Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 23 (2004) 489–497

ELSEVIER

POLYHEDRON

www.elsevier.com/locate/poly

Platinum-alkyl and hydride complexes supported by a tris(phosphino)borate ligand: structural and spectroscopic studies

J. Christopher Thomas, Jonas C. Peters *

Division of Chemistry and Chemical Engineering, Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, CA 91125, USA

Received 30 July 2003; accepted 8 October 2003

Abstract

The synthesis and characterization of platinum-methyl and hydride complexes containing the ligand [$PhBP_3$] ([$PhBP_3$] = [$PhB(CH_2PPh_2)_3$]$^-$) are described. Metalation of [$PhBP_3$][TBA] (**1[TBA]**, [TBA] = [^{n}Bu_4N]$^+$) with platinum methyl precursors provided the corresponding phosphine methyl platinum species [$PhBP_3$]$PtMe_3$ (**2**) and [[κ^2-$PhBP_3$]$PtMe_2$][TBA] (**3**). The reactivity of octahedral **2** and square planar **3** are discussed, and their X-ray diffraction structures are reported. Octahedral Pt(IV) **2** was found to be very thermally and chemically robust. In contrast, the square planar Pt(II) complex **3** demonstrated reactivity at both the platinum center and the unbound phosphine. The reaction of **3** with one equivalent of elemental sulfur provided the corresponding phosphine-sulfide [[κ^2-$PhB(CH_2P(S)Ph_2)(CH_2PPh_2)_2$]$PtMe_2$][TBA] (**4**). Similarly, the reaction of **3** with one equivalent of $BH_3 \cdot SMe_2$ generated the borane-protected complex [[κ^2-$PhB(CH_2P(BH_3)Ph_2)(CH_2PPh_2)_2$]$PtMe_2$][TBA] (**5**). Complex **5** was significantly less reactive than **3** to a variety of substrates under similar conditions; however, the reaction of **5** with additional $BH_3 \cdot SMe_2$ resulted in the formation of the platinum(I) bridged hydride species [[κ^2-$PhB(CH_2P(BH_3)Ph_2)(CH_2PPh_2)_2$]Pt($\mu$-H)]$_2$[TBA]$_2$ (**6**).

Keywords: Zwitterions; Monoanionic ligands; Syntheses; Structures; Methyl; Hydrides

1. Introduction

Trofimenko's tris(pyrazolyl)borate ligands [1] have been widely used in mechanistic C–H activation studies. Several studies of the noble group 9 metals (Rh and Ir) have exploited the scorpionates, such as the recent works of Bergman and Harris [2], as well as that of Jones [3]. Important advances in [Tp]-supported platinum C–H activation chemistry have also emerged ([Tp] = hydrotris(pyrazolyl)borate, [$HB(pz)_3$]$^-$). For example, in an elegant experiment, Goldberg's group showed that the anionic complex K[[κ^2-Tp_2^{Me}]$PtMe_2$] ([Tp_2^{Me}] = hydrotris(3,5-dimethylpyrazolyl)borate) reacts with $B(C_6F_5)_3$ to generate an unobserved, presumed 3-coordinate species, "[κ^2-Tp_2^{Me}]PtMe", that then undergoes oxidative C–H bond addition to afford octahedral platinum(IV) alkyl hydride products, [κ^3-Tp_2^{Me}]Pt(Me)(R)H [4]. A number of interesting studies have followed this early report, including the isolation of a well-defined five-coordinate Pt(IV) species [5], a rare η^2-benzene adduct of platinum(II) [6], and mechanistic investigations of reductive elimination from platinum(IV) [7,8]. Given the considerable momentum behind [Tp]-supported C–H activation studies, it seemed prudent to us to begin examining other tripodal borate ligands for comparison [9]. We have therefore begun to develop the platinum chemistry of a related class of tris(phosphino)borate ligands. These latter ligands resemble the classic scorpionates by virtue of having three donor arms anchored by a borate unit so that they bind most typically in a tripodal fashion. Despite these similarities, the (phosphino)borates appear to be electronically, as well as sterically, quite distinct from [Tp]-type ligands. For example, the monoanionic (phosphino)borate complexes of platinum feature an anionic borate unit that is more spacially separated from the coordinated platinum center in both κ^3- and κ^2-binding modes

---

* Corresponding author.
E-mail address: jpeters@caltech.edu (J.C. Peters).

0277-5387/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2003.11.036

by comparison to structurally related [Tp] complexes (vide infra). Moreover, the absence of simple resonance contributors that would efficiently distribute the anionic borate charge in these (phosphino)borate complexes suggests that they can be reasonably regarded as molecular "zwitterions" [10]. Such a descriptor is not typically attributed to [Tp]-supported complexes, where resonance delocalization of the borate charge is normally presumed [11].

In the present study, we describe for the first time aspects of the platinum coordination chemistry of the tris(phosphino)borate ligand $[PhB(CH_2PPh_2)_3]^-$ (**1**, $[PhBP_3]$). We report on the synthesis and characterization of several methyl and hydride complexes of platinum supported by **1** and emphasize the electronic contribution that the anionic phosphine ligand provides.

2. Experimental

2.1. General

Unless otherwise noted, all syntheses were carried out under a dinitrogen atmosphere in the absence of water and dioxygen, using standard Schlenk or glovebox techniques. Acetonitrile, tetrahydrofuran, diethyl ether, dichloromethane, toluene, benzene, and petroleum ether were deoxygenated and dried by thorough sparging with N_2 gas followed by passage through an activated alumina column. Pentane and hexanes were deoxygenated by repeated evacuation under reduced pressure followed by introduction of dinitrogen and were dried by storing over 3-Å molecular sieves. Hydrocarbon and ethereal solvents were typically tested with a standard purple solution of sodium benzophenone ketyl in tetrahydrofuran in order to confirm effective oxygen and moisture removal. Ethanol and acetone were dried and distilled over calcium sulfate under dinitrogen. Morpholine and TMEDA were dried and distilled from CaH_2 under dinitrogen. Deuterated chloroform, benzene, dichloromethane, THF, acetonitrile, and acetone were purchased from Cambridge Isotope Laboratories, Inc. and were degassed by repeated freeze–pump–thaw cycles and dried over activated 3-Å molecular sieves prior to use. $[PhBP_3][Li(TMEDA)]$ [9a] and $(COD)PtMe_2$ [12] were prepared by literature methods. All other chemicals were purchased from commercial vendors and used without further purification. NMR spectra were recorded on Varian Mercury 300 MHz and Inova 500 MHz, and Joel 400 MHz spectrometers at ambient temperature, unless otherwise noted. ^1H and $^{13}C\{^1H\}$ chemical shifts were referenced to residual solvent as determined relative to Me_4Si (0 ppm). $^{31}P\{^1H\}$ NMR, $^{11}B\{^1H\}$ NMR, and $^{19}F\{^1H\}$ NMR chemical shifts are reported relative to an external standard (0 ppm) of 85% H_3PO_4, neat $BF_3 \cdot Et_2O$, and neat $CFCl_3$ respectively. Abbreviations for reported signal multiplicities are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. IR spectra were recorded at 4 cm^{-1} resolution on a Bio-Rad Excalibur FTS 3000 spectrometer controlled by Win-IR Pro software using either a KBr solution cell or KBr plates. Elemental analyses were performed by Desert Analytics, Tucson, AZ. X-ray diffraction experiments were carried out by the Beckman Institute Crystallographic Facility on a Bruker SMART 1000 CCD diffractometer.

2.2. Syntheses of complexes

2.2.1. $[PhB(CH_2PPh_2)_3][^nBu_4N]$ (**1[TBA]**, $[PhBP_3]$ $[TBA]$)

The previously reported compound $[PhBP_3][Li(TMEDA)]$ [9] (20.987 g, 25.952 mmol) was dissolved in MeOH in air (50 mL). The methanolic solution was quickly filtered through diatomaceous earth and added slowly to tetra-*n*-butyl ammonium bromide (9.603 g, 28.55 mmol) dissolved in water (300 mL), yielding a white gelatinous solid which dispersed into a coarse chunky powder upon addition of Et_2O (40 mL). The mixture was stirred for 5 min, and then the solids were collected by filtration and washed sequentially with water (30 mL), Et_2O (30 mL), water (30 mL), and Et_2O (30 mL). The resulting white solids were dissolved in acetonitrile (100 mL), yielding a somewhat cloudy yellowish solution which was dried by stirring the reaction mixture over sodium sulfate for 10 min. The solution was then filtered over diatomaceous earth affording a clear yellow solution, which was concentrated by rotary evaporation and triturated with Et_2O, yielding white solid **1[TBA]** (16.453 g, 67.3%). This compound is not air or moisture stable and should be stored under inert atmosphere. ^1H NMR (400 MHz, CD_3CN): δ 7.48 (br, 2H, [*ortho*-$C_6H_5BP_3$]), 7.22 (m, 12H, aryl protons), 7.13 (m, 18H, aryl protons), 6.86 (t, 2H, [*meta*-$C_6H_5BP_3$]), 6.74 (t, 1H, [*para*-$C_6H_5BP_3$]), 3.04 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.57 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.33 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.08 (br, 6H, $[PhB(CH_2PPh_2)_3]$), 0.96 (t, 12H, $[(CH_3CH_2CH_2CH_2)_4N]$). $^{31}P\{^1H\}$ NMR (161.9 MHz, CD_3CN): δ −11.31. *Anal.* Calc. for $C_{62}H_{79}BNP_3$: C, 79.05; H, 8.45; N, 1.49. Found: C, 79.36; H, 8.52; N, 1.37%.

2.2.2. $[PhBP_3]PtMe_3$ (**2**)

Solid off-white $[PhBP_3][TBA]$ (263.6 mg, 0.2840 mmol) and $IPtMe_3$ (104.5 mg, 0.2847 mmol) were dissolved in THF (7 mL). The reaction mixture was stirred for 2 h and then concentrated to 4 mL. Upon standing, white solids precipitated. The supernatant was decanted, and the solids were dried under reduced pressure. Benzene (6 mL) was added, and the reaction mixture was stirred for 10 min. The cloudy solution was filtered, and volatiles were removed under reduced pressure from the resulting solution, providing white solid **2** (193.2 mg, 73.5%). Clear, colorless block crystals suitable for X-ray diffraction were obtained from pentane diffusion into a THF solution of **2**. ^{1}H NMR (300 MHz, C_6D_6): δ 7.90 (d, 2H, [*ortho*-$C_6H_5BP_3$]), 7.54 (t, 2H, [*meta*-$C_6H_5BP_3$]), 7.36 (m, 13H, aryl protons), 6.85 (m, 18H, aryl protons), 2.01 (br, 6H, $[PhB(CH_2PPh_2)_3]$), 1.35 (d, 9H, $Pt(CH_3)_3$, $^{2}J_{Pt-H} = 55.5$ Hz, $^{3}J_{P-H} = 7.2$ Hz). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, C_6D_6): δ 136.9, 133.9, 132.4, 129.5, 128.9, 124.9, 15.8 (br, $[PhB(CH_2PPh_2)_3]$), 6.5 (dd, $Pt(CH_3)_3$, $^{1}J_{Pt-C} = 497$ Hz, $^{2}J_{P-C} = 11$, 111 Hz). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, C_6D_6): δ −26.01 ($^{1}J_{Pt-P} = 1094$ Hz). $^{11}B\{^{1}H\}$ NMR (128.3 MHz, C_6D_6): δ −11.9. *Anal.* Calc. for $C_{48}H_{50}BP_3Pt$: C, 62.28; H, 5.44. Found: C, 62.44; H, 5.67%.

2.2.3. *[[κ²-PhBP₃]PtMe₂][TBA] (3)*

Solid off-white $[PhBP_3][TBA]$ (1.6076 g, 1.732 mmol) was dissolved in THF (8 mL). A solution of $(COD)PtMe_2$ (577.0 mg, 1.731 mmol) dissolved in THF (1 mL) was added to the stirring $[PhBP_3][TBA]$ solution, forming a colorless to pale yellow solution. After stirring the reaction mixture for 4 h, the volume of the reaction was reduced by removal of volatiles under reduced pressure. Precipitation with pentane produced off-white to pale yellow solids which were repeatedly triturated with pentane. Drying the solids under reduced pressure resulted in off-white to pale yellow solid **3** (1.8024 g, 90.3%). Clear, colorless rectangular prism crystals suitable for X-ray diffraction were grown by slow evaporation of a saturated toluene solution of **3**. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.64 (br, 4H), 7.44 (br, 4H), 6.86–7.28 (m, 24H), 6.63 (m, 3H), 3.36 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.76 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.55 (br, 4H, $[[PhB(CH_2PPh_2)(CH_2PPh_2)_2]PtMe_2]$), 1.39 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 0.96 (t, 12H, $[(CH_3CH_2CH_2CH_2)_4N]$), 0.65 (br, 2H, $[[PhB(CH_2PPh_2)(CH_2PPh_2)_2]PtMe_2]$), 0.08 (t, 6H, $Pt(CH_3)_2$, $^{2}J_{Pt-H} = 67$ Hz, $^{3}J_{P-H} = 5$ Hz). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, acetone-d_6): δ 122–148 (aryl carbons), 59.9 ($[(CH_3CH_2CH_2CH_2)_4N]$), 25.0 ($[(CH_3CH_2CH_2CH_2)_4N]$), 24 (br), 21.0 ($[(CH_3CH_2CH_2CH_2)_4N]$), 14.6 ($[(CH_3CH_2CH_2CH_2)_4N]$), 6.7 ($Pt(CH_3)_2$, $^{1}J_{Pt-C} = 616$ Hz, $^{2}J_{P-C} = 8.8$, 103 Hz). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, acetone-d_6): δ 18.96 (s, 2P, $^{1}J_{Pt-P} = 1888$ Hz), −9.61 (s, 0.12P), −12.60 (s, 0.88P). $^{11}B\{^{1}H\}$ NMR (160.4 MHz, acetone-d_6): δ −14.10. *Anal.* Calc. for $C_{63}H_{83}BNP_3Pt$: C, 65.86; H, 7.34; N, 1.20. Found: C, 65.51; H, 7.29; N, 1.06%.

2.2.4. *[[κ²-PhB(CH₂P(S)Ph₂)(CH₂PPh₂)₂]PtMe₂][TBA] (4)*

Solid **3** (159.0 mg, 0.1379 mmol) was dissolved in THF (2 mL). While stirring the reaction mixture, a suspension of elemental sulfur (4.6 mg, 0.14 mmol of S atoms) in THF (1 mL) was added to the reaction. After 1h, the sulfur had been visibly consumed and the reaction changed color from colorless to yellow. The reaction mixture was filtered, and volatiles were removed under reduced pressure, providing pale yellow solid **4** (160.7 mg, 97.2%) in > 95% purity. Analytically pure **4** has not yet been isolated. ^{1}H NMR (300 MHz, acetone-d_6): δ 7.62 (br, 4H), 7.46 (br, 4H), 6.8–7.3 (m, 24H), 6.62 (m, 3H), 3.36 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.76 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.6 (br, 4H, $[[PhB(CH_2P(S)Ph_2)(CH_2PPh_2)_2]PtMe_2]$), 1.39 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 0.96 (t, 12H, $[(CH_3CH_2CH_2CH_2)_4N]$), 0.73 (br, 2H, $[[PhB(CH_2P(S)Ph_2)(CH_2PPh_2)_2]PtMe_2]$), 0.07 (t, 6H, $Pt(CH_3)_2$, $^{2}J_{Pt-H} = 68$ Hz, $^{3}J_{P-H} = 5$ Hz). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, acetone-d_6): δ 44.44 (s, 1P), 18.37 (s, 2P, $^{1}J_{Pt-P} = 1875$ Hz).

2.2.5. *[[κ²-PhB(CH₂P(BH₃)Ph₂)(CH₂PPh₂)₂]PtMe₂][TBA] (5)*

Solid **3** (241.2 mg, 0.2092 mmol) was added to a fresh 2 M solution of $BH_3 \cdot SMe_2$ (104.6 μL, 0.2092 mmol) in toluene/THF. After 5 min, concentration of the reaction mixture under reduced pressure followed by addition of petroleum ether precipitated solid **5**. Analytically pure **5** was obtained from repeated washing of the solids with petroleum ether (237.6 mg, 97.3%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 7.72, 7.49, 7.0–7.4, 6.95, 6.54 (m, 35H, aryl protons), 2.96 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.50 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 1.35 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 0.99 (t, 12H, $[(CH_3CH_2CH_2CH_2)_4N]$), 0.04 (t, 6H, $Pt(CH_3)_2$, $^{2}J_{Pt-H} = 67$ Hz, $^{3}J_{P-H} = 5.5$ Hz). $^{13}C\{^{1}H\}$ NMR (125.7 MHz, CD_2Cl_2): δ 161 (br), 140.1 (m), 137.5 (d), 137.2 (d), 134.7 (m), 133.9 (m), 133.3, 132.4 (d), 129.0, 128.4, 128.0, 127.8 (d), 127.5, 127.1, 125.5, 122.3, 59.3 ($[(CH_3CH_2CH_2CH_2)_4N]$), 24.3 ($[(CH_3CH_2CH_2CH_2)_4N]$), 23.5 (br), 22.5 (br), 20.2 ($[(CH_3CH_2CH_2CH_2)_4N]$), 13.9 ($[(CH_3CH_2CH_2CH_2)_4N]$), 5.1 (dd, $Pt(CH_3)_2$, $^{1}J_{Pt-C} = 602$ Hz, $^{2}J_{P-C} = 9.1$, 102 Hz). $^{31}P\{^{1}H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 18.01 (s, 2P, $^{1}J_{Pt-P} = 1878$ Hz), 15.30 (br, 1P). $^{11}B\{^{1}H\}$ NMR (160.4 MHz, CD_2Cl_2): δ −14.8, −30.3. *Anal.* Calc. for $C_{63}H_{86}B_2NP_3Pt$: C, 65.09; H, 7.51; N, 1.19. Found: C, 64.69; H, 7.53; N, 1.02%.

2.2.6. *[[κ²-PhB(CH₂P(BH₃)Ph₂)(CH₂PPh₂)₂]Pt(μ-H)]₂[TBA]₂ (6)*

Solid **3** (277.4 mg, 0.2377 mmol) was dissolved in THF (2 mL). While stirring the reaction mixture, a fresh 2 M solution of $BH_3 \cdot SMe_2$ in toluene/THF was added (250 μL, 0.500 mmol). After 15 min, the solution was concentrated to dryness under reduced pressure. The resulting solids were washed with petroleum ether [5 × 2 mL] and dried under reduced pressure, providing analytically pure **6** (268.4 mg, 99.2%). ^{1}H NMR (500 MHz, C_6D_6): δ 7.97 (br), 7.83 (m), 7.76 (br), 7.54 (br), 7.45 (d), 7.04 (br), 6.93 (m), (m, 35H, aryl protons), 2.66 (m, 8H, $[(CH_3CH_2CH_2CH_2)_4N]$), 2.10 (br, 4H), 1.61 (br, 2H), 1.15 (m, 16H, $[(CH_3CH_2CH_2CH_2)_4N]$ and $[(CH_3CH_2CH_2CH_2)_4N]$), 0.84 (t, 12H, $[(CH_3CH_2CH_2CH_2)_4N]$), −3.17 ("quintet of quintets", 2H, $[Pt(\mu-H)]_2$, $^1J_{Pt–H} = 464$ Hz, $^2J_{P–H} = 40$ Hz). $^{13}C\{^1H\}$ NMR (125.7 MHz, C_6D_6): δ 161 (br), 142.5 (br d), 141.3 (br d), 138.2 (d), 137.5 (d), 134.6 (br m), 134.2 (d), 134.0, 133.2 (d), 133.0 (d), 129.4, 128.9 (m), 127.9 (m), 126.5, 123.1, 58.8 ($[(CH_3CH_2CH_2CH_2)_4N]$), 24.4 ($[(CH_3CH_2CH_2CH_2)_4N]$), 20.2 ($[(CH_3CH_2CH_2CH_2)_4N]$), 20 (br), 14.3 ($[(CH_3CH_2CH_2CH_2)_4N]$). $^{31}P\{^1H\}$ NMR (121.4 MHz, C_6D_6): δ 25.69 (s, 2P, $^1J_{Pt–P} = 2959$ Hz, $^2J_{Pt–P} = 168$ Hz), 16.06 (br, 1P). $^{11}B\{^1H\}$ NMR (160.4 MHz, C_6D_6): δ −15.3, −31.1. ES–MS (CH_3CN, anion observe): Calc. for $[C_{90}H_{90}B_4P_6Pt_2]^{2-}$: 1790.5, found: 1790.9 $[M^{2-} + H^+]$, 1777.1 $[M^{2-} + H^+–BH_3]$, 1763.3 $[M^{2-} + H^+–2BH_3]$. IR (Nujol, cm^{-1}): ν 2368 ($R_3P{:}BH_3$), 2003 (Pt-*H*), 1966 (Pt-*H*). IR (THF, cm^{-1}): ν 2378 ($R_3P{:}BH_3$), 2010 (Pt-*H*), 1969 (Pt-*H*). *Anal.* Calc. for $C_{122}H_{162}B_4N_2P_6Pt_2$: C, 64.64; H, 7.26; N, 1.22. Found: C, 64.26; H, 7.26; N, 1.46%.

2.3. X-ray crystallography

Single crystals of **2** and **3** were grown as described and were mounted on a glass fiber with Paratone N (Exxon) and transferred to the 98 K cold stream of a Bruker CCD X-ray diffraction system controlled by the SMART (v5.060) software package. Collected data were processed using SAINT+ (v6.02). No empirical absorption corrections were calculated. Structures were solved either by direct or Patterson methods using the XS program, followed by difference Fourier methods and refinements carried out with SHELXTL, both part of the SHELXTL software package (v5.1). Non-hydrogen atoms were refined anisotropically by a series of least-squares cycles. All hydrogen atoms were assigned idealized positions and refined isotropically. Crystallographic information is provided in Table 1, and interatomic distances and angles are contained in Table 2.

3. Results and discussion

3.1. Synthesis of a platinum(IV) trimethyl complex

The tridentate phosphine ligand **1** was initially reported as the lithium(TMEDA) salt, $[PhB(CH_2PPh_2)_3]$[Li(TMEDA)] (**1[Li(TMEDA)]**) [9a]. Salt metathesis protocols developed in our laboratories have resulted in the useful thallium adduct, $[PhB(CH_2PPh_2)_3]Tl$ (**1[Tl]**) [13] and the tetra(*n*-butyl)ammonium salt, $[PhB(CH_2PPh_2)_3]$[TBA] (**1[TBA]**) [14]. For the ensuing discussion of platinum chemistry supported by **1**, it was found that **1[TBA]** resulted in clean substitution onto platinum starting materials.

Table 1
Crystal data and refinement parameters of **2 · THF** and **3**

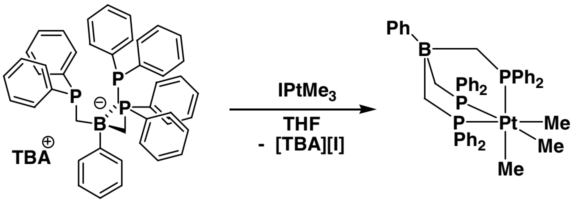
Compound	$[PhBP_3]PtMe_3 \cdot THF$ (**2 · THF**)	$[[\kappa^2\text{-}PhBP_3]PtMe_2][TBA]$ (**3**)
Empirical formula	$C_{48}H_{41}BP_3Pt \cdot C_4H_8O$	$C_{63}H_{83}BNP_3Pt$
Formula weight	925.72 · 72.11	1153.15
Crystal description	colorless block	colorless fragment
Crystal size (mm)	0.19 × 0.15 × 0.15	0.33 × 0.11 × 0.07
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$ (#2)	$P2_1/n$ (#14)
Unit cell dimensions		
a (Å)	12.1517(8)	10.656(3)
b (Å)	13.4760(9)	26.546(6)
c (Å)	15.218(1)	20.462(5)
α (°)	88.345(1)	90
β (°)	67.998(1)	95.821(4)
γ (°)	71.325(1)	90
V (Å^3)	2177.1(2)	5758(2)
Z	2	4
D_{calc} (g cm^{-3})	1.522	1.330
Absorption coefficient (mm^{-1})	3.372	2.559
T (K)	98	98
Radiation λ (Å)	0.71073	0.71073
Reflections collected	40 405	90 893
Unique data/parameters	10 339/526	13 924/628
R_1, wR_2, $[I > 2\sigma(I)]$	0.0263, 0.0557	0.0695, 0.1258
Goodness-of-fit	1.065	1.209
Largest difference peak and hole (e Å^{-3})	1.597 and −0.718	4.398 and −4.510

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$, $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

Table 2
Selected interatomic distances (Å) and angles (°) for **2 · THF** and **3**

2 · THF		**3**	
Interatomic distances (Å)			
Pt1–C46	2.114(3)	Pt–C46	2.082(8)
Pt1–C47	2.112(3)	Pt–C47	2.096(6)
Pt1–C48	2.107(3)	Pt–P1	2.271(2)
Pt1–P1	2.4044(7)	Pt–P2	2.282(2)
Pt1–P2	2.3976(7)	Pt–B	4.058(8)
Pt1–P3	2.4307(7)		
Pt1–B	3.640(3)		
Bond angles (°)			
P–Pt–P (average)	88.33	P2–Pt–P3	90.28(6)
C–Pt–C (average)	82.98	C46–Pt–C47	85.5(3)
C–Pt–P (average)	94.29	C46–Pt–P1	90.9(2)
		C47–Pt–P2	93.2(2)

Reaction of **1[TBA]** in THF with $\mathrm{IPtMe_3}$ led to the formation of a single product, $[\mathrm{PhBP_3}]\mathrm{PtMe_3}$ (**2**), as a colorless, neutral, octahedral Pt(IV) complex Eq. (1). In solution, **2** exhibited C_{3v} symmetry. Protons on the platinum-methyl groups showed coupling to both platinum ($^2J_{\mathrm{Pt-H}} = 55.5$ Hz) and phosphorus ($^3J_{\mathrm{P-H}} = 7.2$ Hz) in the ^{1}H NMR spectrum. Similarly, platinum coupling was seen for the ligand phosphines in the $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectrum ($^1J_{\mathrm{Pt-P}} = 1094$ Hz). Interestingly, the only other *fac*-platinum trimethyl complex supported by trialkyl phosphines that has been reported in the literature is $[(\mathrm{Me_2PhP})_3\mathrm{PtMe_3}][\mathrm{PF_6}]$ [15].



1[TBA] **2** (1)

An X-ray diffraction study carried out on a single crystal of **2** verified the structure (Fig. 1). The X-ray structure of **2** shows the tridentate *fac* coordination of ligand **1**, with P–Pt–P bond angles being very close to 90°. Space-filling models of **2** derived from the crystallographic data show that the phosphino-phenyl groups provide sufficient steric bulk to force the platinum-methyl groups slightly away from octahedral, as evidenced by the average C–Pt–C bond angle of 83.0°. Complex **2** is very robust, being stable to air, moisture, aqueous mineral acids (e.g., 12M HCl (aq)), strong Lewis acids (e.g., $\mathrm{B(C_6F_5)_3}$, $[\mathrm{Ph_3C}][\mathrm{BF_4}]$), and reductants such as methyl lithium and sodium borohydride. Thermolysis of **2** in 1,3-dichlorobenzene showed that the complex was stable for several hours even at 170 °C; however, thermal decomposition occurred relatively quickly (hours) at 180 °C to provide a complex mixture of uncharacterized products. The marked stability of **2** is comparable to that observed for $[(\mathrm{Me_2PhP})_3\mathrm{PtMe_3}][\mathrm{PF_6}]$ by Clark and Manzer [15].[1] Compared to the recently structurally characterized $[\mathrm{Tp}_2^{\mathrm{Me}}]\mathrm{PtMe_3}$, the Pt–C bond lengths of **2** are longer, presumably due to the greater *trans* influence of the phosphine ligands. More importantly, the Pt–B distance (3.640 Å) in **2** is much larger than for its [Tp] analogue (3.184 Å), likely providing a better through space separation of charge for **2**.

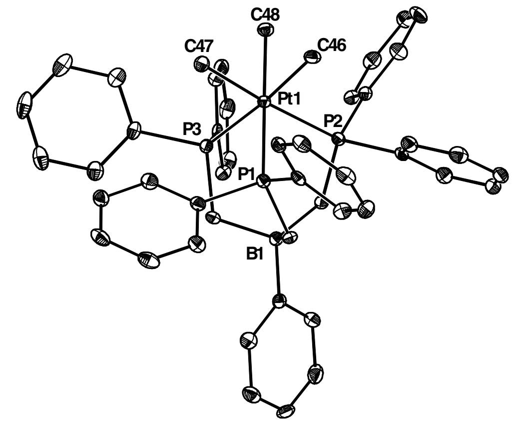
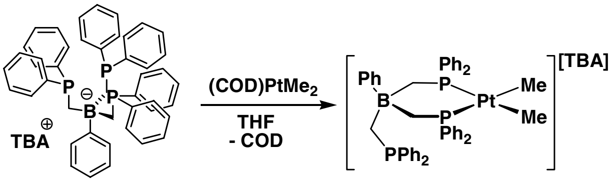


Fig. 1. A 50% displacement ellipsoid representation of **2·THF**. Hydrogen atoms and THF molecule are omitted for clarity.

3.2. Synthesis and reactivity of platinum(II) complexes

Formation of the platinum(II)-methyl compound $[[\kappa^2\text{-}\mathrm{PhBP_3}]\mathrm{PtMe_2}][\mathrm{TBA}]$ (**3**) proceeded cleanly at room temperature by the reaction of **1[TBA]** and $(\mathrm{COD})\mathrm{PtMe_2}$ in THF solution (Eq. (2)). The ability to use $(\mathrm{COD})\mathrm{PtMe_2}$ as a reagent is consistent with previous results using phosphine donor ligands and stands in contrast to (pyrazolyl)borate ligands which require more labile starting materials to achieve substitution [16,17].



1[TBA] **3**

(2)

Examination of the ^{1}H and $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR spectra of **3** shows the C_s symmetry of the platinum complex: the platinum-methyl protons are equivalent, with readily apparent coupling to platinum ($^2J_{\mathrm{Pt-H}} = 67$ Hz) and phosphorus ($^3J_{\mathrm{P-H}} = 5$ Hz). The coordinated phosphines in **3** have a very different chemical shift and platinum coupling constant ($\delta = 18.96$, $^1J_{\mathrm{Pt-P}} = 1885$

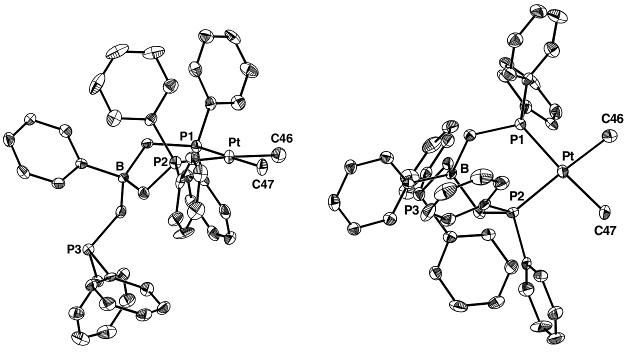
---

[1] Interestingly, the authors observed high stability for $[\mathrm{Pt(CH_3)_3(OH_2)_3}]^+$ and $[\mathrm{Pt(CH_3)_3(NC_2H_5)_3}]^+$ as well, noting that the complexes "are quite stable and exhibit no tendency towards reductive decomposition" [15]. We presume that this is due to the electronic nature of the threefold symmetric octahedral molecules.

Hz) from those in **2** ($\delta = -26.01$, $^{1}J_{\mathrm{Pt-P}} = 1093$ Hz), demonstrating a substantial change in the electronic character of the ligated phosphines between Pt(II) and Pt(IV) states. In contrast to two related $[[\kappa^2\text{-Tp}]\mathrm{PtMe_2}]^-$ complexes, **3** exhibits smaller methyl $^{2}J_{\mathrm{Pt-H}}$ values ($[[\kappa^2\text{-Tp}]\mathrm{PtMe_2}]^-$, $^{2}J_{\mathrm{Pt-H}} = 86$ Hz [16b]; $[[\kappa^2\text{-Tp}_2^{\mathrm{Me}}]\mathrm{PtMe_2}]^-$, $^{2}J_{\mathrm{Pt-H}} = 83$ Hz [4]), consistent with stronger trans influencing phosphine donors. Relative to a series of previously prepared bidentate phosphine platinum-dimethyl compounds [18], $[\mathrm{E(CH_2PPh_2)_2]Pt(CH_3)_2}$ (E $= \mathrm{Ph_2B^-}$, $\mathrm{Ph_2Si}$, $\mathrm{H_2C}$), the phosphorus-platinum coupling constant of **3** is comparable to the anionic bis(phosphino)borate complex $[[\mathrm{Ph_2BP_2]PtMe_2][ASN]}$ ($^{1}J_{\mathrm{Pt-P}} = 1892$ Hz), and both anionic complexes have larger platinum phosphorus coupling constants than similar neutral compounds. A structurally analogous neutral Pt(II) compound, $(\kappa^2\text{-tripod})\mathrm{Pt(CH_3)_2}$, has been previously prepared [19], though it was not thoroughly characterized nor explored further.

Examination of the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum of **3** showed two phosphine environments consistent with two phosphines ligated to a square planar platinum(II) center and one unligated phosphine. The pendant arm of the (phosphino)borate ligand in an analytically pure sample of **3** demonstrated unusual behavior. Two peaks were observed at −9.61 and −12.60 ppm whose integrated intensity corresponded to one phosphine relative to the two phosphines coordinated to platinum in the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum. Both of these signals are similar to the chemical shift of the uncoordinated ligand **1[TBA]** ($^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR ($\mathrm{CD_3CN}$): δ −11.3). The two distinct signals suggest that there is a barrier to rotation about the phosphine-methylene (or the boron-methylene) carbon bond. The difference in chemical shifts between the two signals also suggests that a there is a modest change in the magnetic environment on the pendant phosphine depending on whether the phosphine lone pair is directed toward the metal or away from it. Two possible orientations are depicted in Fig. 2.

An X-ray diffraction experiment confirmed the structure of **3** (Fig. 3), showing that two arms of the tridentate ligand bind to platinum in a *cis* fashion to form a square planar dimethyl platinum complex while one arm of the ligand remains uncoordinated. The uncoordinated arm in the crystal lattice is oriented so that the phosphine lone pair is directed away from the metal. Examination of the bond angles around the platinum center reveals a square planar motif which has been slightly altered due to the steric demands of the aryl rings and the twisted conformation of the chelating ligand. Comparison of the bond lengths and angles observed for **3** with those observed for the related bis(phosphino)borate platinum(II) dimethyl anion $[[\kappa^2\text{-Ph}_2\mathrm{BP_2]PtMe_2][ASN]}$ demonstrate that no significant structural changes occur by replacing the uncoordinated phosphine arm for a more innocent phenyl group pendant to boron [18]. Fortunately, the crystal structure of the related $[[\kappa^2\text{-Tp}_2^{\mathrm{Me}}]\mathrm{PtMe_2}]^-$ has been reported [4]. Similar to **2**, the Pt–C bond lengths (2.09 Å) are longer than for the Tp analogue (2.03 Å). The Pt–B distance in **3** is significantly longer (4.06 Å) than for its Tp analogue (3.37 Å), again suggesting a greater degree of spacial charge separation for $[\mathrm{PhBP_3}]$-ligated complexes. It is interesting to note that for both **3** and $[[\kappa^2\text{-Tp}_2^{\mathrm{Me}}]\mathrm{PtMe_2}]^-$ the pendant donor is directed away from the metal center in the solid state structure. Presumably, interactions between the donor lone pair and the occupied d_{z^2}-type orbital results in electron-electron repulsion.



Side View Top View

Fig. 3. A 50% displacement ellipsoid representation of **3**. Hydrogen atoms and the TBA cation are omitted for clarity.

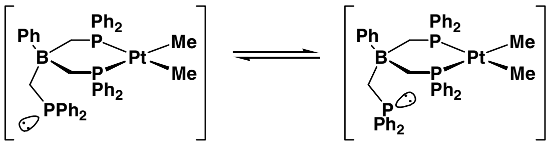
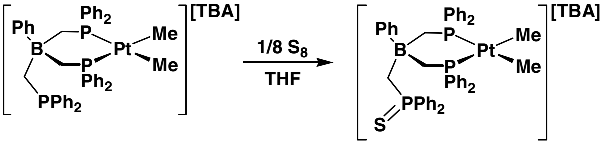


Fig. 2. Possible orientations for the pendant phosphine arm in **3**.

Complex **3** exhibited reactivity with dioxygen, water, protic and Lewis acids (e.g., HCl in $\mathrm{Et_2O}$, HOTf, $[\mathrm{Et_3NH}][\mathrm{BPh_4}]$, $\mathrm{B(C_6F_5)_3}$), and small alkyl halides such as $\mathrm{CH_3I}$, $\mathrm{CH_2Cl_2}$, and $\mathrm{CHCl_3}$. In most cases, complex product mixtures were formed, as determined by $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectroscopy. In particular, reactivity at the pendant phosphine arm was frequently observed, as evinced by new $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR signals without platinum satellites. Related $[[\kappa^2\text{-Tp}]\mathrm{PtMe_2}]^-$ species also show a wide variety of reactivity, including well-characterized reactions with $\mathrm{H_2O}$, and protic and Lewis acids [4,16,20]. Reactivity at the uncoordinated pyrazolyl donor has been primarily limited to protonation [21]. The apparent contrast in reactivity of the uncoordinated donor in **3** is most likely attributed to its greater basicity and lower oxidation potential.

3.3. Protection of the unchelated phosphine

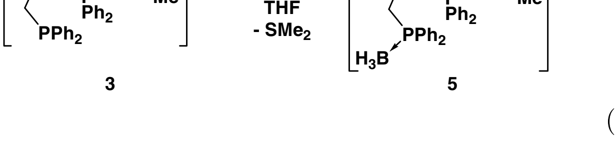
In order to sidestep undesirable reactivity at the pendant phosphine arm, phosphine protection strategies were considered. The pendant arm of the ligand reacted with one equivalent of elemental sulfur to provide a single major product Eq. (3), assigned by NMR spectroscopy as [[κ^2-PhB(CH$_2$P(S)Ph$_2$)(CH$_2$PPh$_2$)$_2$]PtMe$_2$][TBA] (**4**). The chemical shift of a singlet at 44.4 ppm (^{31}P{^{1}H} NMR) suggests an oxidized trialkylphosphine and is consistent with the ^{31}P{^{1}H} NMR chemical shifts of known R$_3$P = S compounds [22]. Additionally, the ^{31}P{^{1}H} NMR chemical shift (18.4 ppm) and coupling ($^1J_{\mathrm{Pt-P}}$ = 1875 Hz) of the coordinated phosphines do not change significantly upon modification of the pendant arm. ^{1}H NMR spectra of **4** showed no significant changes as compared to **3**. Due to the difficulty in stoichiometric control of the sulfur addition, **4** was typically isolated in >95% purity. The addition of excess sulfur provides uncharacterized products.



3 4

(3)

A second protection strategy involved addition of the Lewis acid, BH$_3$ · SMe$_2$. Using one equivalent of a 2.0 M solution of BH$_3$ · SMe$_2$ in toluene (BH$_3$ · THF can also be used), clean formation of the BH$_3$-phosphine adduct **5** can be observed by ^{31}P{^{1}H} NMR spectroscopy Eq. (4). ^{31}P{^{1}H} NMR spectra show the disappearance of the peaks at −9 and −12 ppm (vide supra) and the growth of a broad peak at ca. 15 ppm. This downfield shift is expected for the formation of a phosphine-borane adduct due to the decreased shielding of the phosphorus nucleus upon borane complexation, and the broadness of the new peak results from unresolved coupling to the boron nucleus. Examination of **5** by ^{11}B NMR spectroscopy confirmed the formation of the phosphine-borane adduct with the presence of a new upfield signal (−30.3 ppm) consistent with known phosphine-borane complexes. The resonances from the platinum-bound phosphines demonstrate virtually no change in their ^{31}P{^{1}H} NMR chemical shift and register only a slight change in their coupling to platinum ($^1J_{\mathrm{Pt-P}}$(**5**) = 1870 Hz versus $^1J_{\mathrm{Pt-P}}$(**3**) = 1885 Hz).



3 5

(4)

Protection of the pendant phosphine arm with BH$_3$ provides altered reactivity with various substrates relative to the reactivity found in **3**. For example, **3** begins to react immediately when dissolved in dichloromethane, providing a mixture of products over a period of hours [10].[2] In contrast, **5** shows no spectroscopic change over 2.5 hours when dissolved in dichloromethane. Additionally, **5** shows no reaction with air and water in THF solution over several hours. These examples show that the reactivity of complex **3** is dependent upon the pendant phosphine arm, either as a site of reactivity or as a neutral donor facilitating reactivity at the platinum center. Deprotection of the pendant phosphine · BH$_3$ adduct of **5** can be accomplished by heating **5** to 55 °C for several hours in the presence of excess (∼200 equiv.) morpholine, a common deprotection method [23].

3.4. *Reactivity of protected platinum(II) species*

If **5** is allowed to react with an additional equivalent of BH$_3$ · SMe$_2$ (or BH$_3$ · THF), then clean formation of a new product is observed Eq. (5). Spectroscopic (NMR), mass spectrometric, and combustion analyses are consistent with the formation of the reduced platinum(I) dimeric species, [[κ^2-PhB(CH$_2$P(BH$_3$)Ph$_2$)(CH$_2$PPh$_2$)$_2$]Pt(μ-H)]$_2$[TBA]$_2$ (**6**). BH$_3$ reagents are widely known to act as reducing agents, and, in this case, it appears that BH$_3$ is serving as a reductant and H-atom donor. The fate of the methyl groups on platinum is unknown at this point: possible methyl containing products are methane or methylborane species, neither of which has been spectroscopically observed.

Bridging platinum(I) hydride dimers have been previously described in detail by Schwarz and Andersen [24]. The NMR spectra of **6** are consistent with their observations and those of others [24–26], including the unusual "quintet of quintets" signal for the hydrides (Table 3). The observed trends of the ^{1}H NMR spectroscopic data for several bisphosphine platinum(I) bridged hydrides suggest that the hydrides in **6** are *trans* to a more electron-rich bisphosphine ligand as compared to other neutral bisphosphine platinum(I) hydride dimers, based on the reduced Pt–H coupling constant. The IR data (Nujol) for **6** contain a broad peak at 2368 cm^{-1}, and two peaks at 2003 and 1966 cm^{-1}. The first of these peaks is consistent with previously observed BH$_3$-phosphine adducts, typically observed between 2450 and 2350 cm^{-1} [27]. The two peaks at 2003 and 1966 cm^{-1} are assigned as the Pt–H stretching modes.

---

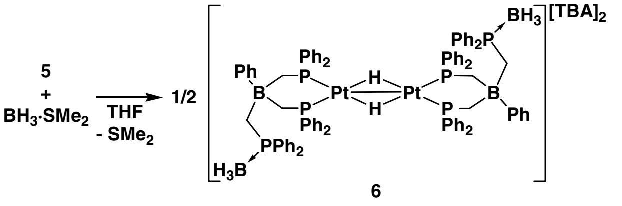
[2] The unligated tris(phosphino)borate [PhBP$_3$][TBA] also demonstrates reactivity with halide-containing solvents such as CH$_2$Cl$_2$ and CHCl$_3$.

Table 3
^{1}H NMR and IR data for bisphosphine platinum(I) dimers

Compound	δ (Pt–H) (ppm)	$^{1}J_{\text{Pt–H}}$ (Hz)	$^{2}J_{\text{P–H}}$ (Hz)	ν (Pt–H) (cm^{-1})Nujol	Ref.
6	−3.17	464	40	2003, 1966	
[(dppe)PtH]$_2$	0.30	564	42	[a]	[25b]
[(dippe)PtH]$_2$	0.49	516	40	1939, 1926	[24]
[(dcype)PtH]$_2$	0.49	512	40	1965, 1937	[24]
[(dtbpe)PtH]$_2$	0.05	570	42	1975, 1951	[24]
[(dfepe)PtH]$_2$	3.55	737	47	[b]	[26]

[a] IR data were not reported.

[b] The authors did not observe Pt–H stretching bands in the IR spectrum (see footnote 7 of [26]).



(5)

4. Conclusions

Several platinum methyl and hydride complexes containing the monoanionic tris(phosphino)borate ligand **1** have been synthesized, and preliminary investigations into their chemistry has begun. In general, a zwitterionic description for complexes ligated by **1** seems more appropriate than for related [Tp]-containing systems, given that comparative structural data often shows similar binding modes for the two ligands but greater separation between the metal center and the anionic borate for [PhBP$_3$] systems. Although the binding modes are similar between [Tp] and [PhBP$_3$], particularly notable for **3** and its [Tp] congener, we have found that much of the reactivity of the anionic dimethyl complex **3** is attributable to the unligated phosphine arm of the trisphosphine ligand. In comparison to related [Tp]-ligated platinum systems, the free phosphine donor readily participates in reactivity due to its greater basicity. Protection of the pendant phosphine arm can be achieved using either BH$_3$ or sulfur. The sulfur-protected complex **4** promises to be an interesting candidate for further reactivity studies based on its donor potential. Studies of the reactivity of the BH$_3$-protected compound **5** have shown it to be significantly less reactive than **3** under comparable conditions, demonstrating the role of the unbound phosphine in reactivity. Future studies of [PhBP$_3$]Pt systems will aim at further understanding the structural and electronic differences between analogous [Tp]- and [PhBP$_3$]-ligated complexes.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited at the Cambridge Crystallographic Data Center, CCDC Numbers 216189 (**2·THF**) and 216190 (**3**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

Acknowledgements

Larry Henling is acknowledged for his assistance with X-ray crystallography. Joseph Duimestra is acknowledged for assistance with the protocol for [PhBP$_3$][TBA]. J.C.T. is grateful to the NSF and to the Moore Foundation for graduate research fellowships. The authors acknowledge financial support from the NSF (CHE-0132216) and the DOE (PECASE).

References

[1] S. Trofimenko, Scorpionates. The Coordination Chemistry of Polypyrazolylborate Ligands, Imperial College Press, London, 1999.

[2] (a) S.E. Bromberg, H. Yang, M.C. Asplund, T. Lian, B.K. McNamara, K.T. Kotz, J.S. Yeston, M. Wilkens, H. Frei, R.G. Bergman, C.B. Harris, Science 278 (1997) 260;
(b) D.M. Tellers, R.G.J. Bergman, J. Am. Chem. Soc. 122 (2000) 954;
(c) J.S. Yeston, R.G. Bergman, Organometallics 19 (2000) 2947;
(d) J.S. Yeston, B.K. McNamara, R.G. Bergman, C.B. Moore, Organometallics 19 (2000) 3442;
(e) D.M. Tellers, R.G. Bergman, Organometallics 20 (2001) 4819;
(f) M.C. Asplund, P.T. Snee, J.S. Yeston, M.J. Wilkens, C.K. Payne, H. Yang, K.T. Kotz, H. Frei, R.G. Bergman, C.B. Harris, J. Am. Chem. Soc. 124 (2002) 10605.

[3] (a) D.D. Wick, T.O. Northcutt, R.J. Lachicotte, W.D. Jones, Organometallics 17 (1998) 4484;
(b) D.D. Wick, W.D. Jones, Organometallics 18 (1999) 495;
(c) D.D. Wick, K.A. Reynolds, W.D. Jones, J. Am. Chem. Soc. 121 (1999) 3974;
(d) T.O. Northcutt, D.D. Wick, A.J. Vetter, W.D. Jones, J. Am. Chem. Soc. 123 (2001) 7257.

[4] D.D. Wick, K.I. Goldberg, J. Am. Chem. Soc. 119 (1997) 10235.

[5] S. Reinartz, P.S. White, M. Brookhart, J.L. Templeton, J. Am. Chem. Soc. 123 (2001) 6425.

[6] S. Reinartz, P.S. White, M. Brookhart, J.L. Templeton, J. Am. Chem. Soc. 123 (2001) 12724.

[7] M.P. Jensen, D.D. Wick, S. Reinartz, P.S. White, J.L. Templeton, K.I. Goldberg, J. Am. Chem. Soc. 125 (2003) 8614.

[8] M.A. Iron, H.C. Lo, J.M.L. Martin, E. Keinan, J. Am. Chem. Soc. 124 (2002) 7041.

[9] (a) J.C. Peters, J.D. Feldman, T.D. Tilley, J. Am. Chem. Soc. 121 (1999) 9871;
(b) J.D. Feldman, J.C. Peters, T.D. Tilley, Organometallics 21 (2002) 4050;
(c) A.A. Barney, A.F. Heyduk, D.G. Nocera, Chem. Commun. (1999) 2379.

[10] J.C. Thomas, J.C. Peters, Inorg. Chem. 42 (2003) 5055.

[11] S.J. Trofimenko, J. Am. Chem. Soc. 89 (1967) 3170.

[12] E. Costa, P.G. Pringle, M. Ravetz, Inorg. Synth. 31 (1995) 284.

[13] I.A. Shapiro, D.M. Jenkins, J.C. Thomas, M.W. Day, J.C. Peters, Chem. Commun. (2001) 2152.

[14] J.C. Peters, J.C. Thomas, Inorg. Synth., in press.

[15] H.C. Clark, L.E. Manzer, Inorg. Chem. 12 (1973) 362.

[16] (a) A.J. Canty, S.D. Fritsche, H. Jin, B.W. Skelton, A.H. White, J. Organomet. Chem. 490 (1995) C18;
(b) A.J. Canty, S.D. Fritsche, H. Jin, J. Patel, B.W. Skelton, A.H. White, Organometallics 16 (1997) 2175.

[17] S.A. O'Reilly, P.S. White, J.L. Templeton, J. Am. Chem. Soc. 118 (1996) 5684.

[18] J.C. Thomas, J.C. Peters, J. Am. Chem. Soc. 125 (2003) 8870.

[19] R.M. Kirchner, R.G. Little, K.D. Tau, D.W. Meek, J. Organomet. Chem. 149 (1978) C15.

[20] A.J. Canty, A. Dedieu, A. Milet, M.K. Richmond, Organometallics 15 (1996) 2845.

[21] S. Reinartz, P.S. White, M. Brookhart, J.L. Templeton, Organometallics 19 (2000) 3854.

[22] V. Mark, C.H. Dungan, M.M. Crutchfield, J.R. Van Wazer, Top. Phosphorus Chem. 5 (1967) 227 (Note: referenced ^{31}P NMR chemical shifts are reported as $-\delta$ being downfield and $+\delta$ being upfield of H_3PO_4, contrary to current standards..

[23] R.M. Stoop, A. Mezzetti, F. Spindler, Organometallics 17 (1998) 668.

[24] D.J. Schwartz, R.A. Andersen, J. Am. Chem. Soc. 117 (1995) 4014.

[25] (a) T.H. Tulip, T. Yamagata, T. Yoshida, R.D. Wilson, J.A. Ibers, S. Otsuka, Inorg. Chem. 18 (1979) 2239;
(b) D. Carmichael, P.B. Hitchcock, J.F. Nixon, A.J. Pidcock, J. Chem. Soc., Chem. Commun. (1988) 1554.

[26] B.L. Bennett, D.M. Roddick, Inorg. Chem. 35 (1996) 4703.

[27] J.M. Brunel, B. Faure, M. Maffei, Coord. Chem. Rev. (1998) 178, pp. 665–698 and references therein.