassium salt of dimethylphosphinous acid leads directly to the neutral oxide *(5)*; yield 82%; m.p. 79 °C; $\nu(BH_2) = 2360$—2395, $\nu(P{=}O) = 1120\ cm^{-1}$; $\delta(PC_3) = -5.45$, $^1J(PB) = 79$ Hz, $\delta(PC_2O) = 50.22$, $^1J(PB) = 123$ Hz; $m/e = 166$ (M^+).



(4) *(5)*

(5) can be metalated with *tert*-butyllithium at −78 °C in tetrahydrofuran (THF)/pentane; loss of alkane takes place with formation of the lithium complex *(6)*, which does not have to be isolated free of solvent but can be reacted further, *in situ*, with metal halides. Thus, *e.g.* with $BeCl_2$ the spirocyclic beryllium complex *(7)*, m.p. 59 °C, subl. at 60—100 °C/10^{-4} torr, is obtained. The colorless, slightly air- and moisture-sensitive crystals are soluble in polar aprotic solvents.



(6) *(7)*

In the mass spectrum the molecular ion appears as base peak ($m/e = 339$, $2 \times {}^{11}B$). In the IR spectrum $\nu(P{=}O)$ is reduced to 1065 cm^{-1} owing to metal coordination. As expected the phosphorus atoms are pairwise non-equivalent: $\delta(PC_3) = -5.07$, qd, $^1J(PB) = 95$, $^2J(PP) = 15$ Hz; $\delta(PC_2O) = 63.62$, qd, $^1J(PB) = 107$, $^2J(PP) = 15$ Hz. The ^{1}H- and ^{13}C-NMR spectra show the sets of doublet signals derivable from the symmetry. The ^{13}C-NMR spectrum, in particular, demonstrates the non-equivalence of the two CH_3 groups on each P-atom, also recognizable on models. In the solid state *(7)* undergoes oligomerization on storage at room temperature, so that aged samples are no longer volatile.

The ligands (B) of complex *(7)* thus correspond to the isoelectronic[2,3,7] chelate type *(A)*, but they favor complexation with highly charged, small, and difficultly polarizable ("hard") metal centers. Beryllium is one of the most favorable candidates for this purpose.

Procedure

Combination of equimolar amounts of $BH_3 \cdot THF$ in excess THF and ethereal HCl at −20 °C leads, with evolution of H_2, to a clear solution of $H_2BCl \cdot THF$, which is allowed to react at 0 °C with one equivalent $(CH_3)_3P$ to give *(1)* quantitatively. The product crystallizes from ether/pentane. Addition of $(CH_3)_2PCl$ (6.32 g) to *(1)* (8.2 g) (66 mmol of each) and heating to 70 °C (without solvent) leads to formation of the salt *(2)*, which for purification is taken up in CH_2Cl_2, filtered, and crystallized at −30 °C by addition of ether (yield 11.2 g; 71%). Reaction of *(2)* (1.97 g) with $NaOCH_3$ (0.48 g) (8.92 mmol of each) in THF at 0—20 °C yields the methoxy derivative *(3)*, which after 16 h is crystallizeable by removal of solvent, dissolution in CH_2Cl_2, filtration and addition of ether to the filtrate at −30 °C (1.74 g; 90%).

$(CH_3)_3P{-}BH_3$ is transformed into $(CH_3)_3P{-}BH_2Br$ in the usual way[5], and 10.3 g (61.2 mmol) of the product *(4)* allowed to react at 0 °C in THF with K $[(CH_3)_2PO]$—freshly prepared from $(CH_3)_2POH$[6] (4.78 g) and KH (2.46 g) (61.24 mmol of each) in 100 ml of THF at 0 °C, but not isolated. After filtration from KBr, *(5)* can be crystallized at −30 °C from ether/pentane (8.3 g; 82%).

A solution of *(5)* (0.96 g, 5.78 mmol) in THF (10 ml) is treated at −78 °C with an equivalent of *t*BuLi (in pentane) and, after 1 hours' stirring, $BeCl_2$ (0.23 g), 2.89 mmol) is added to the mixture. Stirring is continued for 16 h, the mixture allowed to warm to room temperature, the solvent removed and replaced by toluene, the resulting solution filtered, and the residue finally obtained from the filtrate is sublimed (0.11 g; 11%).

All the compounds gave correct elemental analyses and characteristic ^{1}H-, ^{13}C-, ^{31}P-NMR and mass spectra.

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(1), 64160-46-9; *(2)*, 76880-09-6; *(3)*, 76880-08-5; *(4)*, 60228-69-5; *(5)*, 76879-14-6; *(6)*, 76880-11-0; *(7)*, 76880-10-9; $(CH_3)_2PCl$, 811-62-1; $K^+[(CH_3)_2PO]^-$, 76819-15-7

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Synthesis and Crystal Structure of a $(\eta^5\text{-}C_5H_5)(CO)_2$-Molybdenum Bicyclophosphoranide: The first Transition Metal Complex with a "$R_4P^{\ominus}$"-Ligand[**]

By *Joachim Wachter, Bernard F. Mentzen* and *Jean G. Riess*[*]

Phosphoranides, R_4P^-, were postulated as reaction intermediates in nucleophilic substitutions at tricoordinated phosphorus by *Wittig* in 1967[1], but remained elusive until *Granoth* and *Martin* succeeded in producing direct evidence for the existence of a lithium phosphoranide salt in 1978[2]. Fur-

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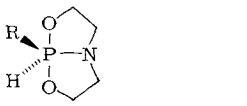
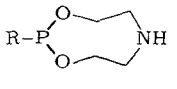
thermore, evidence for the presence of a sodium phosphoranide in an equilibrium mixture in solution has recently been obtained[3]. We report here the isolation and crystal structure of a molybdenum adduct, which is the first transition metal complex with a phosphoranide ion as ligand.

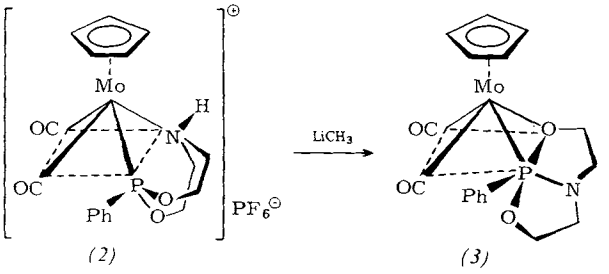
Bicyclic phosphoranes of type *(1a)* react with a variety of transition metal carbonyl complexes to give coordination adducts of their normally undetected tautomeric form *(1b)*. Coordination occurs either *via* P alone or *via* P and N[4]. The reaction of *(1a)* with $C_5H_5(CO)_3MoCl$ can be directed towards substitution of either two carbonyl groups or of one carbonyl and the chloride. In the latter case it yields the cationic species *(2)*[4b]. We selected *(2)* as a substrate on which to attempt the abstraction of the nitrogen bonded proton.



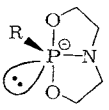
(1a)



(1b)



(2) *(3)*



(4), R = C_6H_5

The action of methyllithium on *(2)* in THF at 60 °C yielded the neutral complex *(3)*, in which the pentacoordinated bipyramidal phosphorus atom is bonded to molybdenum and acts as an anionic phosphoranide ligand *(4)*. The two additional electrons needed by the metal to achieve an 18-electron configuration are provided by one of the oxygen atoms, giving the hitherto unknown MoPO three-membered ring. It is noteworthy that this structural arrangement, rather than one in which the nitrogen acts as the additional donor, avoids the unfavorable location of the oxygen atoms in equatorial positions and the phenyl group in an apical position, which would have resulted had this structural alternative been adopted.

All spectroscopic and analytical data of the red-orange crystalline material, isolated in 21% yield, are in accord with structure *(3)*. It exhibits two ν(CO) vibrations at 1925 and 1835 cm^{-1}; the ν(N—H) vibration of the educt *(2)* has disappeared. The ^{1}H-NMR spectral data exclude the possibility of addition of $CH_3^{\ominus}$. The only sharp signal observed is that of the $\delta(C_5H_5) = 5.32$ (in $CDCl_3$); the signal integrations are also consistent with the abstraction of a proton. $^{31}P\{^1H\}$-NMR spectra of *(3)* show a singlet at an unusual location ($\delta = +23.8$) relative to the free phosphorane *(1a)*: −44.3 and to the metal complexes of the tautomer *(1b)*: +185 to +200[4b].

The structure of *(3)* was further established by X-ray crystal structure analysis[5] and is shown in Fig. 1.

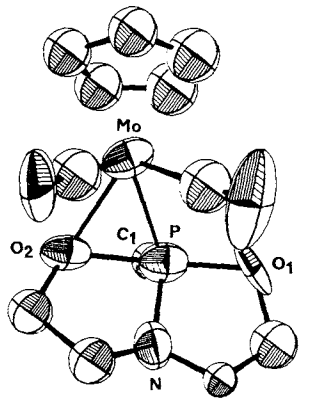


Fig. 1. Molecular structure of complex *(3)* in the crystal; of the phenyl group bonded to phosphorus only C-1 is reproduced (ellipsoids with 50% probability).

The bicyclic phosphoranide ligand whose N-bridgehead is close to planar (sum of angles 345 ± 5°), is almost perpendicularly orientated with respect to the C_5H_5 ring. The P—N bond length (1.69(5) Å) is in the range expected when N is equatorially bound to a bipyramidal pentacoordinated P atom[6]. The P—O2 distance in the coordinated five-membered ring (1.893(4) Å) is 0.24 Å longer than P—O1 in the uncoordinated ring. The P—Mo distance 2.375(2) Å) is 0.07—0.14 Å shorter than in complexes having the $C_5H_5MoPR_3$ pattern (R = OCH_3, C_6H_5)[7]; this may simply result from the contraction of the radii normally observed when going from a tri- to a pentacoordinated phosphorus atom.

Procedure

An equimolar mixture of the PF_6 salt *(2)* (630 mg, 1.1 mmol) and CH_3Li (0.7 cm^3 of 1.6 M solution in diethyl ether) in THF (50 cm^3) is stirred for 60 min at 60 °C. After evaporation of THF the oily residue is dissolved in ether (20 cm^3) and filtered. The concentrated filtrate is chromatographed on SiO_2 (column 20 × 2 cm), the product eluted with ether as an orange band (yield 100 mg, 21%), and recrystallized from ether/pentane (2:1) to give *(3)* as red-orange crystals (decomp. 86 °C)[8].

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CAS Registry Numbers:
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