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# $Pt(PEt_3)(\kappa^2$-P,C-$PEt_2CHMe)(C_6Cl_5)$: An Unexpected Intermediate in the Synthesis of *cis*-$Pt(PEt_3)_2(Cl)(C_6Cl_5)$

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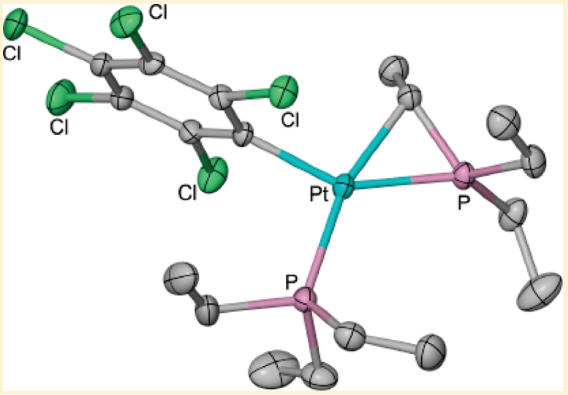
Supporting Information

**ABSTRACT:** Addition of 1 to 6 equiv of $LiC_6Cl_5$ to *cis*-$Pt(PEt_3)_2Cl_2$ gives the unexpected phosphine ligand C—H bond activation product $Pt(PEt_3)(\kappa^2$-P,C-$PEt_2CHMe)(C_6Cl_5)$ (**1**). Aqueous HCl addition to **1** gives the previously reported product of the reaction, *cis*-$Pt(PEt_3)_2(Cl)(C_6Cl_5)$ (**2**).




## INTRODUCTION

A common method for the synthesis of Pt(II) alkyl and aryl complexes involves addition of an organolithium or organomagnesium reagent to a Pt(II) halide followed by an aqueous, often acidic workup to remove excess reagent and coproduct salts.[1,2] It is usually assumed that the Pt alkyl or aryl complex is formed directly in the reaction and is present before and after the workup. Herein, we report an example where this is not the case, and the final Pt(II) aryl complex is obtained only after acidic treatment of an initially formed phosphine ligand metalation product.[3]

## RESULTS AND DISCUSSION

The reported synthesis of Pt(II) aryl complex *cis*-$Pt(PEt_3)_2(Cl)(C_6Cl_5)$ (**2**) employs the reaction of *cis*-$Pt(PEt_3)_2Cl_2$ with excess $LiC_6Cl_5$ or $C_6Cl_5MgCl$ with an HCl(aq) workup.[4] (The steric bulk of the $C_6Cl_5$ ligand was assumed to prevent a second arylation.) In repeating this synthesis, we left out the acidic workup and were surprised to isolate not **2**, but rather a new complex, $Pt(PEt_3)(\kappa^2$-P,C-$PEt_2CHMe)(C_6Cl_5)$ (**1**). Thus, **1** was obtained by reaction of *cis*-$Pt(PEt_3)_2Cl_2$ with 1 to 6 equiv of $LiC_6Cl_5$ in THF followed by a neutral aqueous workup (Scheme 1).

The $^{31}P$ NMR spectrum for **1** in $CDCl_3$ (see Figure 1 for atom numbering) exhibits two doublets at $\delta$ −22.4 ($J_{PtP1}$ = 1545 Hz, $J_{P1P2}$ = 29 Hz, P1) and 19.9 ($J_{PtP2}$ = 3007 Hz, P2), a pattern not unlike that reported for **2**.[5] However, due to the large negative shift of P1, the chemical shift difference between the doublets ($\Delta\delta$ = 42.3) is very much larger than expected for **2**. The shift for P1 is consistent with P1 being part of the three-membered ring[6] of **1**, and P1 is assigned to the metalated phosphine ligand. The doublet at $\delta$ 19.9 is assigned to the "nonmetalated" phosphine, P2. $^{195}Pt-^{31}P$ couplings are also consistent with this assignment.[7,8] P1 is *trans* to the strongly donating anionic $C_6Cl_5$ ligand and has the smallest coupling while P2, with larger coupling, is *trans* to the less strongly donating phosphorus-bonded CHMe group. In the $^{195}Pt$ NMR spectrum of **1** in $CH_2Cl_2$, the expected doublet of doublets appears at $\delta$ −3252 ($J_{P1Pt}$ = 1588 Hz, $J_{P2Pt}$ = 3088 Hz). The $^1H$ NMR spectrum of **1** is less readily interpreted and contains multiple overlapping peaks in the $PEt_3$ region that could only be assigned with the assistance of COSY and HMQC experiments (see Experimental Section). On the other hand, the $^{13}C$ NMR spectrum of **1** is well resolved, and the three-membered-ring carbon atom (C7) is apparent as the lowest frequency signal ($\delta$ 4.3) consisting of a doublet of doublets with satellites ($J_{PC7}$ = 59 and 13 Hz, $J_{PtC7}$ = 197 Hz). The *ipso* carbon atom (C1) of the $C_6Cl_5$ ligand is the highest frequency signal ($\delta$ 167.4) and is also a doublet of doublets with satellites ($J_{PC1}$ = 83 and 6 Hz; $J_{PtC1}$ = 1150 Hz).

A single crystal of **1**, suitable for X-ray diffraction analysis, was obtained by slow vapor diffusion of EtOH into a $CH_2Cl_2$ solution of **1** at room temperature. Complex **1** (Figure 1) shows a planar geometry at the Pt(II) metal center; however, the typical square shape is distorted by the presence of the Pt,P,C ring.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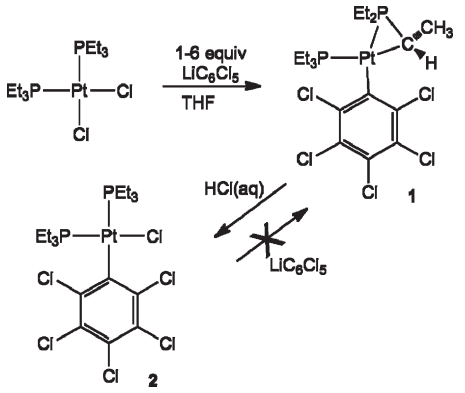
**Scheme 1**



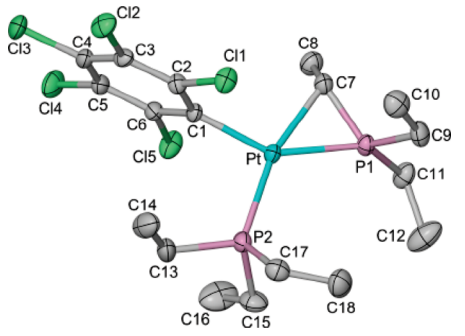




**Figure 1.** Drawing of the solid-state structure of $Pt(PEt_3)(\kappa^2\text{-P,C-}PEt_2CHMe)(C_6Cl_5)$ (**1**) (50% probability ellipsoids). Hydrogen atoms are omitted. The methylene groups of the $PEt_3$ ligand are disordered over two positions. Only the major (70%) positions are shown. Selected bond distances (Å) and angles (deg) for **1**: Pt−P1, 2.226(2); Pt−P2, 2.281(2); Pt−C1, 2.057(5); Pt−C7, 2.158(6); P1−C7, 1.757(6); C7−C8, 1.514(7); P1−Pt−P2, 116.28(5); P2−Pt−C1, 96.5(1); C1−Pt−C7, 100.1(2); C7−Pt−P1, 61.7(1); Pt−C7−P1, 42.8(1); C7−P1−Pt, 64.4(2); Pt−C7−C8, 118.5(3); P1−C7−C8, 122.9(3).

The $Et_2PCHMe$ ligand can be formulated in the extremes as a metalated phosphine ligand where the C atom bonded to the Pt is essentially an anionic alkyl group (**A**) or as a metal-substituted phosphorus ylide ligand with $\pi$-donation to the Pt center from the P−C double bond (**B**). The P1−C7 distance of 1.757(6) Å is shortened relative to the other P−C distances (average = 1.83), consistent with double-bond character and the ylide formulation **B**. Also in agreement with the ylide formulation is the Pt−C7 distance (2.158(6) Å), which is larger than that expected for an alkyl-type interaction (compare to the Pt−C1 distance of 2.057(5) Å). The long distance also agrees with the $^{31}P$ NMR data, which indicate a relatively low *trans* influence for C7 (see above).

The stability and reactivity of **1** were briefly examined. Heating solutions of **1** in THF at 90 °C overnight under inert or atmospheric conditions gave no visible or spectroscopic indication of decomposition. An identical result was observed when **1** was heated in wet THF. As shown in Scheme 1, excess HCl, gaseous or aqueous, gives **2**, consistent with the unrecognized conversion of **1** into **2** by the acidic workup in the reported preparation of **2**.[4] Complex **2** was also acquired from a thick-layer $SiO_2$ chromatographic plate by eluting with hexanes/$CH_2Cl_2$ (90:10) in air. (The source of the HCl is presumably the $CH_2Cl_2$ solvent and adventitious water interacting with the $SiO_2$ surface.) A single crystal of **2** for X-ray diffraction was obtained from slow evaporation of $CH_2Cl_2$ solution of **2** at room temperature (SI).[15]

The above NMR and structural data match well with that reported for related Pt and Pd complexes containing M,P,C three-membered rings.[9−19] Most closely related are the complexes $Pt(PEt_3)(\kappa^2\text{-P,C-}PEt_2CHMe)(R)$ (R = a carboranyl, e.g., $PhC_2B_{10}H_{10}^-$), which are formed in exactly the same way as **1**, that is, from the reaction of $PtL_2Cl_2$ (L = a phosphine) and a carboranyl lithium reagent.[9−13] (The first report of these complexes[9] incorrectly assigns the metalation to the $\beta$-carbon of the phosphine ligands.)

The formation of **1** and its carboranyl analogues is rather curious, and we conducted experiments to learn more about the formation of **1**. The reaction of $Pt(PEt_3)_2Cl_2$ and $LiC_6Cl_5$ was repeated with incremental additions of $LiC_6Cl_5$ and $^{31}P$ NMR monitoring. Other than trace amounts of **2**, **1** and $C_6Cl_5H$ ($^1H$ NMR: $\delta$ 7.54) are the only detected products. With less than stoichiometric amounts of the Li reagent the products are the same but with remaining $Pt(PEt_3)_2Cl_2$. Complex **2** is not an intermediate in the formation of **1**, as there is no reaction between isolated **2** and $LiC_6Cl_5$ under similar conditions (Scheme 1). It seems that either phosphine ligand metalation precedes Pt center arylation or a species other than **2** is formed in the arylation reaction and undergoes rapid phosphine metalation.

Two possible pathways are shown in Scheme 2. A key feature for pathway (a) is $PEt_3$ dissociation, which would probably need to precede the bulky aryl anion attack. Chloride loss from anionic **3** with coordination of a triethylphosphine C−H bond would activate the C−H bond to deprotonation[20] in **4**. Deprotonation by the second aryl anion gives **5**, and $PEt_3$ displacement of chloride, with a geometric rearrangement, would then yield **1**. For this pathway to be successful, free $PEt_3$ must not capture **3** or **4**, or **2** would be the product. While this may be the case with low $PEt_3$ concentrations, capture would be much more likely with added $PEt_3$. In addition, added $PEt_3$ should slow the reaction rate by suppressing $PEt_3$ dissociation in the first step. We added 1 equiv of free $PEt_3$ to the reaction and observed no change in the product distribution or in the qualitative reaction rate, suggesting that pathway (a) is not operative.

Pathway (b) occurs by aryl anion attachment on a coordinated $PEt_3$ to give **7**, either by deprotonation (α-CH deprotonation of alkyl phosphines has been reported[21−24]) to give **7** directly or by attack at the P atom to form metallaphosphorane[25] **6** followed by RH elimination. We favor direct deprotonation given the steric crowding around the P center in **6**. Chloride displacement by the ylidic carbon center in **7** then gives **8**, which would be sterically much more open than $PtCl_2(PEt_3)_2$, allowing aryl anion/chloride exchange to give **1**. Added $PEt_3$ should not affect this pathway.

In conclusion, we find that in the reported synthesis of aryl complex *cis*-$Pt(PEt_3)_2(Cl)(C_6Cl_5)$ (**2**) the primary product is phosphine metalation complex $Pt(PEt_3)(\kappa^2\text{-P,C-}PEt_2CHMe)(C_6Cl_5)$ (**1**), and **2** is only formed after an acidic workup. The analogous formation of **1** and previously reported $Pt(PEt_3)(\kappa^2\text{-P,C-}PEt_2CHMe)(R)$ (R = a carboranyl) complexes probably occurs by direct deprotonation of the coordinated $PEt_3$ ligand.

## EXPERIMENTAL SECTION

**General Procedures.** All procedures were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corporation drybox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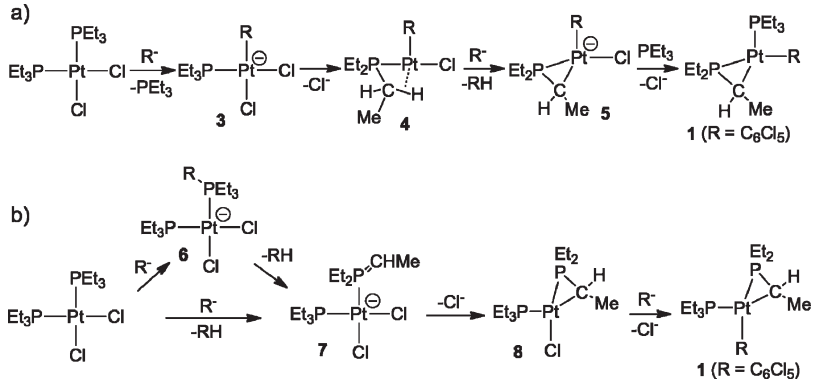
**Scheme 2**




unless otherwise stated. All solvents were dried and degassed by standard techniques and stored under dinitrogen over 4 Å molecular sieves or sodium metal. *n*-Butyllithium and hydrochloric acid were obtained from commercial sources (Aldrich or Acros) and used as received. Commercial hexachlorobenzene was recrystallized from benzene. *cis*-$PtCl_2(PEt_3)_2$[26] and lithiopentachlorobenzene[27] were prepared by literature methods. Hydrogen chloride gas was prepared from NaCl and sulfuric acid. NMR spectra were recorded on Bruker AMX-250, -300, or -500 spectrometers at ambient probe temperature unless otherwise stated. Chemical shifts are given as $\delta$, and coupling constants ($J$) in Hz. $^1$H and $^{13}$C NMR shifts are relative to internal TMS (0 ppm) as referenced to solvent signals. $^{31}$P NMR shifts are relative to external 85% $H_3PO_4$ (0 ppm), and $^{195}$Pt NMR shifts are relative to external $K_2PtCl_4/D_2O$ (−1624 ppm). NMR peak assignments were assisted by COSY, DEPT, and HMQC experiments (SI).

**Pt(PEt$_3$)($\kappa^2$-P,C-PEt$_2$CHMe)(C$_6$Cl$_5$) (1).** A suspension of $C_6Cl_6$ (50.3 mg, 0.177 mmol) in 0.5 mL of THF was cooled to −30 °C in a refrigerator. The $C_6Cl_6$ mixture was removed from the refrigerator, and $^n$BuLi (0.11 mL, 0.176 mmol, 1.6 M in hexanes) was added dropwise into the stirred $C_6Cl_6$ mixture over a 5 min period.[27] The resulting dark brown solution was stirred for another 20 min and then replaced in the refrigerator for ca. 20 min. The cold solution was then slowly added dropwise to a stirred suspension of *cis*-$Pt(PEt_3)_2Cl_2$ (40.8 mg, 0.0812 mmol) in 0.5 mL of THF, previously cooled to −30 °C in the refrigerator. The dark brown mixture was stirred for 20 min and allowed to warm to room temperature. The mixture was filtered through diatomaceous earth, and the volatiles were removed under reduced pressure to give a dark brown oil. The oil was dissolved in $CHCl_3$ and washed 3× with $H_2O$. The volatiles were removed under reduced pressure from the organic fraction, and the resulting dark brown solid was washed with 0.2 mL of EtOH, collected by filtration, and dried under reduced pressure to give crude brown solid **1**. Yield: 33 mg (60%). The brown material is nearly pure by NMR and may be recrystallized from $CH_2Cl_2$/EtOH to give a yellow solid. Yellow single crystals for X-ray analysis were grown by slow vapor diffusion of EtOH into a $CH_2Cl_2$ solution at room temperature.

MS (ESI/APCI) $m/z$ (rel intensity %): $[M + H]^+$ 679 (50), 681 (45), 680 (39), 683 (22), 682 (17), 678 (27), 677 (28), 684 (11), 685 (12), 686 (4), 687 (3); $[M - C_6Cl_5]^+$ 429 (40), 430 (39), 431 (29), 433 (10), 432 (7), 434 (2), 427 (22). $^1$H NMR ($CDCl_3$, 500 MHz): 2.10−1.87 (overlapping m's, 5H, PEt(C$H_2$Me)CHMe and $PEt_2CHCH_3$), 1.68 (br m, 6H, $P(CH_2Me)_3$), 1.28 (overlapping dq, $J_{HH}$ = 7, $J_{PH}$ = 9, 2H, PEt(C$H_2$Me)′CHMe), 1.23 (dt overlapping with 1.28 signal, $J_{HH}$ = 8, $J_{PH}$ = 18, 3H, PEt($CH_2CH_3$)CHMe)), 1.06 (dt, 3H, $J_{HH}$ = 7, $J_{PH}$ = 19, PEt($CH_2CH_3$)′CHMe)), 0.99 (overlapping dt, 9H, $P(CH_2CH_3)_3$). The COSY spectrum indicates that the $PEt_2CHMe$ resonance is buried under the signals around $\delta$ 1.1 and adds 1H to the integration in this region. One line of the expected complex multiplet may be seen at $\delta$ 1.09. There is a possibility that the $PEt_2CHCH_3$ and $PEt_2CHMe$ peak assignments are reversed. The $^1$H−$^{13}$C HMQC spectrum did not show a clear cross-peak for either $^1$H NMR signal, and our assignment was based on integration values (see SI). A previously reported $Ph_2PCHMe$ Pt complex[14] showed the CH peak at $\delta$ 1.63 and the $CH_3$ peak at $\delta$ 0.90, the reverse of our assignment order in $\delta$. $^{13}$C{$^1$H} NMR ($CDCl_3$, 125 MHz): 167.4 (dd with satellites, $J_{PtC}$ = 1150, $J_{PC}$ = 83 and 6, C1), 137.2 (d with satellites, $J_{PtC}$ = 28, $J_{PC}$ = 42, $C_6Cl_5$), 132.3 (s), 129.1 (dd with satellites, $J_{PtC}$ = 73, $J_{PC}$ = 83 and 6, $C_6Cl_5$), 124.9 (s, $C_6Cl_5$), 20.0 (dd with satellites, $J_{PC}$ = 28 and 4, $J_{PtC}$ = 45, $P(CH_2CH_3)_3$), 13.5 (pseudo t, apparent $J_{PC}$ = 7, $PEt_2CHCH_3$), 13.3 (dd, $J_{PC}$ = 25, PEt($CH_2CH_3$)-CHMe)), 11.6 (d with satellites, $J_{PC}$ = 25, $J_{PtC} \approx$ 7, PEt($CH_2CH_3$)-′CHMe)), 10.0 (d with satellites, $J_{PC}$ = 4, $J_{PtC}$ = 28, PEt($CH_2CH_3$)-CHMe)), 9.4 (s with satellites, $J_{PtC}$ = 25), 8.5 (s with satellites, $J_{PtC}$ = 20), 4.3 (dd with satellites, $J_{PtC}$ = 197, $J_{PC}$ = 59 and 13, $PEt_2CHMe$ (C7)). The C7 signal was clearly established as a CH in the DEPT experiments. $^{31}$P{$^1$H} NMR ($CDCl_3$, 101 MHz): 19.7 (d with satellites, $J_{PtP}$ = 3004, $J_{PP}$ = 29, P2); −22.4 (d with satellites, $J_{PtP}$ = 1542, $J_{PP}$ = 29, P1). Essentially identical spectra are obtained in $CH_2Cl_2$, hexanes, THF, and $C_6D_6$. $^{195}$Pt NMR ($CH_2Cl_2$, 64 MHz): −3252 (q, $J_{PPt}$ = 3088 and 1588). $^{195}$Pt NMR (hexanes, 64 MHz): −3260 (q, $J_{PPt}$ = 3063 and 1525).

***cis*-Pt(PEt$_3$)$_2$(Cl)(C$_6$Cl$_5$) (2) from *cis*-(PEt$_3$)Pt($\kappa^2$-P,C-PEt$_2$CHMe)(C$_6$Cl$_5$) (1). (a).** Complex **1** (15.7 mg, 0.0231 mmol) dissolved in 0.2 mL of $CDCl_3$ was placed into a screw-capped NMR tube fitted with a rubber septum. HCl(g) (2.0 mL, 0.065 mol) was injected by syringe into the NMR tube, and the tube was shaken. The volatiles were removed under reduced pressure to give **2** as a brown solid. Yield: 15.1 mg (91.3%). HCl(aq) could be used in place of HCl(g). **(b)** Complex **1** was eluted with hexanes/$CH_2Cl_2$ (90:10) on a thick chromatographic plate and then extracted with $C_6H_6$. The volatiles were removed under reduced pressure to give **2** as a brown solid. Light yellow single crystals for X-ray analysis were grown by slow vapor evaporation of a $CH_2Cl_2$ solution at room temperature. Details of the structure are available in the Supporting Information. The $^{195}$Pt and $^{31}$P NMR data match the literature report.[5]

$^1$H NMR ($CDCl_3$, 300 MHz): 2.03−1.95 (m, $J_{HH}$ = 7.5, 6H, $P(CH_2Me)_3$ *trans* to Cl), 1.79−1.62 (m, $J_{HH}$ = 7.8, 6H, $P(CH_2Me)_3$ *cis* to Cl), 1.24−1.12 (m, $J_{HH}$ = 7.5, 18H, $P(CH_2CH_3)_3$ *trans* to Cl), 1.14−1.04 (m, $J_{HH}$ = 8.1, 9H, $P(CH_2CH_3)_3$ *cis* to Cl). $^{13}$C NMR ($CDCl_3$, 125 MHz): 137.3 (s, $C_6Cl_5$), 130.4 (s, $C_6Cl_5$), 128.3 (s, $C_6Cl_5$), 128.0 (s, $C_6Cl_5$), 18.2 (d, $J_{PC}$ = 37.7, $P(CH_2Me)_3$ *cis* to Cl), 14.6 (d, $J_{PC}$ = 31.4, $P(CH_2Me)_3$ *trans* to Cl), 8.4 (d, $J_{PC}$ = 21.4, $P(CH_2CH_3)_3$). $^{31}$P{$^1$H} NMR ($CDCl_3$, 101 MHz): 7.8 (d with satellites, $J_{PtP}$ = 2034,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$J_{PP}$ = 19, $PEt_3$ *cis* to Cl); −0.18 (d with satellites, $J_{PtP}$ = 3937, $J_{PP}$ = 19, $PEt_3$ *trans* to Cl). $^{31}P\{^1H\}$ NMR ($CH_2Cl_2$, 101 MHz): 7.6 (d with satellites, $J_{PtP}$ = 2053, $J_{PP}$ = 19, $PEt_3$ *cis* to Cl), −0.12 (d with satellites, $J_{PtP}$ = 3903, $J_{PP}$ = 19, $PEt_3$ *trans* to Cl). $^{31}P\{^1H\}$ NMR ($C_6H_6$, 101 MHz): 7.8 (d with satellites, $J_{PtP}$ = 2037, $J_{PP}$ = 19, $PEt_3$ *cis* to Cl), −0.80 (d with satellites, $J_{PtP}$ = 3855, $J_{PP}$ = 19, $PEt_3$ *trans* to Cl). $^{195}Pt$ NMR ($CDCl_3$, 64 MHz): −2,889 (pseudo q, $J_{PPt}$ = 3989 and 2075). $^{195}Pt$ NMR ($CH_2Cl_2$, 64 MHz): −2,889 (pseudo q, $J_{PPt}$ = 3928 and 2037).

## ■ ASSOCIATED CONTENT

**Supporting Information.** X-ray crystallographic files in CIF format for **1** and **2** and selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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## ■ ACKNOWLEDGMENT

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