at −1.251 V. This potential is even more negative than that for the SALEN complexes. Since this complex is as yet uncharacterized, further statements regarding the effect of the electron-donating ability of *o*-aminophenol are not possible at this time.

Registry No. Ce(SALEN)$_2$, 98839-38-4; Ce(SALEN)$_2^-$, 98839-41-9; Ce(5-BrSALEN)$_2$, 98839-39-5; Ce(5-BrSALEN)$_2^-$, 98839-42-0; Ce(5-MeOSALEN)$_2$, 98839-40-8; Ce(5-MeOSALEN)$_2^-$, 98839-43-1; Ce(SALOPHEN)$_2$, 88178-02-3; Ce(SALOPHEN)$_2^-$, 98839-44-2; Ce(DAPSC)$_2$(ClO$_4$)$_3$, 74841-15-9.

Contribution from Gulf Research & Development Company,
Pittsburgh, Pennsylvania 15230

Preparation of a Novel P–P-Bonded Diphosphine

Thomas V. Harris*[1] and Wayne R. Pretzer*[2]

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Both steric bulk and electronic donor/acceptor capability of tertiary phosphine ligands are known to exert quite drastic regiochemical and stereochemical consequences in reactions catalyzed by organometallic complexes. A balance of these steric and electronic factors is important, for example, in such reactions as the oxo or hydroformylation reaction. In general, phosphine ligands with a wide range of steric bulk are known.[3] The donor/acceptor nature of the phosphine is largely limited by the electronic properties of the organic groups bonded to phosphorus. However, there appear to be few or no examples of phosphines in which both the electronic and steric properties were designed and successfully incorporated into the ligand. Control of steric effects in phosphine ligands is well-known,[3] but electronic properties such as basicity are usually indirectly determined by the properties of the groups attached to the phosphorus atom, e.g., aryl vs. alkyl. Attempts to prepare a phosphine ligand with a strongly electron-withdrawing substituent and steric bulk similar to that of a strong donor ligand in which the phosphorus atom is an integral part of a bicyclic ring structure led instead to formation of a P–P-bonded diphosphine[4,5] by rather novel chemistry.

We developed a method to introduce alkyl groups based on quaternization of secondary phosphines with alkyl halides. While this route proved successful for prepn. of tertiary phosphines from alkyl bromides and halides, extension of the reaction to perfluoroalkyl iodides led to formation of P–P-bonded diphosphines by an unusual P–CF$_2$R cleavage reaction. In this note we discuss this unusual reaction and report some interesting synthetic chemistry of the bicyclic phosphine system. Results of cobalt-catalyzed oxo reactions using the diphosphine ligand are also reported.

Experimental Section

All reactions were conducted in a Vacuum Atmospheres Dri-Lab or with conventional vacuum and Schlenk techniques. Solvents were dried and deoxygenated over sodium/benzophenone ketyl. Routine reaction product analysis was obtained by VPC with a $^1/_8$ in. × 1 ft OV-101 column (temperature program: 100–240 °C at 10 °C/min, 4 min initial hold) with comparison to known compounds. Infrared spectra were recorded as Nujol mulls with a Perkin-Elmer 299 spectrophotometer. ^{31}P NMR spectra were recorded on a Varian FT-80A spectrometer at 32.203 MHz operating in the Fourier transform mode, and ^{1}H NMR spectra were obtained with the same instrument. Phosphorus spectra were measured with positive chemical shifts taken as downfield from phosphoric acid. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

The bicyclic phosphines and diphosphines described in this paper are extremely air-sensitive, and when care is not taken in handling, air-oxidation products can be seen by VPC.

HPC$_8$H$_{14}$. This preparation is similar to that previously described.[7] Two isomers of HPC$_8$H$_{14}$ are obtained, i.e., 9-phosphabicyclo[4.2.1]nonane and 9-phosphabicyclo[3.3.1]nonane. The synthesis uses phosphine, PH$_3$, which is highly flammable and toxic, and 1,5-cyclooctadiene, which has a nauseating odor. Appropriate precautions should be taken when handling multigram quantities of phosphine. Careful pressure checking of the autoclave prior to reaction, continual monitoring for phosphine gas, and an isolated, well-ventilated reaction area are highly recommended. The reaction was carried out in an evacuable autoclave system with pressure-release devices and exterior vents. Phosphine was condensed into the autoclave from weighing bombs by cooling with dry ice.

Degassed 1,5-cyclooctadiene (128 mL), hexane (64 mL), and a radical initiator, Vazo-64 (2,2′-azobis(2-methylpropionitrile)) (7.5 g) were charged into the autoclave, and following N$_2$ purge the phosphine (35 g) was added. The reactor was carefully heated to 77–80 °C for 5 h (above 80 °C, reaction rates were excessive). After cooling and purging with N$_2$, the viscous liquid products were drained into a large sublimation apparatus. Excess solvent was evaporated, and the solid white product was obtained by vacuum sublimation at 25 °C to a −78 °C cold finger; yield 73.2 g. IR: ν_{P-H}, 2266 cm^{-1}. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −49.5 (s), −55.7 (s) with respective relative intensities of 1:2 for the two isomers. ^{31}P NMR (undecoupled, C$_6$D$_6$): overlapping doublets of triplets, $^1J_{P-H}$ = 190 Hz, $^2J_{P-H}$ = 28 Hz. The gas chromatogram of HPC$_8$H$_{14}$ showed two compounds in a 1:2 ratio corresponding to 1,4- and 1,5-addition of PH$_3$ to cyclooctadiene, in agreement with ref 7.

C$_6$H$_{13}$PC$_8$H$_{14}$. Quaternization. A solution of 15.0 g (0.106 mol) of HPC$_8$H$_{14}$ and 17.43 g (0.106 mol) of hexyl bromide in 50 mL of octane was placed in a vacuum reaction bulb. The contents were degassed at −78 °C and then heated at 70 °C. A white solid formed, which after 6 days was collected by filtration, washed with octane, and dried under vacuum; yield 23.6 g, 72.7%. Anal. Calcd for C$_{14}$H$_{28}$BrP: C, 54.73; H, 9.18; Br, 26.01; P, 10.08. Found: C, 56.52; H, 9.45; Br, 24.64; P, 9.51. This is consistent with contamination by 2.6 wt % of the starting material C$_8$H$_{15}$P. IR: ν_{P-H}, 2310 cm^{-1}. ^{31}P{^{1}H} NMR (CD$_3$CN): two overlapping singlets, δ 264.8, 262.0 (ratio 1:0.28). ^{31}P NMR (undecoupled, CD$_3$CN): broad doublet, $^1J_{P-H}$ = 517 Hz.

Deprotonation. To a suspension of 39.1 g (0.128 mol) of the quaternary salt in 50 mL of toluene was added 6.13 g (0.128 mol) of 50% NaH/50% mineral oil dispersion (previously washed with hexane). Gas evolution occurred immediately. The reaction mixture was degassed at −78 °C with further periodic degassing over 4 days. The solid was then filtered, suspended in toluene, and treated again with NaH. Both toluene-soluble fractions were combined and filtered. VPC analysis showed the presence of a trace of HPC$_8$H$_{14}$ and a major component presumed to be C$_6$H$_{13}$PC$_8$H$_{14}$, previously prepared by us according to another method.[7] Purification was achieved by vacuum distillation at ca. 15 mmHg. The fraction collected between 145 and 155 °C was retained; yield 10.2 g (92.6% pure by VPC), 32.6%. Only a trace of a second isomer was seen by VPC. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −32.2 (s).

Reaction of HPC$_8$H$_{14}$ with C$_3$F$_7$I. Quaternization. HPC$_8$H$_{14}$ (9.38 g, 0.066 mol) and 20.0 g of C$_3$F$_7$I (0.068 mol) were allowed to react according to the procedure used for hexyl bromide. A white solid was obtained, which was washed with pentane and dried under vacuum; yield 17.36 g. Anal. Calcd for a 50% mixture of C$_{16}$H$_{29}$IP$_2$ and C$_{16}$H$_{28}$I$_2$P$_2$: C, 40.61; H, 6.07; P, 13.09. Found: C, 41.32; H, 6.48; P, 13.83; F, 1.08. Analyses of a replicate reaction showed variable amounts of fluorine from 1 to 6%. ^{31}P{^{1}H} NMR (CD$_3$CN): AB quartet, δ 239.9, J_{P-P} = 323 Hz; AB quartet, δ 220.9, J_{P-P} = 389 Hz; singlet, δ 297.5 (ratio 8.9:1.5:1). ^{31}P NMR (undecoupled, CD$_3$CN): singlet at δ 297.5 became a doublet, $^1J_{P-H}$ = 478 Hz. We were unable to obtain an acceptable IR spectrum.

Deprotonation. The salt from the quarternization reaction was deprotonated at room temperature according to the procedure used for the hexyl bromide reaction. The crude product was purified by three successive crystallizations from toluene cooled to −40 °C; yield 6.4 g (55% based on C$_{16}$H$_{28}$P$_2$). Anal. Calcd for C$_{16}$H$_{28}$P$_2$: C, 68.08; H, 9.99; P, 21.94. Found: C, 68.04; H, 9.97; P, 20.73; F, 0.02. ^{1}H NMR (C$_6$D$_6$): 1.86 (overlapping CH$_2$ and CH resonances). ^{31}P{^{1}H} NMR (C$_6$D$_6$) (Figure 1): δ −27.2 (AB quartet, J_{P-P} = 180 Hz), −48.0 (s).

Reaction of P(C$_8$H$_{14}$)$^-$ Anion with Alkyl Halides. To a chilled (0 °C) solution of 7.1 mL of 2.5 M butyllithium (0.018 mol) in 30 mL of diethyl ether under argon was added dropwise a solution of 2.5 g (0.018 mol) of HPC$_8$H$_{14}$ in ether. The solution turned pale yellow, and a white solid

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(1) Current address: Chevron Research Co., Richmond, CA 94802.

(2) Current address: Amoco Chemicals Co., Naperville, IL 60566.

(3) See, for example: Tolman, C. A. *Chem. Rev.* **1977**, *77*, 313.

(4) The synthesis of diphosphines has been reviewed: Fluck, E. *Prep. Inorg. React.* **1968**, *5*, 103.

(5) Corbirdge, D. E. C. *Stud. Inorg. Chem.* **1980**, *2*, 73.

(6) In U.S. Patent 3 396 197, the synthesis of C$_3$F$_7$PPh$_2$ from C$_3$F$_7$I and LiPPh$_2$ was reported. The reaction was carried out in THF at 0 °C for 16 h.

(7) Mason, R. G.; Van Winkle, J. L. U.S. Patent 3 400 163, Sept 3, 1968 (assigned to Shell Oil Co.).

0020-1669/85/1324-4437$01.50/0

formed. The solid was filtered and washed; yield 2.17 g, 81.3%.

Reaction of a suspension of the anion salt in ether at 0 °C with hexyl bromide gave $C_6H_{13}PC_8H_{14}$ as determined by VPC. A similar reaction of the salt with C_3F_7I gave equal amounts of $C_8H_{14}P–PC_8H_{14}$ and a material believed to be $C_3F_7PC_8H_{14}$[6] by VPC.

Hydroformylation Reactions. The hydroformylation experiments were conducted in standard 300-cm^3 autoclaves available from Autoclave Engineers (Erie, PA). Reaction conditions were 3500 psig (1:1 H_2/CO) and 180 °C. The catalyst was dicobalt octacarbonyl modified by a mono- or diphosphine in a fixed P/Co mole ratio of 2 and was used in the reaction solution at 0.3 or 0.6 wt % Co. In a typical run, 50 g of dodec-1-ene and 0.3 or 0.6 g of $Co_2(CO)_8$ were charged to the reactor, followed by the phosphine dissolved in 50 g of toluene. The reactor contents were then purged with N_2 and synthesis gas and pressurized to two-thirds of the final pressure with synthesis gas before heating. At the final temperature synthesis gas was admitted from a high-pressure reservoir and the pressure was held constant during the reaction. Samples were taken periodically during the reaction and analyzed by VPC.

Results and Discussion

We sought to synthesize a ligand having lower basicity than a trialkyl bicyclic phosphine but retaining the unique bicyclic steric properties by introduction of electron-withdrawing perfluoroalkyl groups into a phosphine. The system chosen was based on a family of bicyclic phosphines $P(C_8H_{14})R$ developed by Shell Oil Co.[7] wherein the bicyclic ring system results from addition of two of the three phosphine P–H bonds to the double bonds of 1,5-cyclooctadiene in the presence of a radical source. Two isomers, 9-phosphabicyclo[4.2.1]nonane and 9-phosphabicyclo[3.3.1]nonane, corresponding to 1,4- and 1,5-addition of two P–H bonds to cyclooctadiene are typically produced in a 0.55:1 ratio, respectively.[7] Reaction of the isomeric secondary phosphines with olefin gives the corresponding bicyclic tertiary phosphines.[7] Space-filling models of these phosphines show that such ligands have quite considerable steric bulk.

However, incorporation of the phosphorus atom in the bicyclic ring system fixes the relative orientation of the phosphorus atom with respect to the alkyl substituents. For example, the C–P–C bond angle in a Ni(II) complex of the bicyclic phosphine ligand 9-phenyl-9-phosphabicyclo[3.3.1]nonane is 96°.[8] Many C–P–C bond angles in tertiary alkyl phosphines are greater than 100°;[3] thus the phosphorus atom in these bicyclic phosphines is more accessible for coordination and reaction. In a different bicyclic phosphine, 1-phosphabicyclo[3.3.1]nonane, in which all three P–C bonds are to ring carbons, the Tolman cone angle was inferred to be 120–125°.[9] Thus, in the bicyclic ring systems 9-phenyl-9-phosphabicyclo[3.3.1]nonane[8] and the two isomeric bicyclic phosphines discussed in this paper, which have only two P–C bonds bound in a ring system, the cone angle should be even larger.

Reaction of the secondary phosphine HPC_8H_{14} with an equimolar amount of 1-bromohexane gave a solid white quaternary phosphonium salt. The ^{31}P NMR spectrum of this salt is consistent with a phosphonium salt containing hydrogen directly bound to phosphorus. The coupling constant, $^1J_{P-H} = 517$ Hz, is comparable to $^1J_{P-H} = 502$ Hz reported for a protonated 1-phosphabicyclo-[3.3.1]nonane.[9] Because the 0.55:1 ratio of isomers in the starting material changed to 0.28:1 in the phosphonium salt, one isomer is presumed to be more reactive than the other. Sodium hydride deprotonation of the salt gave the alkylphosphine $C_6H_{13}PC_8H_{14}$. Phosphorus NMR showed that $C_6H_{13}PC_8H_{14}$ prepared via the quarternary phosphonium salt is identical with the product we obtained by reaction of HPC_8H_{14} and hex-1-ene according to ref 7. However, only a trace of a second isomer was observed in the material prepared by the phosphonium salt method or by us using the method of ref 7, again indicating that one isomer must be more reactive than the other. Other bases used for deprotonation ($LiAlH_4$, $LiHBEt_3$, and the Li^+ form of a cation-exchange resin (Amberlite IR-20)) were not as effective.

Attempts to form the corresponding phosphonium salt $HP(C_8H_{14})C_3F_7{}^+I^-$ with C_3F_7I gave a white solid containing virtually no fluorine. The elemental analysis and phosphorus NMR of this material was consistent with a mixture of the two diphosphonium salts $HP(C_8H_{14})P(C_8H_{14})^+I^-$ and $IP(C_8H_{14})P(C_8H_{14})^+I^-$ contaminated with a trace of fluorine-containing material. Phosphorus NMR showed two AB quartets due to two isomers of the P–P-bonded diphosphonium salt $IP(C_8H_{14})P(C_8H_{14})^+I^-$ containing no direct P–H bonds. A singlet which showed P–H coupling was attributed to a symmetric isomer of $HP(C_8H_{14})P(C_8H_{14})^+I^-$ in which the hydrogen either bridges the two phosphorus atoms or rapidly exchanges between them. No evidence was seen for a second, nonsymmetric isomer of $HP(C_8H_{14})P(C_8H_{14})^+I^-$. The ratios of $IP(C_8H_{14})P(C_8H_{14})^+I^-$ to $HP(C_8H_{14})P(C_8H_{14})^+I^-$, as well as the amount of residual fluorine, varied from reaction to reaction as indicated by elemental analyses. We propose (see below) that the variable salt composition is due to varying degrees of reaction of an intermediate IPC_8H_{14} with either HPC_8H_{14} or IPC_8H_{14}. The fluorine is the result of incomplete reaction of a proposed $HP(C_8H_{14})I^+C_3F_7{}^-$ intermediate (see Scheme I). Similar diphosphonium salts have been prepared by reaction of diphosphines with both polar and nonpolar reactants.[10] Sodium hydride deprotonation of the mixture of salts, followed by repeated extraction with toluene, filtration, and evaporation, gave a white solid in 55% yield. Characterization by elemental analysis and NMR (Figure 1) suggested that the compound was a P–P-bonded diphosphine, $C_8H_{14}PPC_8H_{14}$. The ^{31}P NMR spectrum is consistent with the presence of two of three possible diphosphine isomers based on 1,4- or 1,5-addition of PH_3 to cyclooctadiene. The singlet at δ 27.2 corresponds to the isomer with the highest VPC intensity, and the AB quartet[11] is attributed to an unsymmetrical diphosphine showing both 1,4- and 1,5-addition to PH_3. The third possible isomer, containing only groups with 1,4-addition, was apparently not formed due to steric reasons.[13]

The unusual coupling reaction is the consequence of the extreme electronegativity of the R_f group resulting in a reactive $-CF_2-I$ bond. Due to the electronegativity of the perfluoroalkyl group, the polarity, and therefore the reactivity,[14] of the R_fCF_2-I bond is opposite that of "normal" alkyl halides. We propose that nucleophilic attack of HPC_8H_{14} on the iodine atom of C_3F_7I (Scheme I) results in formation of the salt $(H)(I)P(C_8H_{14})^+C_3F_7{}^-$, followed by elimination of C_3F_7H to give IPC_8H_{14}.[15] (We were not able to collect volatile products to see if C_3F_7H was formed.) Displacement of I^- from IPC_8H_{14} by reaction with HPC_8H_{14} could then give the salt $HP(C_8H_{14})P(C_8H_{14})^+I^-$. A similar reaction of IPC_8H_{14} with itself would give the salt $IP(C_8H_{14})P(C_8H_{14})^+I^-$. Such P–P-bonded phosphonium salts were proposed by Van Wazer[16] as intermediates in the exchange reactions of chlorophosphines with phosphites. A similar phosphonium salt was isolated from the nucleophilic reaction of triethylphosphine with $OPCl_3$ in ether.[17] Deprotonation of these salts with hydride leads to the diphosphine.[18]

The unexpected isolation of $C_8H_{14}PPC_8H_{14}$ from quaternization/deprotonation of HPC_8H_{14} led us to investigate direct routes to the preparation of the diphosphine. Treatment of HPC_8H_{14}

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(8) Smith, A. K. *Inorg. Chem.* **1972**, *11* (12), 3017.

(9) Krech, F.; Issleib, K. *Z. Anorg. Allg. Chem.* **1976**, *425*, 209.

(10) (a) Reference 5, p 386. (b) Appel, R.; Milker, R. *Chem. Ber.* **1975**, *108*, 1783.

(11) A P–P coupling constant of 179.7 Hz was calculated for the symmetrical diphosphine Me_2PPMe_2 from the ^1H spectrum.[12] Since the phosphorus atoms are magnetically equivalent, no coupling was seen in the ^{31}P spectrum. Thus $J_{P-P} = 180$ Hz observed for the unsymmetrical isomer of $C_8H_{14}PPC_8H_{14}$ seems reasonable.

(12) Aime, S.; Harris, R. K. *J. Magn. Reson.* **1974**, *13* (2), 236.

(13) Space-filling models of PC_8H_{14} fragments indicate that for steric reasons 1,5-addition of PH_3 to cyclooctadiene is favored over 1,4-addition. This is not intuitively obvious. The amount of 1,4-compound available for dimerization is therefore less than the amount of 1,5-product. We feel that due to steric reasons dimerization with two 1,4-fragments is less favorable than with two 1,5-fragments or with one 1,4- and one 1,5-fragment.

(14) Banks, R. E. "Fluorocarbons and Their Derivatives"; Olbourne: London, 1964; pp 58–9.

(15) The reaction temperature is probably too low to consider the possibility of radicals generated from C_3F_7I.

(16) Abraham, K. M.; Van Wazer, J. R. *Inorg. Chem.* **1975**, *14*, 1099.

(17) Lindner, E.; Beer, H. *Chem. Ber.* **1972**, *105*, 3261.

(18) Reaction of phosphinous halides with metal hydrides to give secondary phosphines is a general reaction.[4,17]

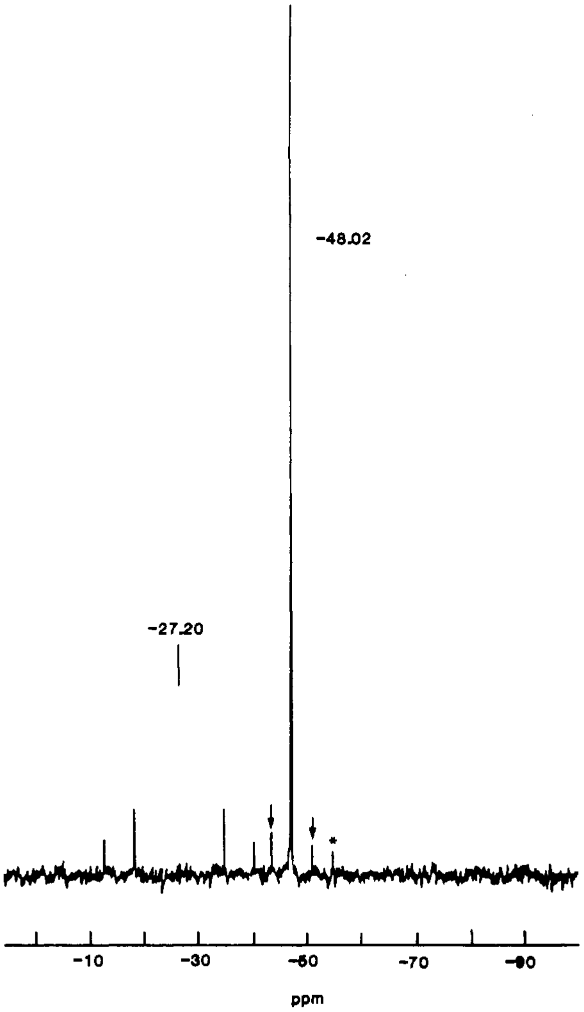
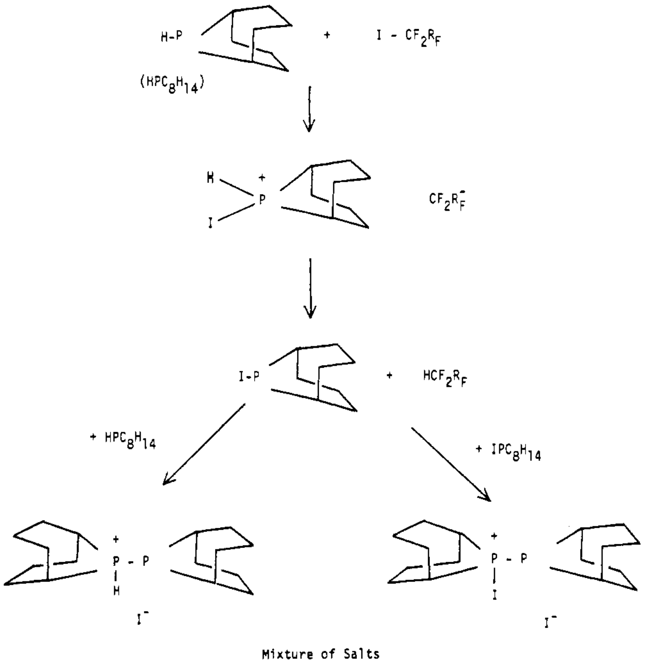


Figure 1. $^{31}P\{^1H\}$ NMR spectrum of $C_8H_{14}PPC_8H_{14}$ in benzene-d_6. The peaks marked with arrows (↓) are 120-Hz sidebands, and the peak marked with an asterisk is due to HPC_8H_{14}.

Scheme I



with *n*-butyllithium in diethyl ether at 0 °C gave the phosphide $LiPC_8H_{14}$ in >80% yield, which reacted with 1-bromohexane to give $C_6H_{13}PC_8H_{14}$. A similar reaction between the phosphide and C_3F_7I gave small amounts of both $C_8H_{14}PPC_8H_{14}$ and a species presumed to be $C_3F_7PC_8H_{14}$.[6]

In another potential synthetic route to $C_8H_{14}PPC_8H_{14}$, HPC_8H_{14} was reacted with triphenylmethyl cation at reflux in THF for 1 week. The product was a salt that was inferred to contain the cation $PC_8H_{14}^+$ [19] by reaction with hexylmagnesium bromide giving $C_6H_{13}PC_8H_{14}$. Reaction of $LiPC_8H_{14}$ (see above) with $PC_8H_{14}^+BPh_4^-$ [19] led to the formation of an unidentified product with only small amounts of the expected diphosphine.

Since bulky phosphines are known to increase the linear/branched ratios (*L*/*B* ratio) of products in the cobalt-catalyzed hydroformylation reaction,[20] we compared the oxo product obtained with the diphosphine-modified catalyst to that obtained with a related tertiary phosphine ($C_6H_{13}PC_8H_{14}$) under identical conditions (3500 psig 1:1 CO/H_2, 180 °C). Periodic product sampling during the reaction showed that the diphosphine gave $L/B = 9$ up to 50% olefin conversion, the same as was observed with the monophosphine $C_6H_{13}PC_8H_{14}$. However, above 50% conversion the *L*/*B* ratio dropped drastically so that $L/B = 1.17$ in the final product was similar to that observed with unmodified cobalt catalysts. This suggests that some thermal decomposition of the diphosphine had occurred. This decrease of the *L*/*B* ratio was not observed with the monophosphine $C_6H_{13}PC_8H_{14}$. Under these conditions, an unmodified cobalt catalyst gives a mixture of aldehyde and alcohol with low linearity ($L/B = 1$), while addition of a phosphine ligand modifier increases production of alcohol product and gives higher *L*/*B* ratios.

The loss of high linear/branched ratio must be due to some ligand decomposition process. Reaction of a tetramethyl diphosphine with an iron complex followed by proton abstraction[21] has been shown to give a coordinated R_2PH ligand. In a recent report,[22] phosphido ligands in phosphido-bridged cobalt carbonyl oxo catalysts apparently reacted with metal hydride or H_2 to give coordinated R_2PH ligands, which reacted further with olefin to give a tertiary phosphine. In the present case, if cleavage of the diphosphine giving phosphido groups occurred, further reaction to give tertiary phosphine ligands did not occur, as the high *L*/*B* product ratios typical of tertiary phosphine oxo modifiers were not maintained through the entire reaction. It is probable that decomposition of the diphosphine involves some other mechanism, such as reaction with the acidic hydrogen of the aldehyde product.

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Registry No. C_3F_7I, 754-34-7; $Co_2(CO)_8$, 15226-74-1; PH_3, 7803-51-2; 9-phosphabicyclo[4.2.1]nonane, 13396-80-0; 9-phosphabicyclo[3.3.1]nonane, 13887-02-0; 2,2′-azobis(2-methylpropionitrile), 78-67-1; hexyl bromide, 111-25-1; dodec-1-ene, 112-41-4.

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[19] Harris, T. V.; Pretzer, W. R., unpublished results.

[20] Slaugh, L. H.; Mullineaux, R. D. *J. Organomet. Chem.* **1968**, *13*, 469.

[21] Cotton, F. A.; Frenz, B. A.; Hunter, D. L. *Inorg. Chim. Acta* **1976**, *16*, 203.

[22] Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. *Organometallics* **1983**, *2*, 53.

Contribution from the Department of Chemistry,
City University of New York—Queens College,
Flushing, New York 11367

Spontaneous Oxidation of Metallotetraphenylporphyrins on Porous Vycor Glass

T. C. Strekas,* H. D. Gafney, and H. W. Goonatilake

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For tetraphenylporphyrin (TPP) and metallotetraphenylporphyrins (MTPP) the first oxidation of the TPP ring occurs at a half-potential of about 1 V (vs. SCE) and gives rise to a well-characterized porphyrin π cation radical.[1] A second oxidation