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Total Diastereoselective Opening of Chiral Hydridophosphorane "Triquinphosphoranes" by Hexacarbonylmolybdenum: An Entry to $Mo(CO)_5$: Chiral Oxazaphospholidine Complex

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Hydridophosphoranes, which can be prepared by an exchange reaction involving alcoholysis or aminolysis of the P^{III}−OR or P^{III}−NR_2 bonds,[1] have aroused interest as ligands for reactive metal complexes.[2] Riess and co-workers[3] have focused on the coordination of bicyclophosphoranes, whereas Lattman and co-workers[4] have been interested in the complexation of tetracyclic cyclen- and cyclamphosphoranes. To our knowledge, chiral bicyclic or tetracyclic hydridophosphoranes have not yet been used for the synthesis of chiral organophosphorus ligands coordinated to a metal center.[5] We previously reported the synthesis of a new class of chiral tricyclic phosphoranes, the "triquinphosphoranes", from chiral enantiopure diaminodiols that present a C_2 symmetry axis.[6] We showed that these phosphoranes exist as two trigonal bipyramid structures (TBP) with opposite absolute configurations at the phosphorus atom, R_P and S_P, in a fast equilibrium by a Berry pseudorotation process (Scheme 1).[6b,7] We also described the first asymmetric addition of chiral triquinphosphorane **1a** to ketopantolactone and to BH_3·SMe_2 complex leading to chiral alkoxyphosphorane **2** and chiral triquinphosphorane−borane adduct **3**, respectively (Scheme 2).[6] The X-ray diffraction structures of **2**[8] and **3**[6b] revealed that the pentacoordinated structure is retained with a deformation percentage of 66 and 6.9%, respectively, along the Berry coordinate from the ideal TBP (0%) toward the ideal SP (100%). As the X-ray structure of **3** showed, the borane group coordinated to the axial nitrogen atom of the TBP structure is in syn position with respect to the P−H bond and in anti position with respect to the adjacent pseudoaxial isopropyl substituent.[6b] Recently, Gavrilov et al. reported the first example in which triquinphosphorane **1b** (R = Et, R′ = H) coordinates to platinum (II) [Pt(COD)Cl_2] as the phosphoranide, based on ^{31}P NMR data. At 60 °C, a ring opening in the phosphorane structure leads to a new Pt^{II} complex in which both the oxazaphospholidine phosphorus P^{III} and the amine nitrogen atoms coordinate the Pt^{II}. However the diastereoselectivity of this coordination was not mentioned.[9] We now report the first asymmetric addition of chiral triquinphosphorane **1c** to hexacarbonylmolybdenum leading to complex **4**.[10] A totally diastereoselective opening of the diazaphospholidine ring occurs and affords an enantiopure bicyclic oxazaphospholidine species, exhibiting an eight-membered ring, fused to the oxazaphospholidine ring by the P−N bond, that is coordinated to the Mo center through the P^{III} phosphorus atom (Scheme 3).

Experimental Section

All reactions and manipulations were carried out in an atmosphere of prepurified dinitrogen. Solvents were rigorously dried over appropriate drying agents, distilled, and deoxygenated prior to use. IR spectra were recorded on a Perkin- Elmer IR−FT spectrophotometer and NMR spectra on a Bruker AC 400, 200, and 100 MHz. $Mo(CO)_6$ was obtained commercially and used without further purification. Triquinphosphorane **1c** was synthesized as described previously.[6b]

4. To a solution of 1 mmol (329 mg) of triquinphosphorane **1c** in 10 mL of toluene was added 1 mmol (264 mg) of hexacarbonylmolybdenum. The mixture was stirred under reflux for 20 min and allowed to cool to room temperature. The mixture was filtered and the filtrate diluted with cold pentane (0 °C) to give a white solid which was recrystallized from chloroform. Yield: 65%; mp 140 °C; IR (KBr) cm^{-1}: 3450, 1990, 1960−1930; ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 7.26-7.18$ (m, 10H, Ar*H*), 4.67−4.60 (m, 2H, C*H*N), 4.22−4.10 (m, 2H, CH_2O), 4.03−3.93 (m, 2H, CH_2O), 2.91−2.76 (m, 4H, CH_2N), 2.05 (s, 1H, N*H*); ^{13}C NMR (200 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 206.3$ (CO), 205.7 (CO), 147.3, 130.4, 128.7, 128.0 (Ar), 71.5 (*C*HN), 68.3 (d, $^2J_{P-C} = 10.2$ Hz, *C*HN), 59.7 (d, $^2J_{P-C} = 7.2$ Hz, *C*H_2O), 58.7 (d, $^2J_{P-C} = 10.3$ Hz, *C*H_2O), 44.6 (d, $^2J_{P-C} = 10.3$ Hz, *C*H_2N), 41.6 (*C*H_2N); ^{31}P NMR (100 MHz, $CDCl_3$, 25 °C, H_3PO_4): $\delta = 141.8$. Anal. Calcd for $C_{21}H_{21}MoN_2O_7P$: C, 46.68; H, 3.92; N, 5.18; P, 5.73. Found: C, 46.54; H, 3.98; N, 5.30; P, 5.83.

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(1) (a) Burgada, R.; Setton, R. *Preparation, Properties and Reactions of Phosphoranes* in *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Patai, Sr., S., Eds.; J. Wiley & Sons: New York, 1994; Vol. 3, p 185. (b) Holmes, R. R. *Pentacoordinated Phosphorus − Structure and Spectroscopy*; ACS Monograph 175; American Chemical Society: Washington, DC, 1980; Vol. 1.

(2) (a) Rauchfuss, T. B. Functionalized Tertiary Phosphines and Related Ligands in Organometallic Coordination Chemistry and Catalysis. In *Homogeneous Catalysis with Metal Phosphine Complexes*; Pignolet, L. H., Ed.; Plenum Press: New York, 1983; pp 239−256. (b) Gavrilov, K. N.; Mikhel', I. S. *Russ. Chem. Rev. (Engl. Transl.)* **1996**, *65* (3), 225−247.

(3) (a) Wachter, J.; Jeanneaux, F.; Riess, J. G. *Inorg. Chem.* **1980**, *19*, 2169. (b) Jeanneaux, F.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1980**, *103*, 4272. (c) Wachter, J.; Mentzen, B. F.; Riess, J. G. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*(3), 284. (d) Dupart, J. M.; Grand, A.; Pace, S.; Riess, J. G. *J. Am. Chem. Soc*. **1982**, *104*, 2316. (e) Vierling, P.; Riess, J. G. *J. Am. Chem. Soc*. **1984**, *106*, 2432.

(4) (a) Burns, E. G.; Chu, S. S. C.; de Meester, P.; Lattman, M. *Organometallics* **1986**, *5*, 2383. (b) Lattman, M.; Chopra, S. K.; Cowley, A. H.; Arif, A. M. *Organometallics* **1986**, *5*, 677. (c) Lattman, M.; Chopra, S. K.; Burns, E. G. *Phosphorus Sulfur Relat. Elem.* **1987**, *30*, 185. (d) Khasnis, D. V.; Lattman, M.; Siriwardane, U. *J. Chem. Soc., Chem. Commun*. **1989**, 1538.

(5) Recently, chiral spirophosphoranes have been used under their hexacoordinate phosphate form as chiral agents in Wittig reactions. (a) Bojin, M. L.; Barkallah, S.; Evans, S. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 1549−1550. (b) Kojima, S.; Takagi, R.; Akiba, K.-Y. *J. Am. Chem. Soc*. **1997**, *119*, 5970−5971.

(6) (a) Vannoorenberghe, Y.; Buono, G. *J. Am. Chem. Soc*. **1990**, *112*, 6142−6143. (b) Marchi, C.; Fotiadu, F.; Buono, G. *Organometallics* **1999**, *18*, 915−927.

(7) We previously described (ref 6b) that AM1 molecular modeling calculations predict two diastereomeric TBP structures in equilibrium for **1a** [R_P (97%), S_P (3%)] and **1b** [R_P (22%), S_P (78%)]. The TBP structure is in accordance with the X-ray diffraction structure of the triquinphosphorane deriving from *N*,*N*′-bis[(−)-norephedrine]ethylene. In this structure, the phosphorus atom adopts a TBP geometry that agrees remarkably well with our computational results. Tlahuextl, M.; Martínez-Martínez, F. J.; Rosales−Hoz, M. J.; Contreras, R. *Phosphorus, Sulfur, Silicon Relat. Elem.* **1997**, *123*, 5−19.

(8) Marchi, C.; Buono, G. *Tetrahedron Lett.* **1999**, *40*, 9251−9254.

(9) Mikhel', I. S.; Gavrilov, K. N.; Lechkin, D. V.; Rebrov, A. I. *Russ. Chem. Bull.* **1997**, *46*(7), 1359−1360.

(10) This triquinphosphorane (6*S*,7*S*)-6,7-diphenyl-2,11-dioxa-5,8-diaza-$1\lambda^5$-phosphatricyclo[6.3.0.01,5]undecane was synthesized from the diaminodiol *N*,*N*′-(bis(hydroxyethyl)ethylene)-(1*S*,2*S*)-1,2-diphenyl-1,2−diamine (see ref 6b).

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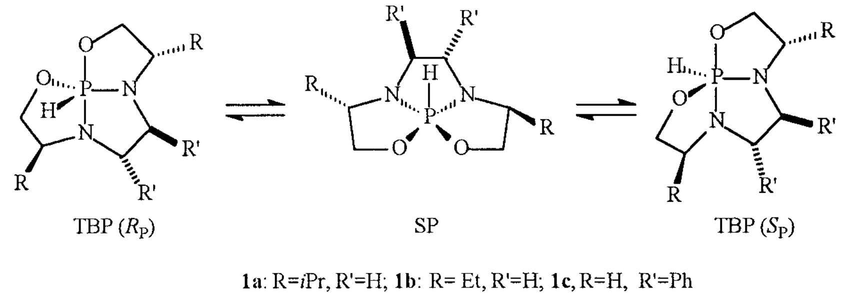
Scheme 1. Equilibration Process of Triquinphosphoranes



Scheme 2. Reactivity of Triquinphosphorane **1a** toward Ketopantolactone and Borane Complex

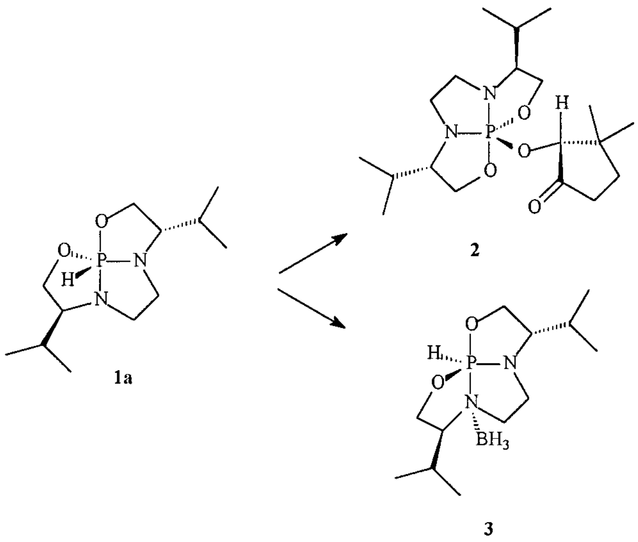


Table 1. Selected Distances (Å), Angles (deg), and Their Estimated Standard Deviations for **4**

Mo−P	2.546(1)	O7−P−N1	111.2(2)
P−O6	1.644(3)	P−O6−C6	116.0(3)
P−O7	1.625(3)	P−O7−C11	123.0(3)
P−N1	1.699(3)	P−N1−C7	110.3(2)
P•••N2	3.57(3)	P−N1−C8	128.5(3)
O6−P−O7	93.0(2)	C7−N1−C8	111.9(3)
O6−P−N1	91.2(2)	C9−N2−C10	119.6(3)

X-ray Crystallographic Data Collection. Single-crystal X-ray diffraction measurements were performed with Mo Kα radiation (λ = 0.71073 Å) on an Enraf-Nonius CAD4 computer-controlled kappa axis diffractometer equipped with a graphite crystal, incident beam monochromator. Crystal data for **4** : $C_{21}H_{21}MoN_2O_7P$, M_r = 540.30, tetragonal, space group *P*212121, *a* = 9.353(1) Å, *b* = 13.585(2) Å, *c* = 18.961(3) Å, *Z* = 4, *V*= 2 409(1) Å^3, ρ_{calcd} = 1.48 g·cm^{-3}, μ(Mo Kα) = 6.4 cm^{-1}, final *R*1 and *wR*2 are 0.028 and 0.035 for 307 parameters and 2418 unique observed reflections with $F_o^2 > 3.0\sigma(F_o^2)$. Selected bond distances and angles are listed in Table 1.

Result and Discussion

The addition of chiral triquinphosphorane **1c** to hexacarbonylmolybdenum led exclusively to complex **4** in which the oxazaphospholidine ligand was coordinated to molybdenum and exhibited a single absolute configuration at the P atom. The exclusive formation of **4** could be monitored by ^{31}P NMR spectroscopy showing only one downfield singlet at 141.8 ppm for the P^{III} coordinated phosphorus atom and the disappearance of the phosphorane signal at −37.8 ppm. Compound **4** was isolated in a 65% yield as colorless crystals (mp 140 °C) that were soluble in common solvents. Those crystals appeared to be indefinitely air and moisture stable at room temperature. The IR spectrum showed five ν(CO) absorptions (1990 cm^{-1}, one CO *trans*, and four signals between 1960 and 1930 cm^{-1}, four CO *cis*) and a NH stretching at 3450 cm^{-1}, characteristic of a noncoordinated nitrogen site.[2] These data are consistent with the presence of a single monodentate ligand in the complex and the coordination of the ligand only by the phosphorus atom. Thus, the carbonyl ligand exchange reaction on molybdenum induced a totally diastereoselective opening of the diazaphospholidine ring. The structure of **4** was confirmed by X-ray diffraction. The molecular structure and atom labeling are presented in Figure 1. The most prominent structural features are, first of all, the nearly tetragonal structure adopted by the phosphorus atom with a S_P absolute configuration; second, the P−N1 bond length [1.699(3) Å] lying in the upper part of the usual range [1.67−1.70 Å],[1b] together with the close to planar sp^2 type configuration of the nitrogen atom [sum of bond angles around N1 is 359(2)°]. The later could be assigned in part to hyperconjugation between the phosphorus center and the nitrogen atom.[11] The monodentate behavior exhibited by the aminophosphine species resulting from the opening of triquinphosphorane **1c** upon complexation is similar to that observed by Riess et al. when complexing cyclamphosphorane to [CpW(CO)$_3$Cl].[12] Furthermore, the distance between the phosphorus and nitrogen N2 atoms [3.57(3) Å] is not in favor of transannular interactions, contrary to what was observed by Lattman for the HcyclenPMo(CO)$_5$ complex **5** in which a P•••N distance of 2.356 (23) Å was found.[13] Thus, as shown by the X-ray

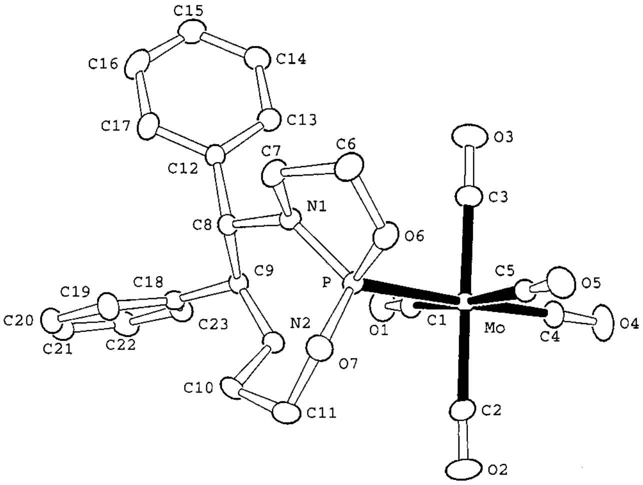


Figure 1. ORTEP drawing of **4**.

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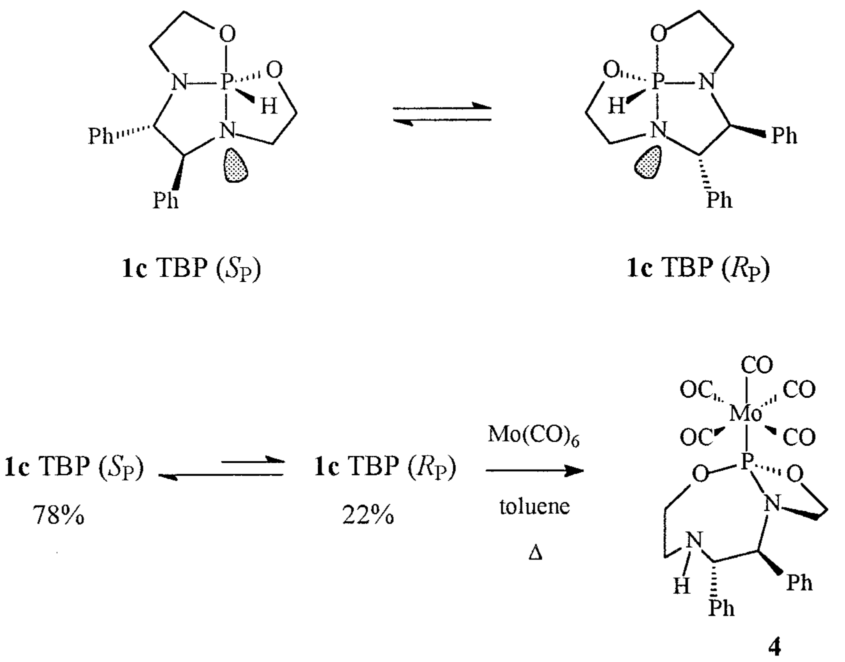
[11] Gilheany, D. G. *Chem. Rev.* **1994**, *94(5)*, 1339−1374.

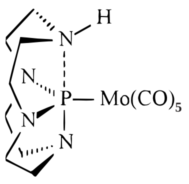
[12] Dupart, J. M.; Grand, A.; Riess, J. G. *J. Am. Chem. Soc.* **1986**, *108*, 1167−1173.

[13] Khasnis, D. V.; Lattman, M.; Siriwardane, U.; Chopra, S. K. *J. Am. Chem. Soc.* **1989**, *111*, 3103−3105.

Scheme 3. Addition of Hexacarbonylmolybdenum to Triquinphosphorane **1c**



structure, the breaking of P−N2 bond upon complexation of triquinphosphorane **1c** with Mo(CO)$_6$ formed an eight-membered ring which is quite difficult to synthesize by classical methods.[14] This eight-membered ring adopted a boat-chair-type conformation.



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Although the mechanism of opening of triquinphosphorane **1c** is still unknown, the formation of complex **4** should not involve the prior opening of the diazaphospholidine ring. Indeed, despite numerous attempts, using variable temperature NMR techniques, such a $P^{III}-P^{V}$ equilibrium has not been detected so far.[6b] We rather propose, as a first step, a complexation of the molybdenum to the less hindered apical nitrogen atom of the diastereomeric phosphorane TBP (R_P),[15] in which the pseudoaxial phenyl group is in an anti position with respect to the P−H bond (Scheme 3). Such a complexation has been observed in the borane addition to phosphorane **1c**, which occurred with a diastereoselectivity of 60%. The total diastereoselectivity observed in the present case could be assigned to the steric hindrance of the hexacarbonylmolybdenum.

In conclusion, this reaction afforded, in a straightforward manner, an enantiopure oxazaphospholidine ligand coordinated to molybdenum. Further studies to extend this approach to synthesize new chiral oxazaphospholidine complexes and explore their applications in asymmetric catalysis are in progress.[16]

Supporting Information Available: Tables listing detailed crystallographic data, atomic positional parameters, and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Quin, L. D. In *Conformational Analysis of Medium-Sized Heterocycles*; Glass, R. S., Ed.; VCH Publishers, New York, 1988; pp 181−216.

(15) The tautomeric equilibrium between the pentacoordinated and tricoordinated forms has never been observed. See ref 6.

(16) For applications of molybdenum complexes in allylic asymmetric synthesis reactions see: Trost, B. M.; Hachiya, I. *J. Am. Chem. Soc.* **1998**, *120*, 1104−1105.