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Chemistry of phosphine–borane adducts at platinum centers: dehydrocoupling reactivity of Pt(II) dihydrides with P–H bonds

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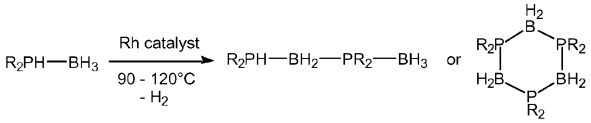
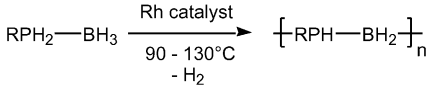
The reaction of the Pt(II) dihydride complex *cis*-[PtH_2(dcype)] (dcype = 1,2-bis(dicyclohexylphosphino)ethane) with the primary or secondary phosphine–borane adducts PhRPH·BH_3 (R = H, Ph) was found to exclusively afford the mono-substituted complexes *cis*-[PtH(PPhR·BH_3)(dcype)] (**1**: R = H; **2**: R = Ph) *via* a dehydrocoupling reaction between Pt–H and P–H bonds. Similar reactivity was observed between the uncoordinated phosphines PhRPH (R = H, Ph) and *cis*-[PtH_2(dcype)], which gave *cis*-[PtH(PPhR)(dcype)] (**4**: R = H; **5**: R = Ph). The complexes were characterized by ^{1}H, ^{11}B, ^{13}C and ^{31}P NMR spectroscopy, IR, MS and, in the case of **2**, X-ray crystallography that confirmed the *cis* geometries. The di-substituted complex *cis*-[Pt(PhPH·BH_3)$_2$(dcype)] (**3**) was prepared from the reaction of *cis*-[$PtCl_2$(dcype)] with two equivalents of Li[PPhH·BH_3]. This suggested that steric reasons alone cannot be used to explain the lack of reactivity with respect to a second dehydrocoupling reaction involving the remaining Pt–H bond in complexes **1**, **2**, **4** and **5**.

Introduction

Catalytic dehydrocoupling has recently emerged as a convenient, mild and versatile route for the formation of new bonds between inorganic elements.[1] In particular, a range of main group hydride species have been shown to undergo both homo- and heterodehydrocoupling reactions in the presence of a variety of early and late transition metal-catalysts. Catalytic dehydrocoupling reactions to form new Si–Si bonds were first discovered in the mid 1980s.[2] Subsequent work has extended this type of method to include, for example, Ge–Ge,[3] Sn–Sn,[4] P–P,[5] Si–P,[6] Si–N[7] and B–C[8] bond forming reactions. Research in our group has focussed on the dehydrocoupling of primary and secondary phosphine–borane adducts (RR′PH·BH_3) in the presence of late transition metal-catalysts, which has afforded six- and eight-membered rings [RR′P–BH_2]$_x$ (x = 3, 4), linear oligomeric species RR′PH–BH_2–RR′P–BH_3 and high molecular weight poly(phosphinoboranes) [RPH–BH_2]$_n$ (eqns. (1) and (2)).[9,10] This method was extended to the metal-catalyzed dehydrocoupling of primary and secondary amine–borane adducts (RR′NH·BH_3), which has afforded cyclic aminoboranes [RR′N–BH_2]$_2$ and borazines [RN–BH]$_3$ under mild reaction conditions (eqns. (3) and (4)).[10,11] In addition, a tandem catalytic dehydrocoupling–hydrogenation reaction involving a variety of Rh (pre)catalysts and Me_2NH·BH_3 as a stoichiometric hydrogen source for the hydrogenation of alkenes at 25 °C has also been recently developed (eqn. (5)).[12] Recent comparative work between the two systems has indicated the presence of a *homogeneous* mechanism for phosphine–borane adducts and a *heterogeneous* mechanism involving Rh(0) colloids in the case of amine–borane analogs.[13] Our attempts to further explore the homogeneous mechanism of phosphine–borane dehydrocoupling involved studies of the chemistry of phosphine–borane adducts at platinum centers.[14,15] During this work an unusual reaction between *cis*-[PtH(PPhH·BH_3)(depe)] (depe = 1,2-bis(diethylphosphino)ethane) and $PhPH_2$·BH_3 was observed, which afforded the di-substituted complex *cis*-[Pt(PPhH·BH_3)$_2$(depe)].[14b] This was formally considered to be a dehydrocoupling reaction involving Pt–H and P–H bonds.



(1)



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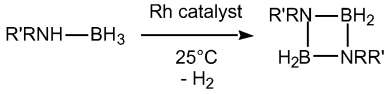

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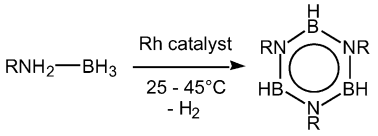

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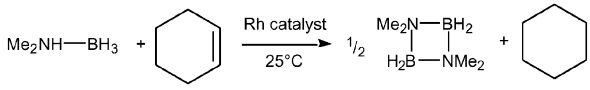

(5)

To date, there are only a few known examples of "dehydrocoupling type" reactions involving either Pt or Pd hydride complexes. For example, Fink and co-workers have reported the reaction of *cis*-[PtH_2(dcype)] with the disilane H_3Si–SiH_3 which afforded a mixture of *cis*-[Pt(SiH_2SiH_3)$_2$(dcype)] and [Pt(μ-SiH_2SiH_2)(dcype)]$_2$.[16] Puddephatt and coworkers have reported the reaction of the dinuclear complex [Pt_2Me_6(μ-H)(bu_2bpy)$_2$]OTf (bu_2bpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine) with HSPh to form the substituted complex [$PtMe_3$(bu_2bpy)(SPh)] and H_2.[17] Recently, Glueck and co-workers have reported the reaction of the bridging Pd hydride complex [Pd_2I_2(μ-dppf)(μ-H)(μ-PPh_2)] (dppf = 1,1′-bis(diphenylphosphino)ferrocene) with Ph_2PH to yield [PdI(μ-PPh_2)(Ph_2PH)]$_2$.[18] However, more detailed investigations into the dehydrocoupling reactivity of Pt hydrides with main group compounds containing E–H bonds have not been performed. In this paper, we report on our detailed investigations of the reactivity of platinum(II) dihydride complexes with phosphines and phosphine–borane adducts bearing P–H bonds.

Results and discussion

The first Pt(II) hydride complexes (*e.g.* *trans*-[PtHCl(PEt_3)$_2$]) were discovered by Chatt and Shaw in 1957.[19] While Pt(IV) hydride species are relevant with respect to C–H bond activation and Pt-catalyzed hydrosilation reactions, they are less well-known than their Pt(II) counterparts.[20] A variety of stable Pt(II)

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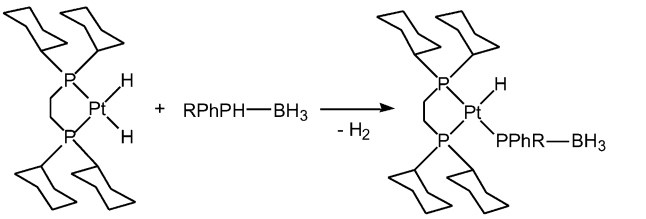
dihydride complexes containing tertiary phosphine ligands have been synthesized with both *cis* and *trans* geometries.[21] However, steric protection in the form of bulky phosphine ligands is usually required to help stabilize these complexes.[22] In addition, the reversible loss of dihydrogen has been observed but can be avoided by exposure of these complexes to a hydrogen atmosphere.[23] The complex *trans*-$[PtH_2(PMe_3)_2]$ is one of the first structurally characterized examples of a mononuclear Pt(II) dihydride complex, which was reported by Trogler and co-workers in 1985.[24] Therefore, for their combination of stability and reactivity, platinum(II) dihydride complexes with both *cis* and *trans* geometries were chosen for preliminary dehydrocoupling studies.

Reaction of *trans*-$[PtH_2(PR_3)_2]$ (R = ^{t}Bu, Me) with $PhPH_2{\cdot}BH_3$

Our first attempts to explore the reactivity of platinum hydrides with the primary phosphine–borane adduct $PhPH_2{\cdot}BH_3$ were performed using the *trans* dihydride complexes *trans*-$[PtH_2(PR_3)_2]$ (R = ^{t}Bu, Me). The reaction of *trans*-$[PtH_2(P^tBu_3)_2]$ with 2 equivalents of $PhPH_2{\cdot}BH_3$ was found to result in partial decomposition of the metal complex with the formation of $^tBu_3P{\cdot}BH_3$ after 5 h at 25 °C, in addition to unreacted starting materials. The reaction of *trans*-$[PtH_2(PMe_3)_2]$ with 2 equivalents of $PhPH_2{\cdot}BH_3$ was performed under an atmosphere of hydrogen, as the dihydride complex has been shown to slowly decompose to eliminate hydrogen under a nitrogen atmosphere.[24] However, displacement of the phosphine ligands was again observed with the formation of $Me_3P{\cdot}BH_3$. The formation of $R_3P{\cdot}BH_3$ (R = ^{t}Bu, Me) in these reactions likely arises due to the fact that the trialkylphosphines are much stronger bases than $PhPH_2$, and thus will undergo exchange with $PhPH_2{\cdot}BH_3$ to afford the tertiary phosphine–borane adducts. In order to avoid this complication, reactions involving platinum dihydrides containing a chelating bis(phosphine) were investigated, as dissociation from the metal center would be inhibited.

Synthesis of *cis*-[PtH(PhRP·BH$_3$)(dcype)] (1: R = H; 2: R = Ph)

It is known that platinum dihydride complexes with a *cis* geometry are prone to hydrogen elimination. However, the use of ligands with bulky substituents can help to stabilize these complexes and prevent decomposition.[22] For this reason, the chelating ligand 1,2-bis(dicyclohexylphosphino)ethane (dcype) was employed as the large cyclohexyl groups should ensure sufficient steric protection. The complex *cis*-$[PtH_2(dcype)]$ was readily prepared from the reaction of the corresponding dichloride *cis*-$[PtCl_2(dcype)]$ with 2 equivalents of "superhydride" $Li[BEt_3H]$. It has been previously shown that *cis*-$[PtH_2(dcype)]$ undergoes slow, reversible loss of hydrogen to afford the binuclear complex $[(dcype)Pt(\mu\text{-}H)]_2$ under a nitrogen atmosphere.[23] However, in our case $[(dcype)Pt(\mu\text{-}H)]_2$ was either not observed, or was formed only in very small quantities (<5%) when the reaction was performed under an atmosphere of nitrogen (1 h, 25 °C). The addition of 1 equivalent of $PhPH_2{\cdot}BH_3$ to a solution of *cis*-$[PtH_2(dcype)]$ (prepared *in situ*) was found to result in a rapid colour change from red to yellow along with the formation of gas bubbles. The gas released was determined to be H_2, as indicated by a resonance at δ 4.46 ppm (lit. δ 4.5 ppm)[5c,25] in the ^{1}H NMR spectrum of the reaction mixture. After 24 h, the ^{1}H, ^{11}B and ^{31}P NMR spectra all indicated the formation of *cis*-[PtH(PPhH·BH$_3$)(dcype)] (**1**) (eqn. (6)). For example, the $^{31}P\{^1H\}$ NMR spectrum showed three distinct resonances (Fig. 1(a)), suggesting inequivalency of the phosphorus nuclei in the dcype ligand. A doublet of doublets was observed at δ 77.9 ppm, which is due to the PCy_2 group that is arranged *trans* to the phosphine–borane moiety (J_{PP} = 264 Hz) and *cis* to the other PCy_2 group (J_{PP} = 2.6 Hz) with additional ^{195}Pt satellites (J_{PPt} = 2282 Hz). A second doublet of doublets was observed at δ 66.5 ppm, which is due the PCy_2 group that is arranged *cis* to both the phosphine–borane moiety (J_{PP} = 15 Hz) and the other PCy_2 group (J_{PP} = 2.6 Hz) with associated ^{195}Pt satellites (J_{PPt} = 1823 Hz). Finally, a broad doublet was observed at δ −50.6 ppm, which is due to the phosphine–borane moiety with a large *trans* coupling to one PCy_2 group (J_{PP} = 266 Hz) and associated Pt satellites (J_{PPt} = 1887 Hz). The ^{1}H NMR spectrum displayed two key resonances associated with **1**. A broad doublet was observed at δ 4.7 ppm, which is due to the PH of the phosphine–borane moiety (J_{HP} = 323 Hz) while a doublet of doublet of doublets was observed at δ −2.63 ppm, which is due to the PtH hydrogen atom with coupling to a *trans* PCy_2 group (J_{HP} = 164 Hz) and *cis* PCy_2 and $PPhH{\cdot}BH_3$ groups (J_{HP} = 26 and 13 Hz), with associated Pt satellites (J_{HPt} = 913 Hz) (Fig. 1(b)). The ^{11}B NMR spectrum of **1** displayed only a broad signal at δ −33.6 ppm. The IR spectrum of **1** in CH_2Cl_2 showed absorptions at 2358, 2197 and 2004 cm^{-1} due to B–H, P–H and Pt–H stretches, respectively.



1: R = H
2: R = Ph (6)

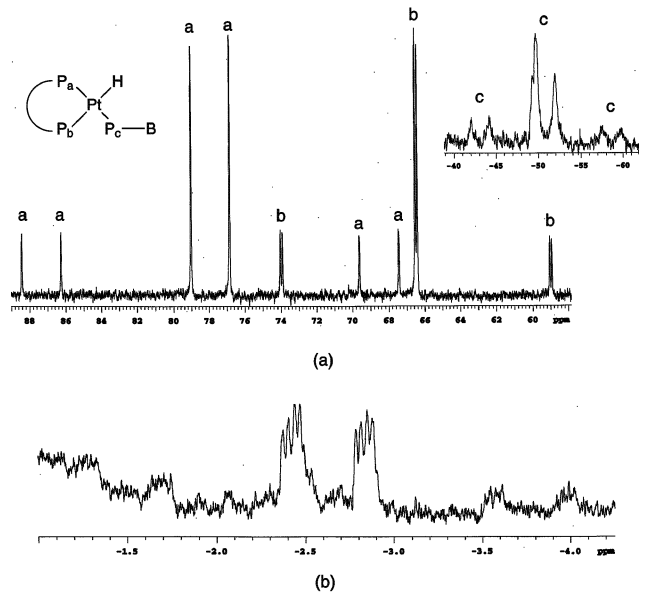


Fig. 1 Selected NMR spectra of *cis*-[PtH(PPhH·BH$_3$)(dcype)] **1**. (a) $^{31}P\{^1H\}$ NMR: For P_a: $J_{PP\,cis}$ = 2.6 Hz, $J_{PP\,trans}$ = 264 Hz, J_{PtP} = 2282 Hz. P_b: $J_{PP\,cis}$ = 2.6 Hz, $J_{PP\,cis}$ = 15 Hz, J_{PtP} = 1823 Hz. P_c: $J_{PP\,trans}$ = 266 Hz, J_{PtP} = 1887 Hz. A small amount of unreacted $PhPH_2{\cdot}BH_3$ at *ca.* δ −49 ppm overlaps with the signal due to P_c yielding the observed unequal doublet. (b) ^{1}H NMR (hydride region): $J_{HP\,cis}$ = 13 and 26 Hz, $J_{HP\,trans}$ = 164 Hz, J_{PtH} = 913 Hz. The increasing baseline at the left edge of the spectrum is due to the impending intense resonances of the protons in the cyclohexyl groups.

The reaction of *cis*-$[PtH_2(dcype)]$ with $Ph_2PH{\cdot}BH_3$ was found to afford the corresponding secondary phosphine–borane complex *cis*-[PtH($PPh_2{\cdot}BH_3$)(dcype)] (**2**), which has many analogous spectroscopic characteristics to those of **1**. For example, the $^{31}P\{^1H\}$ NMR spectrum again showed three different resonances due to the inequivalent PCy_2 groups (δ 77.5 and 67.3 ppm) and the $PPh_2{\cdot}BH_3$ moiety (δ −5.8 ppm). The hydride region of the ^{1}H NMR spectrum displayed a doublet of doublet of doublets at δ −1.84 ppm due to coupling with three different phosphorus nuclei, while the ^{11}B NMR spectrum consisted of a broad resonance at δ −30.5 ppm.

X-Ray quality crystals of **2** were grown from THF–hexanes,[26] and the molecular structure is shown in Fig. 2. The geometry around the Pt center is distorted square planar, with the hydride and the phosphine–borane moiety in a *cis* arrangement. Large angles of 170(2) and 176.10(8)° were observed between the *trans* substituents (H–Pt–P and P–Pt–P, respectively). The Pt–H bond length was determined to be 1.70(7) Å, slightly longer than the 1.59(4) Å found in the analogous complex *cis*-[PtH(PPh_2·BH_3)(depe)].[14b] For the phosphine–borane moiety, Pt–P and P–B bond lengths of 2.332(2) and 1.944(11) Å were found, respectively. For the chelating phosphine, Pt–P bond lengths of 2.269(2) and 2.312(2) Å were observed with a P–Pt–P bite angle of 87.12(7)°. The Pt–P bond *trans* to the hydride ligand was found to be much longer than the Pt–P bond *cis* to the hydride, which likely arises from the larger *trans* influence exerted by the hydride ligand compared to the phosphine–borane moiety. Similar bonding behaviour has been observed in the complexes *cis*-[PtH(PPh_2·BH_3)(depe)][14b] and *cis*-[PtH{P(O)Ph_2}{PPh_2(OH)}(PEt_3)].[27]

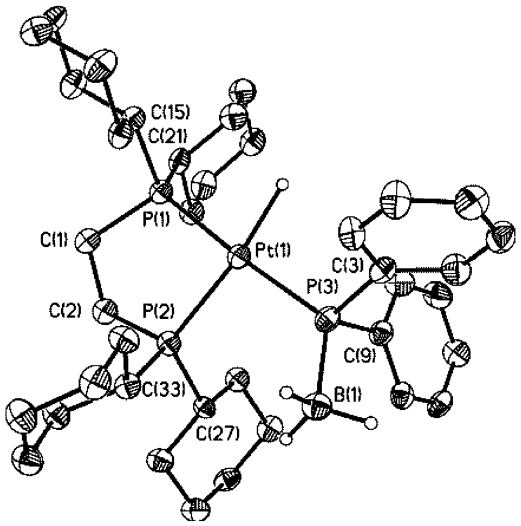
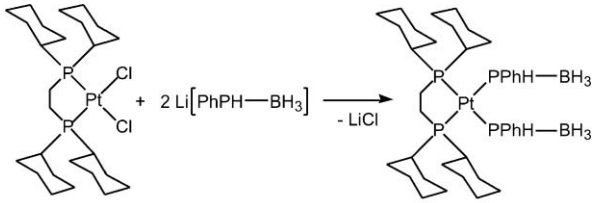


Fig. 2 Molecular structure of *cis*-[PtH(PPh_2·BH_3)(dcype)] **2**. Selected bond lengths (Å) and angles (°): Pt(1)–P(1) 2.269(2), Pt(1)–P(2) 2.312(2), Pt(1)–P(3) 2.332(2), Pt(1)–H(1Pt) 1.70(7), P(3)–B(1) 1.944(11), P(1)–C(1) 1.855(8), P(2)–C(2) 1.839(8), P(1)–C(21) 1.861(7), P(2)–C(27) 1.832(7), P(3)–C(3) 1.819(8), P(3)–C(9) 1.823(7), C(1)–C(2) 1.554(10); P(1)–Pt(1)–H(1Pt) 83(2), P(2)–Pt(1)–H(1Pt) 170(2), P(3)–Pt(1)–H(1Pt) 93(2), P(1)–Pt(1)–P(2) 87.12(7), P(1)–Pt(1)–P(3) 176.10(8), P(2)–Pt(1)–P(3) 96.77(8), B(1)–P(3)–Pt(1) 123.7(4).

Synthesis of *cis*-[Pt(PhPH·BH_3)$_2$(dcype)] (3)

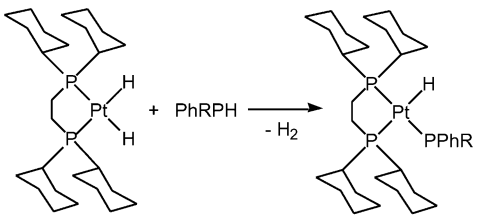
One noteworthy observation for the reactivity of **1** and **2** was that only mono-substituted complexes were formed during the dehydrocoupling reactions. For example, the treatment of **1** with a second equivalent of $PhPH_2$·BH_3 was found to result in no further reaction at 25 °C. This reactivity is in contrast to the initial dehydrocoupling reaction observed in which the di-substituted complex *cis*-[Pt(PPhH·BH_3)$_2$(depe)] was formed from the reaction of *cis*-[PtH(PPhH·BH_3)(depe)] with $PhPH_2$·BH_3.[14b] The larger cyclohexyl substituents on the dcype ligand in **1** and **2** might be expected to sterically shield the Pt center and prevent close approach of a second phosphine–borane adduct. This would explain the lack of reactivity towards di-substitution compared to the previously reported depe complex that contains smaller ethyl substituents.[14b] Contrary to this explanation, it was found that the di-substituted species *cis*-[Pt(PhPH·BH_3)$_2$(dcype)] (**3**) resulted from the reaction of *cis*-[$PtCl_2$(dcype)] with 2 equivalents of Li[PPhH·BH_3] (eqn. (7)). For complex **3**, the $^{31}P\{^1H\}$ NMR spectrum showed the presence of two species with resonances at δ 64.6 and −36.6 ppm for **3′** and δ 65.3 and -46.3 ppm for **3″**. These isomers are expected to be a mixture of *rac* (*R*,*R* and *S*,*S*) and *meso* (*R*,*S* and *S*,*R*) diastereomers due to the four different substituents on phosphorus (Pt, H, B and Ph). Based on the previous assignment of *cis*-[Pt(PPhH·BH_3)$_2$(depe)] and the trend in the ^{31}P chemical shifts,[14b] we can tentatively assign **3′** to be the *rac* diastereomer and **3″** to be the *meso* diastereomer. However, structural determination by X-ray crystallography would be required to confirm this assignment. In addition, the complex multiplets observed at δ 64.6 and 65.3 ppm occur as a result of a non-first order AA′XX′ spin system due to the chiral phosphorus centers.[14b] However, as **3** was synthesized by a salt metathesis reaction and not by a consecutive oxidative-addition/reductive-elimination reaction sequence, steric hindrance can not be completely eliminated as a valid reason to explain the lack of reactivity. For example, the insertion of the Pt center in **1** into the P–H bond of $PhPH_2$·BH_3 would likely give an intermediate octahedral Pt(IV) complex [PtH_2(PPhH·BH_3)$_2$(dcype)], which could reductively eliminate H_2 to give **3**. However, if this intermediate complex is too sterically hindered, the initial oxidative-addition reaction would not be favoured and only monosubstitution might result. In addition, reactions involving **1** and $PhPH_2$·BH_3 may require more forcing conditions that were not investigated during the course of this study.



3 (7)

Synthesis of *cis*-[PtH(PhRP)(dcype)] (4: R = H; 5: R = Ph)

With the reactivity of *cis*-[PtH_2(dcype)] with primary and secondary phosphine–borane adducts established, the reaction of uncoordinated phosphines bearing P–H bonds was also investigated. The treatment of *cis*-[PtH_2(dcype)] with $PhPH_2$ was found to result in a colour change from red to yellow and the formation of H_2 gas. Again, the spectroscopic characteristics were consistent with the formation of *cis*-[PtH(PhPH)(dcype)] (**4**) (eqn. (8)). For example, the $^{31}P\{^1H\}$ NMR spectrum showed the presence of three resonances due to three different phosphorus nuclei. The two PCy_2 groups displayed resonances at δ 79.3 and 65.5 ppm, while the PPhH group showed a signal at δ −29.5 ppm with a resolved *cis* coupling of J_{PP} = 13 Hz. The ^1H coupled ^{31}P NMR spectrum of **4** showed that the latter signal was further split into a doublet of doublets with a large coupling to the PH hydrogen atom (J_{PH} = 269 Hz). The ^1H NMR spectrum showed two key resonances associated with **4**. A broad doublet at δ 6.06 ppm due to the PH hydrogen atom was observed, as well as a doublet of doublet of doublets at δ −2.63 ppm with associated ^{195}Pt satellites, which is due to the PtH hydrogen atom. Similarly, the reaction of *cis*-[PtH_2(dcype)] with Ph_2PH was found to result in the formation of *cis*-[PtH(PPh_2)(dcype)] (**5**), as evidenced by three ^{31}P NMR resonances at δ 75.8, 61.8 and 13.8 ppm and a ^1H NMR hydride resonance at δ −3.38 ppm, which occurred as the expected doublet of doublet of doublets with associated ^{195}Pt satellites.



4: R = H
5: R = Ph (8)

As the P–H hydrogen substituents in borane-complexed phosphines would be expected to be more acidic those of the corresponding free phosphines, phosphine–borane adducts might be anticipated to undergo more facile reaction with basic transition metal hydrides to form dihydrogen due to this greater inherent polarity difference. However, no difference in reactivity between coordinated and uncoordinated free phosphine was observed in this study, suggesting that the acidity of the P–H hydrogen substituents does not affect the reactivity in this case.

Mechanism for the formation of 1, 2, 4 and 5

The formation of complexes **1**, **2**, **4** and **5** may be expected to occur by consecutive oxidative-addition/reductive-elimination reactions. For example, the insertion of the Pt center in *cis*-[PtH_2(dcype)] into a P–H bond may give an intermediate octahedral polyhydride complex (*e.g.* [$Pt(H)_3(PPh_2)$(dcype)] in the case of **5**), which could undergo reductive-elimination of H_2 to yield a mono-substituted complex. Alternatively, the reductive-elimination of H_2 from *cis*-[PtH_2(dcype)] may give [Pt(dcype)], which could undergo oxidative-addition with a P–H bond to afford the mono-substituted complex. Unfortunately, no evidence for any intermediate complexes were observed in the NMR spectra of the reaction mixtures. Notably, Böhm and Brookhart and co-workers have reported the catalytic dehydrocoupling of secondary phosphines using the late transition metal catalyst [Cp*Rh(CH_2=CH($SiMe_3$))$_2$].[5c] They found that the P–H bonds of two phosphine ligands underwent oxidative-addition at the Rh(I) center to afford a detectable Rh(V) dihydride intermediate [Cp*Rh$(H)_2(PR_2)_2$]. This intermediate was then observed to reductively eliminate H_2 and R_2P–PR_2 and return to the Rh(I) oxidation state. This type of reaction sequence may parallel the observed reactivity of the phosphine or phosphine–borane species at the Pt center in our case.

Summary

The reaction of the dihydride complex *cis*-[PtH_2(dcype)] with primary and secondary phosphine–borane adducts or phosphines has been shown to afford the mono-substituted complexes **1**, **2**, **4** and **5** *via* dehydrocoupling between the Pt–H and P–H bonds. The formation of di-substituted species were not observed, which may be due to the potentially unfavourable steric hindrance present in a Pt(IV) intermediate. With further development, this dehydrocoupling route may prove to be a general method for the formation of new Pt–P bonds which does not rely on metathesis-type salt elimination reactions.

Experimental

General procedures and materials

All reactions and product manipulations were performed under an atmosphere of dry nitrogen using standard Schlenk techniques or in an inert atmosphere glovebox filled with dry nitrogen unless otherwise specified. Hexanes was dried *via* the Grubb's method[28] while THF and CH_2Cl_2 were dried over Na/benzophenone and CaH_2, respectively, and distilled prior to use. Li[BEt_3H] (1.0 M in THF), Na (Aldrich), dcype, Ph_2PH, $PhPH_2$ (10 wt% in hexanes) (Strem Chemicals) were purchased and used as received. Naphthalene (Aldrich) was sublimed prior to use. *trans*-[$PtH_2(P^tBu_3)_2$],[29] *cis*-[$PtCl_2(PMe_3)_2$],[24] $(PhCN)_2PtCl_2$,[30] $Ph_2PH{\cdot}BH_3$[9b] and $PhPH_2{\cdot}BH_3$[9b] were synthesized by literature procedures.

Equipment

NMR spectra were recorded on a Varian Gemini 300 MHz or a Varian Unity 400 MHz spectrometer. Chemical shifts are reported relative to residual protonated solvent peaks (^1H, ^{13}C) or external $BF_3{\cdot}Et_2O$ (^{11}B) or H_3PO_4 (^{31}P) standards. NMR spectra were obtained at 300 or 400 MHz (^1H), 96 MHz (^{11}B), 75 or 100 MHz (^{13}C) or 121 MHz (^{31}P). Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact (EI) mode. Melting points were performed in sealed capillary tubes and are uncorrected. Infrared spectra were obtained on a Perkin Elmer Spectrum One FT-IR spectrometer using KBr windows.

X-Ray structural characterization

Diffraction data were collected on a Nonius Kappa-CCD using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data were integrated and scaled using the Denzo-SMN package.[31] The structure was solved and refined with the SHELXTL-PC V5.1 software package.[32] Refinement was by full-matrix least squares on F^2 using all data (negative intensities included). The molecular structure is presented with thermal ellipsoids at a 30% probability level and all hydrogen atoms attached to carbon are omitted for clarity. The hydrogen atoms bonded to carbon were included in calculated positions and treated as riding atoms, while those attached to boron or platinum were located and refined with isotropic thermal parameters.

Crystallographic data and summary of data collection and refinement for 2. Empirical formula: $C_{38}H_{62}BP_3Pt$, M_r = 817.69, T = 150(1) K, λ = 0.71073 Å, monoclinic, space group $P2_1/n$, crystal size = 0.10 × 0.10 × 0.06 mm, a = 10.7765(6), b = 20.0924(12), c = 17.4561(12) Å, β = 100.571(3)°, V = 3715.5(4) Å^3, Z = 4, D_c = 1.462 g cm^{-3}, μ = 3.931 mm^{-1}, $F(000)$ = 1672, θ range = 2.58–24.99°, index ranges: $-12 \le h \le 12$, $-21 \le k \le 23$, $-20 \le l \le 20$, reflns. collected = 18649, ind. reflns. = 6408, R_{int} = 0.0861, GoF on F^2 = 1.031, $R1$ ($I > 2\sigma(I)$) = 0.0478, $wR2$ (all data) = 0.1154, peak/hole = 1.609/−2.218 e Å^{-3}.

CCDC reference number 249141. See http://www.rsc.org/suppdata/dt/b4/b416114a/ for crystallographic data in CIF or other electronic format.

Synthesis of *cis*-[$PtCl_2$(dcype)]

To a solution of $(PhCN)_2PtCl_2$ (0.369 g, 0.781 mmol) in CH_2Cl_2 (5 mL), a solution of dcype (0.329 g, 0.778 mmol) in CH_2Cl_2 (2 mL) was added dropwise at 25 °C. The solution was stirred for 4 h and the volatiles were removed to give *cis*-[$PtCl_2$(dcype)] as a pale yellow solid. Yield: 0.526 g (98%). ^1H NMR (300 MHz, CD_2Cl_2): δ 2.7 (br, PCH_2), 2.34 (m, Cy), 2.2 (br, Cy), 2.0–1.6 (m, Cy), 1.4–1.2 (m, Cy). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 64.7 (s, J_{PPt} = 3574 Hz).

Reaction of *trans*-[$PtH_2(P^tBu_3)_2$] with 2 equiv. $PhPH_2{\cdot}BH_3$

To a solution of *trans*-[$PtH_2(P^tBu_3)_2$] (0.054 g, 0.090 mmol) in C_6D_6 in a 5 mm NMR tube, a solution of $PhPH_2{\cdot}BH_3$ (0.023 g, 0.19 mmol) in C_6D_6 was added at 25 °C. After 5 h, the ^{11}B and ^{31}P NMR spectra of the reaction mixture showed the presence of unreacted *trans*-[$PtH_2(P^tBu_3)_2$] and $PhPH_2{\cdot}BH_3$, and also $^tBu_3P{\cdot}BH_3$ (δ_P 58.9 (q, J_{PB} = 56 Hz), δ_B −40.8 (d, J_{BP} = 56 Hz); lit. δ_P 58.5 (J_{PB} = 59 Hz), δ_B −40.8 (J_{BP} = 58 Hz)).[33]

Reaction of *trans*-[$PtH_2(PMe_3)_2$] with 2 equiv. $PhPH_2{\cdot}BH_3$

A green solution of Na[naphthalide] was prepared from the reaction of Na (0.178 g, 7.74 mmol) and naphthalene (0.277 g, 2.16 mmol) in THF (7.8 mL) at 25 °C for 1.5 h. *Under a H_2 atmosphere*, the above solution of Na[naphthalide] (3.6 mL, ca. 1.0 mmol) was added to a solution of *cis*-[$PtCl_2(PMe_3)_2$] (0.208 g, 0.497 mmol) in THF (15 mL) at 0 °C. The mixture was stirred for 30 min, then warmed to 25 °C to give a brown solution of *trans*-[$PtH_2(PMe_3)_2$]. To this solution, $PhPH_2{\cdot}BH_3$ (0.123 g, 0.992 mmol) in THF (3 mL) was added. After 3.5 h, the ^{11}B and ^{31}P NMR spectra of the reaction mixture showed the presence of

$Me_3P{\cdot}BH_3$ (δ_P −1.1 (q, J_{PB} = 60 Hz), δ_B −36.9 (d, J_{BP} = 59 Hz); lit. δ_P −1.8 (J_{PB} = 59.8 Hz), δ_B −36.0 (J_{BP} = 59.8 Hz)).[34]

Synthesis of *cis*-[(dcype)PtH(PPhH·BH$_3$)] (1)[26]

In a 5 mm NMR tube, *cis*-[$PtCl_2$(dcype)] (0.039 g, 0.057 mmol) was suspended in C_6D_6, and a solution of Li[BEt_3H] in THF (0.11 mL, 0.11 mmol) was added *via* syringe. After 1 h at 25 °C, the formation of *cis*-[PtH_2(dcype)] was complete as indicated by $^{31}P\{^1H\}$ NMR: δ 77.2 (s, J_{PPt} = 1875 Hz); lit. δ 78.2 (s, J_{PPt} = 1822 Hz).[23] A solution of $PhPH_2{\cdot}BH_3$ (0.007 g, 0.06 mmol) in C_6D_6 was added *via* syringe and the formation of bubbles were observed. The initial orange–red solution turned yellow in colour after 24 h at 25 °C. The solution was filtered and the volatiles were removed *in vacuo*. The residue was washed with hexanes (4 × 10 mL), and the residual solvent removed to give **1** as a yellow solid. Crude yield: 0.020 g (48%). Attempts at recrystallization from THF–hexanes by vapour diffusion first afforded a dark yellow oil in which pale yellow crystals of **1** were embedded and could not be cleanly separated. The crystals were determined to be *ca.* 95% pure by ^1H NMR. Attempts at recrystallization by other methods (slow evaporation, solvent layering, cooling saturated solutions) all resulted in the precipitation of either impure powders or oils. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.84 (m, Ph), 7.70 (m, Ph), 4.7 (d br, J_{HP} = 323 Hz, PH), 2.0–1.5 (m, PCH_2 and Cy), 1.4–1.0 (m, Cy), −2.63 (ddd, $J_{HPtrans}$ = 164 Hz, J_{HPcis} = 26 Hz, J_{HPcis} = 13 Hz, J_{HPt} = 913 Hz, PtH). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −33.6 (br). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 135.9 (Ph), 129.5 (Ph), 128.2 (d, J_{CP} = 8.8 Hz, Ph), 36.5–35.8 (PCH_2), 29.6 (m, Cy), 27.6–27.0 (m, Cy), 26.6–26.2 (m, Cy). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 77.9 (dd, J_{PPcis} = 2.6 Hz, $J_{PPtrans}$ = 264 Hz, J_{PPt} = 2282 Hz, PCy_2), 66.5 (dd, J_{PPcis} = 2.6 Hz, J_{PPcis} = 15 Hz, J_{PPt} = 1823 Hz, PCy_2), −50.6 (d br, $J_{PPtrans}$ = 266 Hz, J_{PPt} = 1887 Hz, PHPh). IR (CH_2Cl_2): 2358 (ν_{BH}), 2197 (ν_{PH}), 2004 (ν_{PtH}) cm^{-1}. EI-MS (70 eV): *m*/*z* 725 (M^+ − BH_3 − 2H, 3%).

Synthesis of *cis*-[(dcype)PtH($PPh_2{\cdot}BH_3$)] (2)[26]

Complex **2** was prepared by a procedure similar to **1** using *cis*-[$PtCl_2$(dcype)] (0.039 g, 0.057 mmol), Li[BEt_3H] in THF (0.11 mL, 0.11 mmol) and $Ph_2PH{\cdot}BH_3$ (0.011 g, 0.055 mmol). Crude yield: 0.016 g (32%). Attempts at recrystallization from THF/hexanes by vapour diffusion afforded a brown oil in which colourless, X-ray quality crystals of **2** were embedded and could not be cleanly separated. The crystals were determined to be *ca.* 97% pure by ^1H NMR. Similar to that of **1**, all other attempts at recrystallization by different methods (slow evaporation, solvent layering, cooling saturated solutions) resulted in the precipitation of either impure powders or oils. ^1H NMR (300 MHz, C_6D_6): δ 8.31 (m, Ph), 7.21 (m, Ph), 7.05 (m, Ph), 2.59 (m, PCH_2), 2.24 (m, PCH_2), 1.7 -1.4 (m, Cy), 1.23 (m, Cy), 1.03 (m, Cy), −1.84 (ddd, $J_{HPtrans}$ = 171 Hz, J_{HPcis} = 13 Hz, J_{HPcis} = 6.4 Hz, J_{HPt} = 961 Hz, PtH). $^{11}B\{^1H\}$ NMR (C_6D_6): δ −30.5 (br). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 134.6 (br, *ipso*-Ph), 128.5 (Ph), 128.1 (Ph), 127.7 (d, J_{CP} = 8.4 Hz, Ph), 32.2 (Cy), 30.3 (Cy), 28–26 (m, PCH_2), 23.2 (Cy), 14.4 (Cy). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 77.5 (dd, J_{PPcis} = 3.2 Hz, $J_{PPtrans}$ = 266 Hz, J_{PPt} = 2220 Hz, PCy_2), 67.3 (dd, J_{PPcis} = 3.2 Hz, J_{PPcis} = 9.7 Hz, J_{PPt} = 1873 Hz, PCy_2), −5.8 (d br, $J_{PPtrans}$ = 254 Hz, J_{PPt} = 2121 Hz, PPh_2). IR (CH_2Cl_2): 2358 (ν_{BH}), 2032 (ν_{PtH}) cm^{-1}. EI-MS (70 eV): *m*/*z* 817 (M^+, 1%), 803 (M^+ − BH_3, 2%).

Attempted reaction of *cis*-[PtH_2(dcype)] with 2 equiv. of $PhPH_2{\cdot}BH_3$

In a 5 mm NMR tube, *cis*-[$PtCl_2$(dcype)] (0.021 g, 0.030 mmol) was dissolved in C_6D_6, and a solution of Li[BEt_3H] in THF (0.06 mL, 0.06 mmol) was added *via* syringe. After 1 h at 25 °C, a solution of $PhPH_2{\cdot}BH_3$ (0.008 g, 0.06 mmol) in C_6D_6 was added *via* syringe. Upon complete conversion to **1** (18 h, 25 °C), a second equivalent of $PhPH_2{\cdot}BH_3$ (0.007 g, 0.06 mmol) in C_6D_6 was added. After 24 h, the ^{31}P NMR spectrum indicated the presence of **1** and unreacted $PhPH_2{\cdot}BH_3$ with no evidence of any di-substituted species.

Synthesis of *cis*-[(dcype)Pt(PPhH·BH$_3$)$_2$] (3)

A solution of ^{n}BuLi in hexanes (1.05 mL, 1.68 mmol) was added dropwise to a solution of $PhPH_2{\cdot}BH_3$ (0.209 g, 1.69 mmol) in THF (14 mL) cooled to 0 °C. The mixture was warmed to 25 °C, and 3 mL of solution (corresponding to *ca.* 0.36 mmol of Li[$PPhH{\cdot}BH_3$]) was removed and added dropwise to a solution of *cis*-[$PtCl_2$(dcype)] (0.123 g, 0.179 mmol) in CH_2Cl_2 (5 mL) at 25 °C. After stirring the mixture for 18 h, the volatiles were removed, and the yellow oily residue was dissolved in CH_2Cl_2 (10 mL). The solution was filtered and hexanes (40 mL) added to precipitate a solid. The supernatant was decanted and the residual solvent was removed *in vacuo* to give **3** as a yellow solid. Pale yellow crystals were obtained by slow evaporation of a CH_2Cl_2–hexanes solution (1 : 1) over 3–4 days at 25 °C. Despite confirming the purity of **3** by ^1H NMR spectroscopy, suitable elemental analysis could not be obtained. Yield: 0.096 g (62%). Mp 129–131 °C. IR (Nujol): 2335 (ν_{BH}), 2247 (ν_{PH}) cm^{-1}. EI-MS (70 eV): *m*/*z* 833 (M^+ − 2 BH_3 − 2H, 4%), 435 (dcypeBH_2^+, 12%).

3′ (*rac* diastereomer): ^1H NMR (CD_2Cl_2): δ 7.58 (m, Ph), 7.24 (m, Ph), 4.7 (d br, J_{HP} = 341 Hz, PH), 2.68 (m, PCH_2), 2.30 (m, PCH_2), 1.9–1.6 (m, Cy), 1.4–1.0 (m, Cy). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −36.7 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 135.2 (d, J_{CP} = 8.4 Hz, Ph), 134.1 (d, J_{CP} = 34 Hz, *ipso*-Ph), 129.4 (s, Ph), 128.3 (d, J_{CP} = 8.3 Hz, Ph), 36.3 (m, PCH_2), 33.0 (m, Cy), 30.3 (m, Cy), 27.6–26.8 (m, Cy), 26.6 (s, Cy). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 64.6 (m, $J_{AX'}$ = $J_{A'X}$ = 224 Hz, J_{AX} = $J_{A'X'}$ = −20 Hz, $J_{XX'}$ = 8.4 Hz, $J_{AA'}$ = 0 Hz, J_{PPt} = 2170 Hz, PCy_2), −36.6 (d br, $J_{PPtrans}$ = 244 Hz, J_{PPt} = 1725 Hz, PHPh).

3′ (*meso* diastereomer): ^1H NMR (CD_2Cl_2): δ 7.84 (m, Ph), 7.30 (m, Ph), 4.7 (d br, J_{HP} = 341 Hz, PH), 2.68 (m, PCH_2), 2.30 (m, PCH_2), 1.9–1.6 (m, Cy), 1.4–1.0 (m, Cy). $^{11}B\{^1H\}$ NMR (CD_2Cl_2): δ −36.7 (br). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ *ipso*-Ph not observed, 135.8 (d, J_{CP} = 7.6 Hz, Ph), 129.5 (s, Ph), 128.2 (d, J_{CP} = 8.4 Hz, Ph), 36.2 (m, PCH_2), 30.7 (m, Cy), 29.6 (m, Cy), 27.6–26.8 (m, Cy), 26.1 (s, Cy). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 65.3 (m, $J_{AX'}$ = $J_{A'X}$ = 223 Hz, J_{AX} = $J_{A'X'}$ = −20 Hz, $J_{XX'}$ = 7.0 Hz, $J_{AA'}$ = 0 Hz, J_{PPt} = 2135 Hz, PCy_2), −46.3 (d br, $J_{PPtrans}$ = 257 Hz, J_{PPt} = 1755 Hz, PHPh).

Synthesis of *cis*-[(dcype)PtH(PPhH)] (4)[26]

Complex **4** was prepared by a procedure similar to **1** using *cis*-[$PtCl_2$(dcype)] (0.042 g, 0.061 mmol), Li[BEt_3H] in THF (0.12 mL, 0.12 mmol) and $PhPH_2$ in hexanes (0.008 g, 0.073 mmol). Crude yield: 0.024 g (55%). Attempts at recrystallization from THF–hexanes by vapour diffusion afforded small clusters of pale yellow microcrystals of **4** embedded in a brown oil which could not be cleanly separated. The crystals were determined to be *ca.* 93% pure by ^1H NMR. All attempts to recrystallize **4** by other methods (*e.g.* slow evaporation, solvent layering, cooling saturated solutions) did not result in pure samples. Mp 150 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.69 (m, Ph), 7.27 (m, Ph), 6.06 (d br, J_{HP} = 250 Hz, PH), 2.1–1.5 (m, PCH_2 and Cy), 1.4–1.0 (m, Cy), −2.63 (ddd, $J_{HPtrans}$ = 122 Hz, J_{HPcis} = 19 Hz, J_{HPcis} = 9 Hz, J_{HPt} = 682 Hz, PtH). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2): δ 128.4 (d, J_{CP} = 9 Hz, Ph), 37–35 (m, PCH_2), 31–30 (m, Cy), 30–29 (m, Cy), 27.5–27 (m, Cy), 26.7–26.3 (m, Cy). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 79.3 (d, $J_{PPtrans}$ = 228 Hz, J_{PPt} = 2310 Hz, PCy_2), 65.5 (d, J_{PPcis} = 13 Hz, J_{PPt} = 1806 Hz, PCy_2), −29.5 (dd, J_{PPcis} = 13 Hz, $J_{PPtrans}$ = 228 Hz, J_{PPt} = 1642 Hz, PHPh). Selected ^{31}P NMR (C_6D_6): δ −29.4 (dd br, J_{PH} = 269 Hz). IR (Nujol): 2308 (ν_{PH}), 2000 (ν_{PtH}) cm^{-1}. EI-MS (70 eV): *m*/*z* 617 (dcypePt, 23%).

Synthesis of *cis*-[(dcype)PtH(PPh_2)] (5)[26]

Complex **5** was prepared by a procedure similar to **1** using *cis*-[$PtCl_2$(dcype)] (0.040 g, 0.058 mmol), Li[BEt_3H] in THF (0.12 mL, 0.12 mmol) and Ph_2PH (0.011 g, 0.059 mmol). Crude yield: 0.030 g (64%). Attempts at recrystallization from THF/hexanes by vapour diffusion occasionally produced pale brown crystals of **5** that were embedded in a dark brown oil and could not be cleanly separated. The crystals were determined to be *ca*. 90% pure by ^{1}H NMR. All other attempts at recrystallization by other methods (*e.g.* slow evaporation, solvent layering, cooling saturated solutions) did not result in crystalline material, only impure powders or oils. Mp 149–153 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.77 (m, Ph), 7.39 (m, Ph), 7.30 (m, Ph), 2.2–1.7 (m, PCH_2 and Cy), 1.5–1.1 (m, Cy), −3.38 (ddd, $J_{HPtrans}$ = 121 Hz, J_{HPcis} = 21 Hz, J_{HPcis} = 7.8 Hz, J_{HPt} = 656 Hz, PtH). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2): δ 128.6 (d, J_{CP} = 11 Hz, Ph), 128.3 (br, Ph), 127.8 (d, J_{CP} = 9 Hz, Ph), 37–36 (m, PCH_2), 30.5–29.5 (m, Cy), 28.9–28.6 (m, Cy), 27.7–27 (m, Cy), 26.8–26.2 (m, Cy). ^{31}P{^{1}H} NMR (C_6D_6): δ 75.8 (dd, J_{PPcis} = 5.2 Hz, $J_{PPtrans}$ = 283 Hz, J_{PPt} = 2263 Hz, PCy_2), 61.8 (d, J_{PPcis} = 14 Hz, J_{PPt} = 2004 Hz, PCy_2), 13.8 (dd, $J_{PPtrans}$ = 228 Hz, J_{PPcis} = 10 Hz, J_{PPt} = 2006 Hz, PPh_2). IR (Nujol): 1997 (ν_{PtH}) cm^{-1}. EI-MS (70 eV): m/z 802 (M^+ − H, 3%).

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