Ion-Pair Structure as a Determinant of Solvent Dependence. Solvent-Selective Formation of *tert*-Butylbis(indenyl)phosphine and *tert*-Butyl(*n*-butyl)indenylphosphine

Tshepo J. Malefetse,† Gerhard F. Swiegers,*,‡ Neil J. Coville,*,† and Manuel A. Fernandes†

Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Private Bag 3, Wits 2050, South Africa, and Division of Molecular Science, Commonwealth Scientific and Industrial Research Organisation (CSIRO), Bag 10, Clayton South, Victoria 3169, Australia

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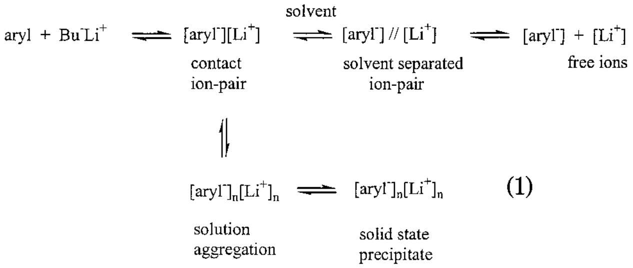
The reaction of *tert*-butyldichlorophosphine with freshly prepared lithium indene is shown to exhibit an unusual solvent dependence. In diethyl ether the reaction proceeds to the achiral *tert*-butylbis(3-indenyl)phosphine via a series of chiral intermediates. The reaction is catalyzed in-situ by the presence of solvent-separated indenyl ions in the solution. In toluene, *tert*-butyl(*n*-butyl)indenylphosphine is formed because of the selective precipitation of an unusual mixed indenyl-butyllithium aggregate prior to the addition of *tert*-butyldichlorophosphine. These mechanisms explain the solvent dependence of a range of related reactions.

Introduction

Numerous reactions involving indenyllithium exhibit a marked solvent dependence. For example, a range of alkyl,[1] boryl,[2] and other indenyl systems[3] undergo 1-indenyl substitution in nonpolar solvents but 3-indenyl substitution in more polar solvents. Another example involves a diboryl species which undergoes monoindenyl substitution when neat toluene is used as the solvent, but disubstitution when toluene containing 1.5% v/v tetrahydrofuran is used.[2a] Solvent influences such as these often appear to depend on temperature, time, or concentration, so that many researchers have attributed them to simple kinetic versus thermodynamic control.[1b,c,2c−e,3a] However, well-defined and distinct causes may underlie and be common in many such solvent effects.



(1)

Rausch[1a] has, for example, proposed that 1-indene substituents are spontaneously tautomerized to their corresponding 3-indenes by small amounts of the more basic solvent-separated indenyl ions that are present in strongly solvating solvents (Scheme 1).[1e] As such species do not exist in nonpolar solvents, this would explain why 3-indenyl products are formed in polar solvents but 1-indenyl products in nonpolar solvents.

The structure of organolithium compounds in various solvents has been a subject of some interest over the years. In weakly solvating nonpolar solvents, such as toluene or hexane, aryllithiums typically form peripherally solvated, "tight" or contact ion pairs, in which state they aggregate into solvated oligomeric units (eq 1).[4−7] These are usually poorly soluble in nonpolar solvents, so that they precipitate immediately. In more strongly

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* Corresponding authors. E-mail: g.swiegers@molsci.csiro.au, ncoville@aurum.chem.wits.ac.za.

† The University of the Witwatersrand.

‡ Commonwealth Scientific and Industrial Research Organisation (CSIRO).

[1] For example: (a) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem*. **1999**, *583*, 11. (b) Licht, E. H.; Alt, H. G.; Milius, W.; Abu-Orabi, S. *J. Organomet. Chem*. **1998**, *560*, 69. (c) Steinhorst, A.; Erker, G.; Grehl, M.; Frölich, R. *J. Organomet. Chem*. **1997**, *542*, 191. (d) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem*. **1996**, *519*, 21. (e) Meurling, L. *Acta Chem. Scand. B* **1974**, *28*, 295. (f) Gridnev, I.; Meller, A. *Main Group Met. Chem*. **1998**, *21*, 271.

[2] For example: (a) Knizek, J.; Krossing, I.; Nöth, H.; Ponikwar, W. *Eur. J. Inorg. Chem*. **1998**, 505. (b) Ashe, A. J., III; Fang, X.; Kampf, J. W. *Organometallics* **1999**, *18*, 2288. (c) Barday, E.; Frange, B.; Hanquet, B.; Herberich, G. E. *J. Organomet. Chem*. **1999**, *572*, 225. (d) Herberich, G. E.; Barday, E.; Fischer, A. *J. Organomet. Chem*. **1998**, *567*, 127. (e) Braunschweig, H.; von Koblinski, C.; Neugebauer, M.; Englert, U.; Zheng, X. *J. Organomet. Chem*. **2001**, *619*, 305.

[3] For example: (a) Schumann, H.; Karasiak, D. K.; Muhle, S. H.; Halterman, R. L.; Kaminsky, W.; Weingarten, U. *J. Organomet. Chem*. **1999**, *579*, 356. (b) Kerber, R. C.; Hodos, M. A. *J. Org. Chem*. **1968**, *33*, 1169. (c) Melera, A.; Claesen, M.; Vandergaege, H. *J. Org. Chem*. **1964**, *29*, 3705.

[4] (a) Elschenbroich, C.; Salzer, A. *Organometallics*, 2nd ed.; Weinheim: 1992; p 20 and p 24, and references therein. (b) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: Oxford, 1974; p 8, and references therein. (c) Haiduc, I.; Zuckerman, J. J. *Basic Organometallic Chemistry*; Walter de Gruyer: Berlin, 1985; p 48, and references therein.

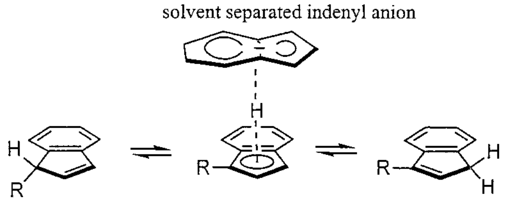
[5] Cox, R. H.; Terry, H. W.; Harrison, L. W. *J. Am. Chem. Soc.* **1971**, *93*, 3297.

[6] Vos, H. W.; Blom, H. H.; Velthorst, N. H.; MacLean, C. *J. Chem. Soc., Perkin Trans. 2* **1972**, 635, and references therein.

[7] Cox, R. H.; Terry, H. W., Jr. *J. Magn. Reson.* **1974**, *14*, 317.

10.1021/om010736k CCC: $22.00

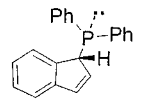
Scheme 1



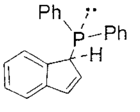
solvating solvents such as diethyl ether or tetrahydrofuran, uncontrolled precipitation typically does not occur. Instead tiny proportions of the ion pairs become solvent separated or may even form free ions, as depicted in eq 1.[4−7] Such species have quite different physical properties compared to the contact ion pairs and solution aggregations.[8−12]

In this work we describe a reaction whose solvent dependence is influenced by the composition of its solid state precipitate, the nature of its solvated aggregates, and the presence of solvent-separated ion pairs. The origin of the solvent dependence is shown to be common to other reactions involving indenyllithium.

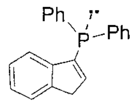
Indenyl phosphines and their group 4 metallocene complexes exhibit interesting isomeric and stereoisomeric properties associated with solvent dependence. For example, the reaction of Ph_2PCl with indenyllithium in diethyl ether produces diphenyl(1-indenyl)phosphine as the *racemic* mixture (*R*)- and (*S*)-**1**.[13] When left to stand in solution or if treated with a catalytic amount of acid or base, **1** spontaneously converts to the achiral 3-indene isomer **2**.[13]



(*R*)-**1**

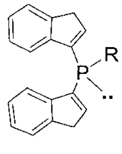


(*S*)-**1**

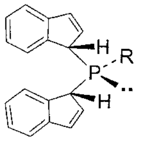


2

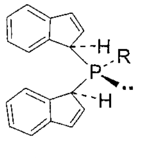
A more complex mixture is generated in the preparation of phenylbis(indenyl)phosphine. When treating $PhPCl_2$ with 2 equiv of indenyllithium in tetrahydrofuran, the achiral, 3-indene-substituted **3a** is obtained.[14] However, when toluene is used as the reaction solvent, the 1-indene product **4a** is isolated as a mixture of three diastereomers: *meso* (1*R*,1′*S*)-**4a**, *meso* (1*S*,1′*R*)-**4a**, and *racemic* (1*R**,1′*R**)-**4a**. Mixture **4a** does not spontaneously isomerize to **3a** in toluene; however it is readily converted to **3a** upon treatment with base.[14]



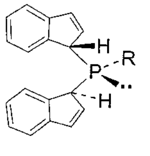
3a R=Ph
b R=^{t}Bu



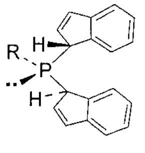
(*1S,1′R*)-**4a** R=Ph
b R=^{t}Bu



(*1R,1′S*)-**4a** R=Ph
b R=^{t}Bu

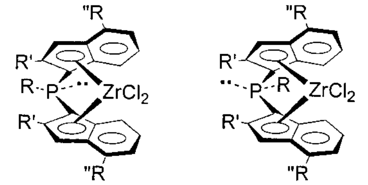


(*1S,1′S*)-**4a** R=Ph
b R=^{t}Bu

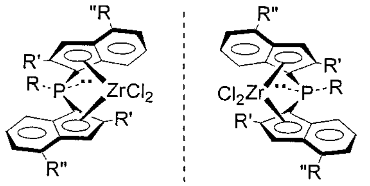


(*1R,1′R*)-**4a** R=Ph
b R=^{t}Bu

Racemic-**5** (R = Ph or ^{i}Pr; R′ = H, Me, R″ = H, Ph) has recently been shown to be an exceedingly active olefin polymerization catalyst. The isopropyl derivative (R = ^{i}Pr) is 3−5 times more active in propylene polymerization than its phenyl-substituted analogue (R = Ph).[15,16] Attempts were therefore made to prepare the *tert*-butyl-substituted derivative (R = ^{t}Bu). However the corresponding free ligand **3** (R = ^{t}Bu, R′ = Me, R″ = Ph) could reportedly not be prepared.[15]



meso-**5**



racemic-**5**

In this work we describe a detailed study of the reaction of ${}^{t}BuPCl_2$ with indenyllithium in diethyl ether and toluene. The results of this study indicate an unusual solvent dependence whose origin has been elucidated using, in part, the stereoisomeric properties of the intermediates. The preparation and isolation of the borane adducts of **3b** and **9** are also described.

Experimental Section

General Information. All reactions were performed under an inert atmosphere using Schlenk techniques. Diethyl ether

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(8) Streitwieser, A., Jr.; Chang, C. J.; Hollyhead, W. B.; Murdoch, J. R. *J. Am. Chem. Soc.* **1972**, *94*, 5288.

(9) The structure of indenyllithium ion pairs/aggregates in solution can be studied using ^{13}C NMR, e.g.: (a) Edlund, U. *Org. Magn. Reson.* **1979**, *12*, 661. (b) Eliasson, B.; Johnels, D.; Wold, S.; Edlund, U. *Acta Chem. Scand. B* **1982**, *36*, 155, and references therein. (c) Lejon, T.; Edlund, U. *Acta Chem. Scand.* **1989**, *43*, 275.

(10) The structure of indenyllithium ion pairs/aggregates in solution can be studied using ^{1}H NMR, e.g.: Gooijer, C.; Velthorst, N. H. *Org. Magn. Reson.* **1979**, *12*, 684.

(11) The structure of indenyllithium ion pairs/aggregates in solution can be studied using fluorescence spectroscopy, e.g.: Vos, H. W.; MacLean, C.; Velthorst, N. H. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 63.

(12) The structure of indenyllithium ion pairs/aggregates in solution can be studied using combinations of the techniques described in refs 9−11, for example: Edlund, U.; Eliasson, B.; Kowalewski, J.; Trogen, L. *J. Chem. Soc., Perkin Trans. 2* **1981**, 1260.

(13) Fallis, K. A.; Anderson, G. K.; Rath, N. P. *Organometallic* **1992**, *11*, 885.

(14) Lensink, C.; Gainsford, G. J. *Aust. J. Chem.* **1998**, *51*, 667.

(15) Schaverien, C. J.; Ernst, R.; Terlouw, W.; Schut, P.; Sudmeijer, O.; Budzelaar, P. H. M. *J. Mol. Catal. A* **1998**, *128*, 245.

(16) Other P-bridged *ansa*-metallocene group IV complexes have also been reported. For example: (a) Shin, J. H.; Hascall, T.; Parkin, G. *Organometallics* **1999**, *18*, 6. (b) Leyser, N.; Schmidt, K.; Brintzinger, H.-H. *Organometallics* **1998**, *17*, 2155. Phospholyl rings have also been employed in *ansa*-zirconocene olefin polymerization catalysts, e.g.: (c) Janiak, C.; Lange, K. C. H.; Versteeg, U.; Lenz, D.; Budzelaar, P. H. M. *Chem. Ber.* **1996**, *129*, 1517. (d) de Boer, E. J. M.; Gilmore, I. J.; Korndorffer, F. M.; Horton, A. D.; van der Linden, A.; Royan, B. W.; Ruisch, B. J.; Schoon, L.; Shaw, R. W. *J. Mol. Catal. A Chem.* **1998**, *128*, 155.

was distilled over sodium benzophenone ketyl. Toluene was distilled over calcium hydride. $^{31}P\{^1H\}$, ^{13}C, and ^1H NMR spectra were recorded at 20 °C on a Bruker AC200 instrument operating at a proton frequency of 200 MHz. $^{31}P\{^1H\}$ NMR spectra were referenced to external aqueous H_3PO_4 (85%). $^7Li\{^1H\}$ NMR spectra were recorded on a Bruker DRX500 spectrometer operating at a lithium frequency of 500 MHz. A solution of 1 M LiCl in D_2O was used as an external standard ($\delta = 0$). One drop of benzene-d_6 was added to test solutions in order to lock the signal. Mass spectra were recorded on the following mass spectrometers: JEOL DX303 (EI and FAB) and a VG Platform (ES). Elemental analyses were carried out by staff at the University of Queensland. *tert*-Butyldichlorophosphine was prepared by the method described in ref 17. Indene was purified by stirring with 6 M HCl for 24 h (to remove basic nitrogenous material), then refluxing with 40% NaOH for 2 h (to remove benzonitrile), followed by fractional distillation.[18] Borane methyl sulfide complex and butyllithium (2.0 M solution in hexanes) were obtained from Aldrich. Silica 60 (240−400 mesh ASTM) was supplied by Merck. Compound **3a** was prepared by a previous method[14] and converted to **3a**·BH_3 by the addition of borane methyl sulfide complex as described below.

X-ray Structure Determinations of 3b·BH_3, 9·BH_3, and 3a·BH_3. Suitable crystals were obtained by recrystallization from hot ethanol (**3b**·BH_3) and dichloromethane−hexane (**9**·BH_3, **3a**·BH_3). Full crystallographic details including data collection and processing parameters, atomic coordinates and anisotropic displacement parameters, and bond distances and angles are provided as Supporting Information. Intensity data were collected on a Bruker SMART 1K CCD area detector diffractometer with graphite-monochromated Mo Kα radiation (50 kV, 30 mA). The collection method involved ω-scans of width 0.3°. Data reduction was carried out using the program SAINT+[19] and further processed using the program SADABS.[20] The crystal structure was solved by direct methods using SHELXTL.[21] Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full matrix least-squares calculation based on F^2 using SHELXTL. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. Diagrams and publication material were generated using SHELXTL and PLATON.[22]

Synthesis of *tert*-Butylbis(indenyl)phosphine-borane, 3b·BH_3. ^nBuLi (1.6 M in hexanes) (10.76 mL, 17.22 mmol, 2 equiv) was added to a stirred mixture of distilled indene (2.00 g, 2.0 mL, 17.22 mmol, 2 equiv) in anhydrous diethyl ether (200 mL) which had been cooled to −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 5 h. During this time the solution became yellow. After again cooling to −78 °C, a mixture of $^tBuPCl_2$ (1.36 g, 8.61 mmol, 1 equiv) in diethyl ether (50 mL) was added dropwise with stirring. The reaction was allowed to warm to room temperature and stirred overnight. Neat $Me_2S·BH_3$ (0.86 mL, 8.61 mmol) was then added dropwise and the mixture heated at reflux for 1 h. After cooling to room temperature, the solution was filtered and evaporated in vacuo, leaving an orange oil. The oil was taken up in dichloromethane, and hexane was added until the mixture was at the point of turbidity. After standing overnight, **3**·BH_3 formed as colorless crystals, which were filtered and air-dried. The remaining solution was evaporated and chromatographed on silica using 1:1 hexane−diethyl ether as eluant. The first major band (R_f 0.69) was collected. The combined solids were recrystallized from ethanol as colorless air-stable needles. Total yield: 2.13 g (75%), mp 186.0 °C. Anal. Calcd (found) for $C_{22}H_{26}BP$: C, 79.6 (79.5); H, 8.0 (7.9). ^1H NMR (200 MHz, $CDCl_3$): δ 7.47 (t, $^3J = 6$ Hz, 4H, ArH), 7.30 (d, $^3J = 6$ Hz, 2H, 2-indene CH), 7.15 (q, $^3J = 6$ Hz, 4H, ArH), 3.62 (s, 4H, 3-indene CH), 1.45 (d, $^3J_{PH} = 14$ Hz, 9 H, ^{t}Bu-H), 0.8 (br s, 3H, BH). ^{13}C NMR (200 MHz, $CDCl_3$): δ 146.7, 146.6, 143.8, 143.4, 143.2, 132.5, 131.5, 126.3, 125.3, 123.6, 123.2, 40.5, 40.3, 31.5, 30.8, 26.9. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 17.6, 16.9 (d, $^1J_{PB} = 41$ Hz). EI-MS (m/z) 347.0 $[M{=}O]^+$.

Synthesis of *tert*-Butyl(*n*-butyl)(indenyl)phosphine-borane, 9·BH_3. ^nBuLi (2.0 M in hexanes) (8.61 mL, 17.22 mmol, 2 equiv) was added to a stirred mixture of distilled indene (2.00 g, 2.0 mL mL, 17.22 mmol, 2 equiv) in anhydrous toluene (200 mL) which had been cooled to −78 °C. The mixture was allowed to warm to room temperature and stirred for a further 5 h. After again cooling to −78 °C, a mixture of $^tBuPCl_2$ (1.36 g, 8.61 mmol, 1 equiv) in toluene (50 mL) was added dropwise with stirring. The reaction was allowed to warm to room temperature and stirred for 24 h. Neat $Me_2S·BH_3$ (0.86 mL, 8.61 mmol) was then added dropwise and the mixture heated at reflux for 1 h. After cooling to room temperature, the solution was filtered and evaporated in vacuo, leaving an orange oil. The oil was chromatographed on silica using hexane as eluent until all of the unreacted indene was removed. The solvent was then changed to 1:1 hexane−diethyl ether. The first major band (R_f 0.85) was collected, evaporated, and recrystallized from dichloromethane−hexane as colorless needles. Yield: 1.91 g (81%), mp 98−100 °C. Anal. Calcd (found) for $C_{17}H_{28}BP$: C, 74.5 (74.7); H, 10.3 (10.0). ^1H NMR (200 MHz, $CDCl_3$): δ 7.97 (d, $^3J = 8$ Hz, 1H, ArH), 7.16 (m, 3H, ArH), 6.70 (d, $^3J = 8$ Hz, 1H, 2-indene CH), 3.0 (s, 2H, 3-indene CH), 1.96 (m, 2H, $-CH_2-$), 1.68 (m, 2H, $-CH_2-$), 1.29 (m, 2H, $-CH_2-$), 1.09 (d, $^3J_{PH} = 14$ Hz, 9 H, ^{t}Bu-H), 0.79 (t, 3H, ^{3}J 8 Hz, CH_3-), 1.60−1.00 (br, 3H, BH). ^{13}C NMR (200 MHz, $CDCl_3$): δ 149.6, 149.5, 126.8, 125.6, 124.2, 123.5, 40.3, 30.0, 29.4, 26.0, 25.7, 24.9, 24.7, 20.2, 19.5, 13.8. $^{31}P\{^1H\}$ NMR (200 MHz, $CDCl_3$): δ 27.2, 28.1 (d, $^1J_{PB} = 41$ Hz). EI-MS (m/z): 290.0 $[^tBu^nBu(indenyl)P(O)BH_3]^+$. The second chromatography band contained **3b**·BH_3 in 0.16 g yield.

Results and Discussion

Reaction in Diethyl Ether. A diethyl ether solution containing 2 equiv of indene was cooled to −78 °C and treated with 2 equiv of *n*-butyllithium. The mixture was allowed to warm to room temperature and stirred for a further 5 h to allow complete formation of indenyllithium. When then treated with 1 equiv of $^tBuPCl_2$ in diethyl ether, a pale yellow solution was obtained which contained an air-sensitive mixture of phosphines (Scheme 2). $^{31}P\{^1H\}$ NMR of the mixture revealed multiple resonances which could not be assigned. However, the addition, after stirring for 24 h, of borane methyl sulfide complex, $Me_2S·BH_3$, converted the free phosphines to their corresponding borane adducts, which are air-stable and readily chromatographed. The $^{31}P\{^1H\}$ NMR spectrum of this mixture contained resonances at δ 17.4 (84%), 19.1 (8%), and 38.9 (8%). Accurate quantifications of the relative proportions of the *P*-containing materials in the mixture were made by employing long delay times (>50 s) in the NMR experiments.[23]

The mixture of borane adducts was separated by chromatography on silica using diethyl ether−hexane

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[17] Fild, M.; Stelzer, O.; Schmutzler, R.; Doak, G. O. *Inorganic Syntheses*; Wiley: New York. 19XX; Vol. XIV, p 4.

[18] Perrin, D. D.; Armarego, W. L. F. *Purification of Organic Chemicals*, 3rd ed.; Pergamon Press: Oxford, 1988.

[19] *SAINT+*, version 6.02 (includes XPREP and SADABS); Bruker AXS Inc.: Madison, WI, 1999.

[20] Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 1996.

[21] *SHELXTL*, version 5.1. (includes XS, XL, XP, XSHELL); Bruker AXS Inc.: Madison, WI, 1999.

[22] Spek, A. L. *Acta Crystallogr.* **1990**, *A46*, C34.

[23] As used in: Dogan, J.; Schulte, J. B.; Swiegers, G. F.; Wild, S. B. *J. Org. Chem.* **2000**, *65*, 951. Correction: *J. Org. Chem.* **2000**, *65*, 4782.

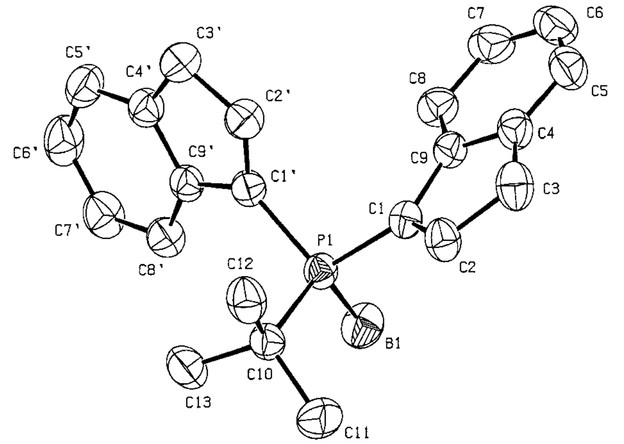
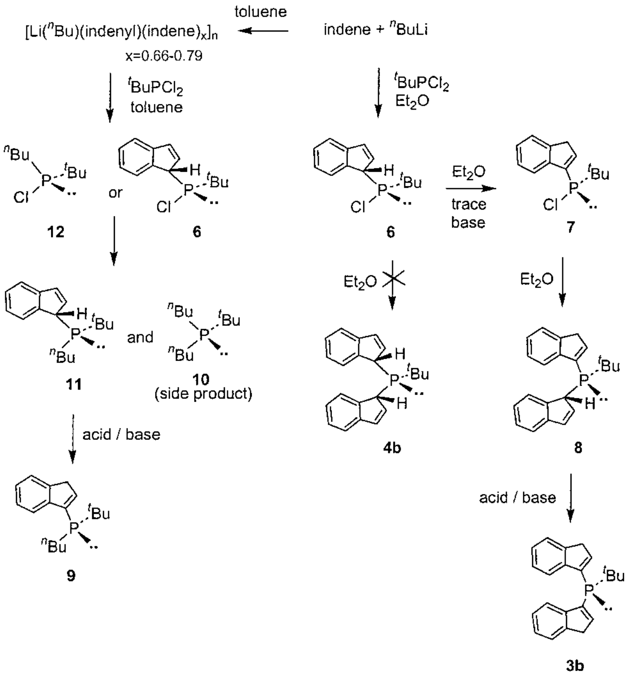


Figure 1. ORTEP diagram of **3b**·BH_3 showing the atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids drawn at the 50% probability levels.

Scheme 2



as eluent. The first band contained the major product (δ 17.4), which was isolated as colorless needles after recrystallization from ethanol. This solid analyzed as the bis(3-indenyl) isomer **3b**·BH_3. A single-crystal X-ray structure determination (Figure 1) confirmed its composition.

The second chromatography band was isolated as an amorphous solid which contained the two minor species observed in the mother liquor (δ 19.1 and δ 38.9). The ^1H NMR spectrum ($CDCl_3$) of this material was extremely complex, containing four major and at least two minor ^{t}Bu doublets, four 3-indenyl 1-C*H* singlets, and four 1-indenyl P-C*H* multiplets. The number of resonances present and the large integrations of the 3-indenyl 1-C*H* singlets compared to the four 1-indenyl P-C*H* multiplets indicated that the solid consisted of **7**·BH_3 (1 diastereomer) and **8**·BH_3 (3 diastereomers), with effectively no **4b**·BH_3 present. Mass spectrometry (EI, FAB, and ES) was consistent with this assignment. The $^{31}P\{^1H\}$ NMR resonances were therefore assigned to **7**·BH_3 (δ 38.9) and **8**·BH_3 (δ 19.1). Attempts to separate the mixture by fractional crystallization or HPLC were unsuccessful, as were attempts to regenerate the free phosphines by removal of the borane adducts using standard release techniques (e.g., heating in the presence of diethylamine).[24]

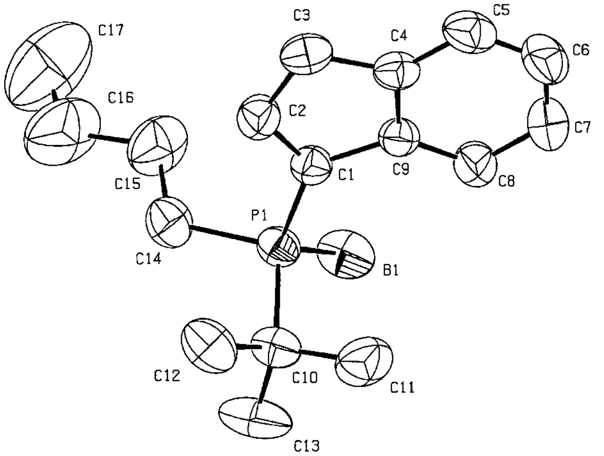


Figure 2. ORTEP diagram of **9**·BH_3 showing the atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids drawn at the 50% probability levels.

Reaction in Toluene. A toluene solution containing 2 equiv of indene was treated with 2 equiv of *n*-butyllithium. A white precipitate was immediately seen to commence formation. The mixture was stirred for a further 5 h. The resulting slurry was then treated with 1 equiv of ^{t}BuPCl_2 in toluene and stirred for 24 h, giving a solution that contained an air-sensitive mixture of phosphines (Scheme 2). $^{31}P\{^1H\}$ NMR of the solution indicated a complex mixture of resonances which could not be assigned. Treatment with borane methyl sulfide produced a pale yellow mixture displaying $^{31}P\{^1H\}$ NMR resonances at δ 37.9 (5%), 31.8 (10%), 27.8 (81%), and 17.3 (**3b**: 4%). The major product (δ 27.8) was separated by chromatography and recrystallized as colorless needles from dichloromethane–hexane. NMR, mass spectrometry, and an X-ray crystal structure determination (Figure 2) established this product to be the borane adduct of (*tert*-butyl)(*n*-butyl)indenyl phosphine, **9**·BH_3. A substantial quantity of free indene was recovered as a fast-moving band during the chromatography step.

The species exhibiting an NMR resonance at δ 31.8 could be relatively enriched by heating the toluene reaction mixture for an extended period. The reaction in toluene was therefore repeated with heating to 100 °C for 3 days prior to the addition of borane methyl sulfide. $^{31}P\{^1H\}$ NMR of the mixture after the addition of the borane produced only the resonance at δ 31.8. Filtration of the solution, followed by evaporation in vacuo and isolation by chromatography, produced an oil which could be recrystallized from dichloromethane–hexane to yield colorless crystals. These analyzed as **10**·BH_3 by elemental analysis, mass spectrometry, and ^1H/^{13}C NMR spectroscopy. The $^{31}P\{^1H\}$ NMR resonances in the original reaction mixture in toluene could therefore be assigned to **6**·BH_3 or **11**·BH_3 (δ 37.9), **10**·BH_3 (δ 31.8), **9**·BH_3 (δ 27.8), and **3b**·BH_3 (δ 17.3). Substantial quantities of unreacted indene were isolated during the

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[24] Imamoto, T.; Kusumoto, T.; Suzuki, N.; Sato, K. *J. Am. Chem. Soc.* **1985**, *107*, 5301.

chromatography step. The isolated yield of **10**·BH$_3$ was <5%, suggesting that the other species present in the reaction mixture decomposed during the extended heating.

Origin of *n*-Butyl Substituents in 9 and 10. To understand the origin of the *n*-Bu substituents in **9** and **10**, the formation and composition of the indenyllithium precipitate formed in toluene was studied.

When an appropriate quantity of *n*-butyllithium (as a solution in hexane) was added to toluene, a clear, colorless solution was obtained which displayed a major ^{7}Li NMR resonance at δ 1.21 and a minor one at δ 1.82. Depending on the concentration of the *n*-BuLi solution used, the proportion of the peaks was found to vary from 95:5 respectively (using a ca. 0.35 M solution of *n*-BuLi in hexane) to 51:49 respectively (using a 2.20 M solution of *n*-BuLi in hexane). A 5 s delay time was provided in these experiments to allow for complete relaxation of the nuclei and therefore accurate integrations. The presence of the two resonances suggests that two different aggregations exist in solution since the same samples of *n*-BuLi in hexanes display only one, sharp ^{7}Li NMR resonance (at δ 0.02) when added to THF. The relative quantity of hexane present in the toluene solutions appeared to influence the proportions of the aggregates.

Upon addition of the appropriate amount of indene, a white precipitate immediately commenced formation. The rate of its formation could be followed by tracking changes in the signal:noise ratio of the ^{7}Li NMR peaks in the supernatant solution. A 5 s delay time was employed in these experiments to allow for complete relaxation of the nuclei and accurate integrations. The reaction was found to occur very rapidly in the first 30 min (ca. 75% complete). After 2 h, it was 95% complete with little further change thereafter. As the indenyllithium solutions employed in the preparation of **9** and **10** were stirred for 5 h prior to treatment with *t*-BuPCl$_2$, the *n*-butyl substituents in **9** and **10** could not have come from unreacted butyllithium present in the solution.

After stirring 5 h, the white precipitate was allowed to settle and the supernatant tested for the presence of indene. Comparative integrations of HPLC traces of samples taken before and after precipitate formation indicated that ca. 8%−19% of the original indene present remained dissolved in the supernatant solution. This is approximately consistent with the ^{7}Li NMR results and indicates that a large portion of the indene was incorporated in the precipitate.

The precipitate was then filtered under inert atmosphere and washed with toluene. When dissolved in THF, it produced a deep yellow-brown solution which exhibited two broad ^{7}Li NMR resonances centered at ca. δ 1.15 (55%) and −4.8 (45%). The latter is characteristic of aryllithiums, being near the expected shift for indenyllithium in THF (δ −6.12).[5,7] The former is characteristic of alkyllithiums. The precipitate must therefore have contained a substantial proportion of *n*-butyllithium, this being the only alkyllithium available.

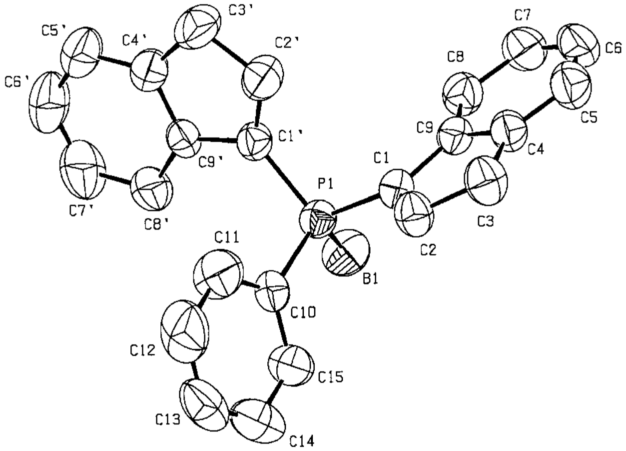

Figure 3. ORTEP diagram of **3a**·BH$_3$ showing the atom-labeling scheme for non-hydrogen atoms. Thermal ellipsoids drawn at the 50% probability levels.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 3b·BH$_3$, 9·BH$_3$, and 3a·BH$_3$

	3b·BH$_3$	**9**·BH$_3$a	**3a**·BH$_3$
P(1)−C(1)	1.807(3)	1.809(2)	1.794(2)
P(1)−C(1′)	1.818(3)	1.812(2)	1.798(2)
P(1)−C(10)	1.862(3)	1.853(3)	1.806(2)
P(1)−B(1)	1.932(3)	1.927(3)	1.919(3)
C(2)−C(3)	1.494(4)	1.487(3)	1.492(3)
C(2′)−C(3′)	1.484(4)		1.498(3)
C(1)−C(2)	1.345(4)	1.347(3)	1.335(3)
C(1′)−C(2′)	1.335(4)		1.334(3)
C(1)−P(1)−C(1′)	102.96(12)	104.91(10)	104.92(9)
C(1)−P(1)−C(10)	110.96(12)	106.98(10)	105.53(9)
C(1′)−P(1)−C(10)	104.63(12)	106.02(11)	104.57(9)
C(1)−P(1)−B(1)	108.2(2)	115.3(1)	113.1(1)
C(1′)−P(1)−B(1)	116.1(2)	110.7(1)	114.7(1)
C(10)−P(1)−B(1)	113.5(2)	112.3(1)	113.1(1)

[a] C(1′) replaced by C(14) in **9**·BH$_3$.

To test the reactivity of the precipitate, a sample was suspended in fresh toluene and the appropriate quantity of *t*-BuPCl$_2$ was added. The reaction was then continued to completion as described in the previous section. TLC of the resulting mixture indicated that the major product was **9**·BH$_3$. Therefore the *n*-butyl substituents in **9** and **10** originate from the formation of a mixed *n*-butyl-indenyllithium precipitate during the reaction of indene with *n*-butyllithium in toluene.

The weight percentage of lithium in the precipitate was determined by treating a weighed, dry sample with water and then titrating this with HCl. By this measure 4.99%−5.35% w/w of the precipitate was Li$^+$; this corresponds to an empirical formula [Li$_2$(indenyl)(*n*-butyl)(indene)$_x$], where $x = 0.66-0.79$. The release of free indene during the formation of **9**·BH$_3$ in toluene is consistent with the presence of unreacted indene in the precipitate. The extreme reactivity of the dried precipitate (even with the trace hydrogen gas required in a drybox atmosphere) precluded a conventional elemental analysis.

Crystal Structures of 3b·BH$_3$ and 9·BH$_3$. Figures 1, 2, and 3 show ORTEP views of **3b**·BH$_3$, **9**·BH$_3$, and **3a**·BH$_3$ respectively. A summary of the important bond lengths and angles in these compounds is compiled in Table 1.

Indicators of steric strain at the central P atom in **3a**·BH$_3$ and **3b**·BH$_3$ are the bond angles and bond lengths associated with the groups attached to the P atom. The bond lengths of *all* groups attached to P in **3b**·BH$_3$ (Table 1) are longer than those in **3a**·BH$_3$, suggesting larger steric interactions between the groups in the

Table 2. Crystal Data and Structure Refinement Details for 3a·BH_3, 9·BH_3 and 3b·BH_3

	3b·BH_3	**9**·BH_3	**3a**·BH_3
empirical formula	$C_{22}H_{26}BP$	$C_{17}H_{28}BP$	$C_{24}H_{22}BP$
fw (g mol^{-1})	332.21	274.17	352.20
temperature (K)	293(2)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
unit cell dimens			
a (Å)	10.2392(6)	7.5080(10)	14.455(2)
b (Å)	14.9110(9)	12.7232(17)	7.2529(10)
c (Å)	12.6693(8)	19.642(2)	21.973(3)
α (deg)	90	90	90
β (deg)	102.9860(10)	109.996(5)	118.729(7)
γ (deg)	90	90	90
volume (Å^3)	1884.8(2)	1763.2(4)	2020.1(5)
Z	4	4	4
density(calcd) (Mg/m^3)	1.171	1.033	1.158
abs coeff (mm^{-1})	0.146	0.143	0.140
$F(000)$	712	600	744
cryst size (mm)	0.40 × 0.08 × 0.04	0.49 × 0.17 × 0.06	0.42 × 0.34 × 0.10
θ range for data collection (deg)	2.14 to 26.00	1.94 to 27.45	1.61 to 25.00
index ranges	$-12 < h < 12$, $-16 < k < 18$, $-15 < l < 11$	$-9 < h < 9$, $-16 < k < 16$, $-13 < l < 25$	$-17 < h < 13$, $-8 < k < 8$, $-23 < l < 25$
no. of reflns collected	10078	11524	7396
no. of ind reflns	3669 [R(int) = 0.0439]	4014 [R(int) = 0.0383]	3398 [R(int) = 0.0212]
completeness to maximum θ	98.9%	99.5%	95.4%
abs corr	empirical	empirical	empirical
max. and min. transmn	0.9942 and 0.9441	0.9915 and 0.9333	0.9861 and 0.9436
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3669/0/221	4014/0/117	3398/0/236
goodness-of-fit on F^2	1.141	1.037	1.099
final R indices [$I > 2\sigma(I)$] (R, R_w)	0.0697, 0.1204	0.0523, 0.1334	0.0428, 0.1183
R indices (all data) (R, R_w)	0.0986, 0.1307	0.0985, 0.1521	0.0628, 0.1281
largest diff peak and hole (e·Å^{-3})	0.314 and −0.239	0.301 and −0.276	0.270 and −0.224

former complex than in the latter complex. In addition, the C(indenyl)−P−C(indenyl) angle in **3b**·BH_3 is 102.97°. In **3a**·BH_3 it is 104.92°. The tighter angle and greater strain in **3b**·BH_3 are consistent with the bulk of the ^{t}-Bu group when compared to the Ph group.

The introduction of a tetrahedral bridgehead carbon in the indenyl substituents when going from **3** to **4** increases the strain. Thus, for example, previous work has shown that the C(indenyl)−P−C(indenyl) angle of 103.7° in the sulfide of **4a** is 2.8° less than the 106.1° angle in the sulfide of **3a**.[14] By this measure, **4b**·BH_3 should have a C(indenyl)−P−C(indenyl) angle of ca. 100.2° and free **4b** a still smaller angle. The comparable free *tert*-butylbis(1-indenyl)arsine displays a C(indene)−As−C(indene) bond angle of 96.4° despite the larger arsenic center and significantly longer heteroatom−C(indene) bonds.[25]

By comparison, **9**·BH_3 is considerably less strained, having a C(indenyl)−P−C(butyl) angle of 104.91°; **10**·BH_3 is presumably still less strained.

Summary. Under otherwise identical conditions, the reaction of indene and BuLi, followed by the addition of ^{t}BuPCl$_2$, produces predominantly **3b** in diethyl ether but **9** in toluene.

The formation of **3b** in diethyl ether has been shown to involve the intermediates **6**, **7**, and **8**, which are observed as side-products. The data indicate that **6** does not form **4b** in significant quantities. Instead it is spontaneously tautomerized in solution to **7**, which then forms **8**. While both **8** and **4b** contain two indenyl groups and are therefore sterically strained, one of the indenyl groups in **8** is a less hindered 3-indenyl substituent. The reaction therefore selectively proceeds along the least strained pathway. This can only occur if an acid- or base-catalyzed tautomerization of **6** → **7** takes place in situ. The only possible catalyst of this type available in the reaction solution is solvent-separated indenyl anions; these must induce the rearrangement.[26] This sequence of events therefore verifies the correctness of Rausch's proposal[1a] regarding the influence of solvent-separated indenyl anions in strongly solvating solvents and indicates its generality to a range of reactions involving indenyllithium.[1−3]

The mechanism by which **8** is isomerized to **3b** most likely involves solvent-separated indenyl ions but could also result from the addition of the borane methyl sulfide.

The reaction of butyllithium and indene in toluene results in the precipitation of an unusual, mixed salt having the empirical formula [Li$_2$(indenyl)(n-butyl)(indene)$_x$] (x = 0.66−0.79). Since indenyllithium is undoubtedly the thermodynamically preferred product, this material must be an intermediate aggregation whose poor solubility causes its precipitation as a kinetic product.

When the salt is treated with ^{t}BuPCl$_2$, **6** or **12** and then **11** are formed, along with some **10** as byproduct. The addition of borane methyl sulfide presumably induces the conversion of **11** to **9**. The resulting mixture contains disproportionately tiny amounts of **3b**, pre-

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[25] Rufanov, K.; Avtomonov, E.; Kazennova, N.; Kotov, V.; Khvorost, A.; Lemenovskii, D.; Lorbeth, J. *J. Organomet. Chem.* **1997**, *536−537*, 361.

[26] The mechanism of base-catalyzed prototropic indene isomerizations of this type is known: Almy, J.; Uyeda, R. T.; Cram, D. J. *J. Am. Chem. Soc.* **1967**, *89*, 6768, and references therein.

sumably because it would have to be formed via the intermediacy of the strained **4b**. Because it is substantially less hindered than **3b** and **9**, **10** appears to be significantly more stable to decomposition at elevated temperature.

These results explain the previous report involving the reaction of a diboryl moiety with indenyl in which monosubstitution was observed when neat toluene was used as solvent but disubstitution when toluene containing 1.5% v/v THF was used.[2a] The lithium salt precipitated in neat toluene was presumably also a mixed species. The addition of 1.5% THF most likely solubilized the aggregation, allowing its rearrangement to the conventional, thermodynamically favored indenyllithium salt.

The previously reported formation of **4a** in toluene[14] cannot be directly compared to the formation of **9**, since the indenyllithium used in that reaction was not prepared in toluene. The use of borane methyl sulfide would, additionally, have transformed **4a** into **3a**·BH_3.

Conclusions

Solvent dependence in the formation of *t*-Bu-substituted indenyl phosphines has been shown to arise from the composition of solid state precipitates (in toluene) or the presence of solvent-separated ion pairs (in diethyl ether). The reaction of *tert*-butyldichlorophosphine and indenyllithium in diethyl ether proceeds via the less hindered intermediates **7** and **8**, to generate **3b** as the final product. This progression can only occur because of the presence of solvent-separated indenyl anions which catalyze the in-situ transformation of 1-indene substituents to 3-indenes. In toluene, a poorly soluble, mixed indenyl-butyllithium aggregate—which is normally an intermediate in the reaction—precipitates. Treatment with *tert*-butyldichlorophosphine then produces **11**. Treatment with borane methyl sulfide causes the 1-indenyl substituent in **11** to be transformed to a 3-indenyl, yielding **9**·BH_3 as the final product.

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Supporting Information Available: A listing of the atomic coordinates, bond lengths, bond angles, anisotropic displacement parameters, and torsion angles for the crystal structures of **3a**·BH_3, **3b**·BH_3, and **9**·BH_3 is available. This material can be obtained, free of charge, via the Internet at http://pubs.acs.org.

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