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# (π-Allyl)palladium Complexes of Norcamphene. Structure and Reactivity

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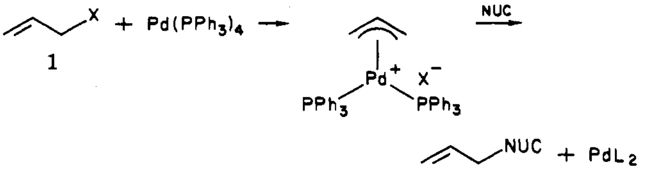
Bis(phosphine) complexes (allyl)Pd$L_2$X were prepared by the reaction of the π-allyl chloride dimer **5** with triphenylphosphine. Study of the $^1$H NMR, conductivity, and chemical reactivity of these complexes indicates that the complex with X = Cl at room temperature in $CDCl_3$, $CH_2Cl_2$, or acetone is best characterized as a contact ion pair, whereas at low temperature it is best envisioned as a free ion pair. In THF, rapidly equilibrating mono(phosphine) halides are the major species present. The complex with X = $PF_6^-$ (**15**) uniformly behaves like a cationic entity, (allyl)Pd$L_2^+X^-$. The crystal structure of the bis(phosphine) cation **15** was determined. The cell dimensions are $a$ = 10.328 (1) Å, $b$ = 17.767 (1) Å, $c$ = 21.984 (1) A, $\beta$ = 100.21 (1)°, and $V$ = 3972.9 Å$^3$. The crystals are monoclinic of space group $P2_1/n$ with $Z$ = 4. The regiochemistry of addition of nucleophiles is discussed in terms of asymmetry in the π-allyl complex.

## Introduction

The tremendous utility of (π-allyl)palladium chemistry in organic synthesis has been thoroughly demonstrated.[1] The exact nature of the intermediates present in this important reaction however, remains unclear and has been a source of considerable controversy. Initial studies by Trost[2] led to the prediction that a bis(phosphine) allyl cationic complex was formed on reaction of $Pd(PPh_3)_4$ and **1** (X = Cl, OAc, etc.) and that this complex was responsible for the observed enhanced electrophilicity of the allyl substrate. In support of this suggestion Trost demonstrated that the species generated by the addition of 1 equiv of (diphenylphosphino)ethane (diphos)/Pd to the π-allyl chloride dimer derived from methylenecyclohexane and an independently prepared bis(phosphine) cation ($BF_4^-$ counterion) of the same substrate gave identical regioisomeric product mixtures when reacted with carbon nucleophiles.[3]



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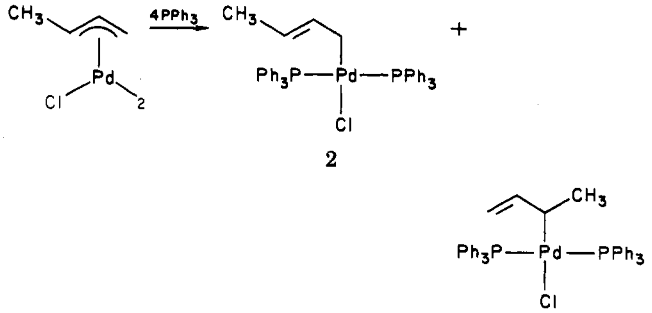
In contrast, in recent work by Akermark[4] involving conductivity studies he concluded that the species formed on reaction of crotyl chloride and $Pd(PPh_3)_4$ in THF was not a bis(phosphine) cation. However, the possibility of a nonconducting contact ion pair species being present was not considered. In a related experiment, Akermark suggested that the compound formed by reaction of (π-crotyl)palladium chloride dimer and 4 equiv of $PPh_3$ was a mixture of the $\eta^1$ complexes **2** and **3**. This suggestion was based on the observation that the addition of amines to the species made in this way gave significantly different products than those from reaction of the amines with a "specifically" generated bis(phosphine) cation ((π-crotyl)palladium chloride dimer, $AgBF_4$, $PPh_3$). Amines however have been demonstrated to be capable of adding by two mechanisms, i.e., directly on the allyl ligand or via the metal. The choice of mechanism may well be a function of counterion ($Cl^-$ vs. $BF_4^-$) and could be responsible for the product variation observed.



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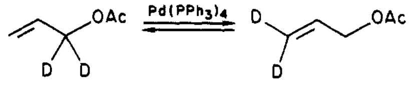
Yamamoto[5] has also probed this problem and found that no observable products ($^1$H NMR) were formed in the reaction of the allyl acetate **4** and $Pd(PPh_3)_4$, although significantly a 1,3 shift in allyl-$d_2$ acetate was seen under these reaction conditions, presumably via the intermediacy of a bis(phosphine) cation. This demonstrates that NMR alone is not a good probe for the intermediates in this reaction, as the species responsible for the observed chemistry may be present in nondetectable amounts.



4-$d_2$

Fiaud[6] found that reaction of sodium dimethylmalonate with the –(diop)– tetrafluoroborate cationic complex of bis(μ-chloro)bis($\eta^3$-cyclohexenyl)palladium(2+) gave an alkylation product with a lower enantiomeric excess than the palladium-catalyzed alkylation of the corresponding

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[2] Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* 1978, *100*, 3401.

[3] Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* 1978, *100*, 3416.

[4] Akermark, B.; Akermark, G.; Hegedus, L. S.; Zetterberg, K. *J. Am. Chem. Soc.* 1981, *103*, 3037.

[5] Yamamoto, T.; Saito, O.; Yamamoto, A. *J. Am. Chem. Soc.* 1981, *103*, 5600.

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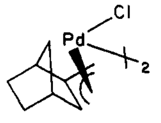
allylic acetate. This result is inconsistent with the exclusive involvement of a π-allyl cationic intermediate for the catalyzed reaction. In contrast, Trost[7] studied the reaction of a structurally very similar optically active cyclohexenyl precursor and observed a racemic product supporting a symmetrical cationic intermediate. The simultaneous rationalization of both of these experiments is difficult.

These studies that have provided a variety of conflicting results are typically flawed by the use of a narrow selection of probes by which to judge the nature of the intermediates present in this important reaction.

We have undertaken a study aimed at gathering information regarding the fundamental nature of this reaction employing $^1$H NMR, X-ray, and conductivity measurements in conjunction with chemical reactivity. Our efforts have centered on the preparation of complexes by the addition of varying amounts of $PPh_3$ to the π-allyl chloride dimer **5** and assay of these species. We chose a norbornyl derivative as the substrate for this study because of its stereochemically rigid nature and its inherent asymmetry with regard to its allylpalladium complex. Previous work by Petit[8] on reactions of the π-allyl chloride dimer **5** and "hard" nucleophiles (e.g., $(CH_3)_2Cd$, $CH_3MgX$) have been reported and have provided evidence for exo-alkylation, presumably via attack at the metal by these anions.



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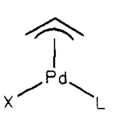
## Results and Discussion

**$^1$H NMR Studies.** Numerous $^1$H NMR studies[9-19] have been undertaken to elucidate the nature of the species formed on addition of phosphines to (π-allyl)palladium chloride dimers. These investigations indicate that depending on the nature of the allyl ligand, the amount and kind of phosphine and the medium, a mono(phosphine)allylpalladium halide (**6**), a bis(phosphine) cation (**7**), a bis(phosphine) pentacoordinate complex (**8**), or an $\eta^1$ species (**9**) may be produced. Furthermore, these complexes are often found to be fluxional at room temperature with a variety of reactions being responsible for equilibrating these species.



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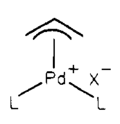

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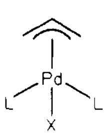

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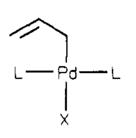

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The $^1$H NMR studies discussed below were performed at 400 MHz employing $CDCl_3$ as solvent at $PPh_3$/Pd ratios of 0.5, 1.0, ~2.0, and >2.0.

Table I. $^1$H NMR of (π-Allyl)palladium Complexes[a]

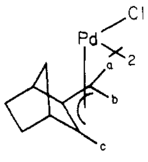
| complex | δ(Ha) | δ(Hb) | δ(Hc) |
|---|---|---|---|
| 5 | 3.62 | 3.12 | 3.88 |
| 10 | 3.01 (1.3) | 2.75 | 4.40 (10.2) |
| 11 | 4.6 (6.3) | 3.8 (9.2) | 2.8 (2.0) |
| 12FIP | 4.1[b] (4.2) | 2.98[b] (8.8) | 3.95[b] (10.2) |
| 12CIP | 4.0 | 3.7 | 4.5 |
| 15 | 3.9 (4.9) | 3.25 (9.8) | 4.1 (10.2) |

[a] Spectra recorded at 400 MHz in $CDCl_3$ chemical shifts in ppm (δ); $J_{P-H}$ (Hz) values given in parentheses. [b] Recorded at −65 °C.

**$PPh_3$/Pd = 0.5.** The π-allyl chloride dimer **5** was prepared from norcamphene by the method of Trost.[20] $^1$H NMR in $CDCl_3$ at ambient temperature exhibited three allyl resonances as singlets at 3.02 ($H_b$), 3.62 ($H_a$), and 3.88 ($H_c$) ppm (Table I).[21] On addition of 1 equiv of $PPh_3$ ($PPh_3$/Pd = 0.5) a nonfluxional spectrum[22] resulted that consisted of resonances of the chloride dimer **5** and a mixture of two mono(phosphine) chlorides **10** and **11** in a ratio of 1.3:1 (**10**/**11**). Assignments of the allyl protons in **10** and **11** were made on the basis of the known[9-19] larger $^{31}$P coupling to trans allyl protons and the well-established larger trans $^{31}$P coupling to the syn H over the anti H (Table I).

**$PPh_3$/Pd = 1.0.** Addition of 2 equiv of $PPh_3$ ($PPh_3$/Pd = 1.0) to the chloride dimer **5** resulted in the observation of a nonfluxional spectrum that indicated the presence of only the mono(phosphine) chlorides **10** and **11** in a ratio of 1.3:1.

**$PPh_3$/Pd = 1.1–2.0.** The addition of greater than 2 equiv of $PPh_3$ ($PPh_3$/Pd > 1) produced a fluxional spectrum at ambient temperature that was probed at various phosphine concentrations by low-temperature $^1$H NMR. The most extensive variable-temperature NMR studies were run at a $PPh_3$/Pd ratio of 1.9; at precisely a $PPh_3$/Pd of 2.0 (where most of the chemical reactivity was investigated) a small amount of precipitate formed that unduly complicated the $^1$H NMR experiment. The ambient-temperature $^1$H NMR of the allyl resonances for $PPh_3$/Pd = 1.9 appeared as three very broad signals centered at 4.3, 3.6, and 3.4 ppm. On cooling, a nonfluxional spectrum was obtained at −35 °C which consisted of the mono(phosphine) chloride **11** (~5%) and a bis(phosphine) π-allyl species (**12**) with resonances at 3.1 (d, $J_{P-H}$ 8.8 Hz, Hb) and 4.0 ppm (br s, Ha, Hc). On further cooling to −40 °C the degeneracy at 4.0 ppm was broken with Ha moving downfield to 4.05 ppm ($J_{P-H}$ = 4.2 Hz) and Hc moving somewhat upfield to 3.95 ppm ($J_{P-H}$ = 10.2 Hz). At −65 °C Ha had moved to 4.1 ppm, Hc remained at 3.95 ppm, and Hb moved to 2.98 ppm (Table I). Warming back to room temperature produced the original spectrum.



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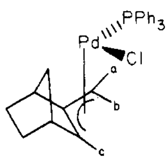

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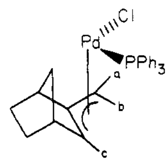

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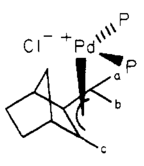

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Additional low-temperature $^1$H NMR studies with intermediate amounts of $PPh_3$ were also conducted. The onset of fluxional processes took place as soon as any excess

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(7) Trost, B. M.; Schmuff, N. R. *Tetrahedron Lett.* **1981**, 2999.
(8) Petit, F.; Castanet, Y. *Tetrahedron Lett.* **1979**, 3221.
(9) Powell, J.; Robinson, S. D.; Shaw, B. L. *J. Chem. Soc., Chem. Commun.* **1965**, 78.
(10) Powell, J. *J. Am. Chem. Soc.* **1969**, *91*, 4311.
(11) Powell, J.; Shaw, B. L. *J. Chem. Soc. A* **1967**, 1839.
(12) Powell, J. *J. Chem. Soc. A* **1971**, 2233.
(13) Oslinger, M.; Powell, J. *Can. J. Chem.* **1973**, *51*, 274.
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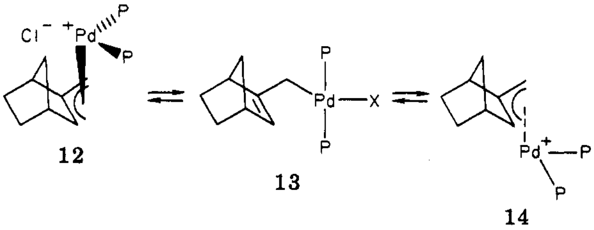
(16) Vrieze, K.; Cossee, P.; Praat, A. P.; Hilbers, C. W. *J. Organomet. Chem.* **1968**, *11*, 353.
(17) Stratton, G. L.; Ramey, K. C. *J. Am. Chem. Soc.* **1966**, *88*, 1327.
(18) Cotton, F. A.; Faller, J. W.; Musco, A. *Inorg. Chem.* **1967**, *6*, 179.
(19) Tibbetts, D. L.; Brown, T. L. *J. Am. Chem. Soc.* **1979**, *92*, 3031.
(20) Trost, B. M.; Strege, P. E. *Tetrahedron Lett.* **1974**, 2603.
(21) Assignments made by using other allyl chloride dimers as models, see ref 15 and 17.
(22) This is in contrast to other Pd-allyl systems that are fluxional even at $PPh_3$ < 1; see ref 11.

$PPh_3$ ($PPh_3/Pd > 1$) was present. The −40 °C spectrum at $PPh_3/Pd = 1.1 \rightarrow 1.5$ are comparable to those at $PPh_3/Pd = 1.9$ except that they showed the mono(phosphine) chloride **10** in addition to **11** and **12**. As expected, the less phosphine that was present, the more of the mono(phosphine) chlorides that was observed. Compound **10** was always present in smaller concentrations than **11**. Beyond $PPh_3/Pd = 1.5$ the species **10** was no longer detectable.[23,24]

As the formation of the bis(phosphine) complex **12** is clearly driven by the addition of phosphine, the presence of a large excess of $PPh_3$ should effectively allow **12** to be present exclusively (i.e. no **10** or **11**) at ambient temperature. The spectrum produced by the addition of 20 equiv of $PPh_3$ ($PPh_3/Pd = 10.0$) however consisted of sharp singlets (no phosphine coupling due to rapid exchange) at 4.5 (Hc), 4.0 (Ha), and 3.7 (Hb) ppm (Table I). Clearly, this spectrum is significantly different than that of the bis(phosphine) species obtained at low temperature. Initially we rationalized that the chemical shifts of Ha, Hb, and Hc at ambient temperature could have been due to an additional equilibration between **12** and an $\eta^1$ complex (**13**) or to an endo-π-allyl bis(phosphine) complex (**14**) via **13**, but neither of these species ever appears in the low-temperature spectra.[25]



12 13 14

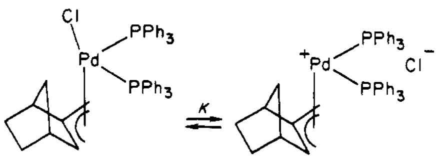
Two additional $^1H$ NMR experiments greatly aided in our discernment of the nature of the low-temperature bis(phosphine) species and the ambient-temperature high phosphine moiety. The first involved slow cooling of the $PPh_3/Pd = 10$ mixture to −65 °C with repeated $^1H$ NMR analysis. The freezing out of phosphine exchange occurs at comparable temperature to the $PPh_3/Pd = 2$ case, and what was observed was the gradual transformation of the ambient-temperature spectrum into a spectrum identical with the $PPh_3/Pd = 2$ spectrum at −65 °C.[26]

The second experiment involved obtaining the $^1H$ NMR spectrum of a bis(phosphine) cation of this system that contained a noncoordinating counterion. To this end, the chloride dimer **5** was treated with 4 equiv of $PPh_3$ in THF, followed by $NH_4PF_6$. A precipitate formed immediately that was isolated and characterized by $^1H$ NMR, elemental analysis, and X-ray structure and found to be the bis(phosphine) $PF_6^-$ complex **15**. The allyl resonances of **15** were nonfluxional at ambient temperatures and were δ 4.1 ($J$ = 10.2 Hb (Hc)), 3.9 ($J$ = 4.9 Hz (Ha)), and 3.25 ($J$ = 9.3 Hz (Hb)) (Table I) that were very similar to the low-temperature species **12**. Conclusively, the −40 °C spectrum of **15** was found to be virtually identical with that of **12** at the same temperature.

These results when coupled with the conductivity measurements (vide infra) led to the following conclusions:

(1) The fluxional nature of the spectrum ($PPh_3/Pd = 2.0$) at ambient temperature is in part due to the rapid interconversion of the mono(phosphine) chloride **11** and a bis(phosphine) allyl complex (**12**) caused by association and dissociation of triphenylphosphine. At low [$PPh_3$] ($PPh_3/Pd$ = 1.1–1.5) both **11** and **10** are present and are equilibrating with **12**.

(2) A further equilibration exists between two bis(phosphine) allyl species with the former being depicted as a contact ion pair (**12CIP**) or pentavalent complex[27] and the later as a free, noncoordinating counterion system (**12FIP**). The equilibrium constant, $K$, defining the relative concentrations of these species is extremely temperature dependent, favoring **12CIP** at ambient temperature and **12FIP** at low temperatures. The assignment of **12FIP** as a free ion pair is based on the close agreement of the allyl resonances of **12FIP** and those of $PF_6^-$ complex **15**. The allyl resonances of **12CIP** differ significantly from those of **15**, but it is also clear that **12CIP** cannot be formulated as either mono(phosphine) halide or an $\eta^1$ species because of the chemical shifts of Ha, Hb, and Hc.



12CIP 12FIP

The suggested temperature dependence of $K$ is well established[28] for classical organic ion pairs with low temperatures consistently favoring the free ion pair. Our conductivity measurements fully support these conclusions.

The further question of the precise structure of **12CIP**, i.e., contact ion pair or pentavalent species, remains difficult to discern, but the exact duplication of classical organic ion pair behavior as a function of temperature strongly suggests the former as a more accurate description.[29]

Because of the known sensitivity of the nature of the intermediates present in these processes to solvent and also to allow maximum correspondence to the conductivity and chemical reactivity data, the $PPh_3/Pd = 2$ and $PPh_3/Pd = 8$ variable-temperature $^1H$ NMR experiments were repeated in $CD_2Cl_2$, THF-$d_8$, and acetone-$d_6$. The $CD_2Cl_2$ and acetone-$d_6$ studies were in good qualitative agreement with the $CDCl_3$ work, showing for $PPh_3/Pd \approx 2$ a fluxional spectra that on cooling revealed the presence of a bis-

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[23] In a single experiment at $PPh_3/Pd = 2.0$ the spectrum at −40 °C was essentially identical with the $PPh_3/Pd = 1.9$ spectrum.

[24] An additional piece of information was gleaned in the low-temperature $^1H$ NMR of the $PPh_3/Pd = 1.5$ mixture. Namely, at −15 °C $^{31}P$ coupling to Ha of **11** was observed while no $^{31}P$ coupling to Hc in **10** or Ha, Hb, and Hc in **12** could be discerned. At −30 °C all the expected $^{31}P$ couplings were now seen. This suggests that the attack of $PPh_3$ on **11** to provide **12** and allow equilibration with **10** (and thereby phosphine exchange) is more difficult than the analogous attack on **10**. This may explain the smaller concentrations of **10** consistently observed in the $PPh_3/Pd > 1$ spectra.

[25] Preparation of both the *exo*- and *endo*-methylenenorbornyl chlorides and treatment of them with $Na_2PdCl_4$ gave rise to only the exo-π-allyl chloride dimer **5**, demonstrating a rapid isomerization of endo-π-allyl species to the considerably more stable exo derivative via an usual syn–anti exchange process.

[26] Additional information was discovered in this experiment by the observation that at −20 °C $^{31}P$ coupling was observed to Hc whereas coupling of $^{31}P$ to Ha and Hb could not be seen until −30 °C, indicating greater liability to the $PPh_3$ trans to Ha and Hb.

[27] Analogous pentavalent bis(phosphine)allylnickel bromides have been structurally characterized. They exhibit anomalously long Ni–Br bonds and conductivities intermediate between nonconducting species and 1:1 electrolytes, also supporting the ion pair hypothesis: Cameron, T. S.; Prout, C. K. *Acta Crystallogr. Sect. B* **1978**, *B28*, 2021. Churchill, M. R.; O'Brien, T. A. *J. Chem. Soc. A* **1970**, 206.

[28] Szwarc, M. "Ions and Ion Pairs in Organic Reactions"; Wiley Interscience: New York, 1972; p 85 ff.

[29] Assignments of Ha, Hb, and Hc throughout this series are based on the well-established magnitudes of coupling constants to phosphorous in these complexes$^{9-19}$ and are further supported by the duplication of all these experiments with a sample of the chloride dimer **5** which consisted of 25% **5**-$d_2$ with deuteriums positioned at Ha and Hb, 25% Da and Hb, 25% Ha and Db, and 25% Ha and Hb.

Table II. Bond Lengths (Å) for Crystal Structure of 15[a]

| | | | |
|---|---|---|---|
| P(2)-Pd(1) | 2.331 (1) | P(3)-Pd(1) | 2.321 (1) |
| C(40)-Pd(1) | 2.182 (5) | C(41)-Pd(1) | 2.197 (5) |
| C(42)-Pd(1) | 2.231 (5) | C(4)-P(2) | 1.832 (5) |
| C(10)-P(2) | 1.820 (5) | C(16)-P(2) | 1.832 (5) |
| C(22)-P(3) | 1.810 (4) | C(28)-P(3) | 1.831 (4) |
| C(34)-P(3) | 1.816 (5) | C(5)-C(4) | 1.401 (7) |
| C(9)-C(4) | 1.382 (8) | C(6)-C(5) | 1.399 (9) |
| C(7)-C(6) | 1.381 (11) | C(8)-C(7) | 1.401 (7) |
| C(9)-C(4) | 1.382 (8) | C(6)-C(5) | 1.399 (9) |
| C(7)-C(6) | 1.381 (11) | C(8)-C(7) | 1.362 (10) |
| C(9)-C(8) | 1.390 (9) | C(11)-C(10) | 1.389 (8) |
| C(15)-C(10) | 1.400 (7) | C(12)-C(11) | 1.395 (8) |
| C(13)-C(12) | 1.380 (11) | C(14)-C(13) | 1.389 (13) |
| C(15)-C(14) | 1.370 (9) | C(17)-C(16) | 1.378 (8) |
| C(21)-C(16) | 1.398 (7) | C(18)-C(17) | 1.388 (9) |
| C(19)-C(18) | 1.383 (10) | C(20)-C(19) | 1.379 (11) |
| C(21)-C(20) | 1.388 (9) | C(23)-C(22) | 1.398 (7) |
| C(27)-C(22) | 1.389 (6) | C(24)-C(23) | 1.391 (7) |
| C(25)-C(24) | 1.377 (8) | C(26)-C(25) | 1.388 (8) |
| C(27)-C(26) | 1.378 (7) | C(29)-C(28) | 1.390 (7) |
| C(33)-C(28) | 1.391 (7) | C(30)-C(29) | 1.381 (8) |
| C(31)-C(30) | 1.377 (9) | C(32)-C(31) | 1.376 (8) |
| C(33)-C(32) | 1.377 (7) | C(35)-C(34) | 1.383 (7) |
| C(39)-C(34) | 1.396 (7) | C(36)-C(35) | 1.389 (8) |
| C(37)-C(36) | 1.376 (9) | C(38)-C(37) | 1.370 (9) |
| C(39)-C(38) | 1.379 (8) | C(41)-C(40) | 1.392 (6) |
| C(42)-C(41) | 1.422 (6) | C(46)-C(41) | 1.506 (7) |
| C(43)-C(42) | 1.478 (6) | C(44)-C(43) | 1.563 (8) |
| C(47)-C(43) | 1.544 (8) | C(45)-C(44) | 1.543 (8) |
| C(46)-C(45) | 1.558 (8) | C(47)-C(46) | 1.537 (7) |
| F(49)-P(48) | 1.572 (5) | F(50)-P(48) | 1.553 (5) |
| F(51)-P(48) | 1.595 (4) | F(52)-P(48) | 1.539 (5) |
| F(53)-P(48) | 1.571 (5) | F(54)-P(48) | 1.534 (6) |

[a] C-H bonds range from 0.82 to 1.07 Å with a mean esd of 0.07.

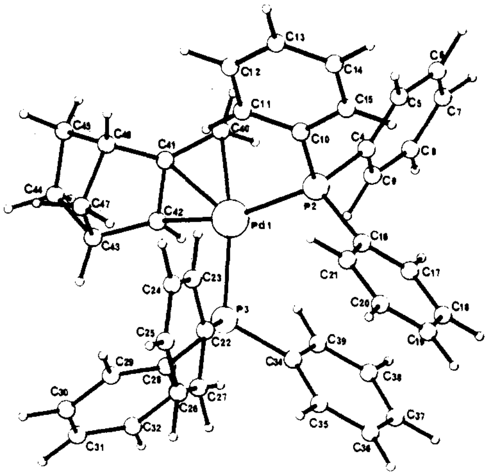


Figure 1. X-ray structure of 15.

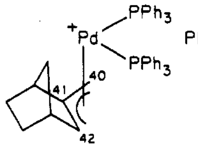
(phosphine) species (12FIP) and the mono(phosphine) halide 11. The $PPh_3$/Pd = 8 spectrum again differed significantly from the low-temperature $PPh_3$/Pd = 2 spectrum at ambient temperature but was virtually identical at low temperature. The THF-$d_8$ studies were markedly different. The $PPh_3$/Pd = 2 sample was fluxional at room temperature but showed only a mixture of **10** and **11** and no bis(phosphine) cation (12CIP or 12FIP) at low temperature. The $PPh_3$/Pd = 8 spectra remained fluxional even at −90 °C. The $^1H$ NMR of $PF_6$ salt **15** served as a model for 12FIP in THF, acetone-$d_6$, and $CD_2Cl_2$.

**X-ray Studies.** The major species formed on addition of 4 equiv of $PPh_3$ to the chloride dimer **5** were not readily isolable to allow for X-ray analysis. The bis(phosphine) hexafluorophosphate allyl system **15** however provided satisfactory crystals for X-ray study, and the resulting data are shown below (Figure 1, Table II). This unequivocally establishes that **15** exists as an exo-bis(phosphine) cationic complex[30] and serves as a structural model for 12FIP.

Table III. Electrical Conductivities of $\pi$-Allyl Complexes in Acetone

| complex | $\Lambda_{eq}$, $cm^2$/($\Omega$ mol) | temp, °C |
|---|---|---|
| **10** and **11** (1.3:1) | 2.95 | 25 |
| **5** + $4PPh_3$ | 11.0 | 25 |
| **5** + $16PPh_3$ | 38.0 | 25 |
| **15** | 117 | 25 |
| **5** + $16PPh_3$ | 55.2 | −15 |
| **15** | 92.9 | −15 |
| **5** + $16PPh_3$ | 39.1 | −55 |
| **15** | 54.2 | −55 |

The degree of asymmetry in **15** although not overwhelming is real: Pd–C(40) = 2.182 Å and Pd–C(42) = 2.231 Å. An important question in addition to the Pd–C distances is whether C(40)–C(41) or C(41)–C(42) is reflecting more "olefin" character in this complex. The most clear-cut answer to the question can be obtained by comparison of the bond lengths C(40)–C(41) and C(41)–C(42) in **15** to that in compounds containing exo and endo cyclic norbornyl olefins. Selected examples are listed below.



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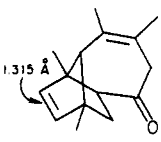

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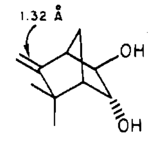

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Although considerable variations exist in examining model systems, the conclusion we draw is that the bond length of C═C exo cyclic = C═C endo cyclic in norbornyl rings. As a result C(40)–C(41) = 1.392 Å vs. C(41)–C(42) = 1.422 Å indicates more olefin character in C(40)–C(41) despite the shorter Pd–C(40) distance. This "contradictory" bond length situation is precedented in other allyl systems.[33] The chemistry of these systems will subsequently be discussed in light of these results.

**Conductivity Studies.** Electrical conductivity studies have often been used to gather information regarding the nature of the ($\pi$-allyl)Pd species present in solution.[4,16] Our results, summarized in Table III, were first determined in acetone at the indicated temperature.[34] An ideal 1:1 electrolyte will exhibit a value of 100–140 $cm^2$/($\Omega$mol) at 25 °C for a 1 mM solution.[35] Table III shows that the mono(phosphine) halides **10** and **11** and the species obtained by addition of 4 equiv of $PPh_3$ to the chloride dimer **5** are essentially nonconducting. The later results agree well with the solution $^1H$ NMR data obtained in acetone-$d_6$ which indicate that the species obtained by mixing **5** and 4 equiv of $PPh_3$ is not well represented as a "free bis-

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(30) Other X-ray structure determinations of ($\pi$-allyl)Pd complexes: Maitlis, P. M. "The Organic Chemistry of Palladium"; Academic Press: New York, 1971; Vol. 1, p 59 ff.

(31) Bear, C. A.; Trotter, T. *J. Chem. Soc., Perkin Trans. 2* **1974**, 330.

(32) Spencer, S. A.; Trotter, J. *Acta Crystallogr., Sect. B* **1979**, *B35*, 3110.

(33) McCrindle, R.; Alyea, A. C.; Ferguson, G.; Dias, S. A.; McAvees, A. J.; Parvez, M. *J. Chem. Soc., Dalton Trans.* **1980**, 137. Barnett, B.; Bussemeier, B.; Heimbach, P.; Jolly, P. W.; Kruger, C.; Tkatchenko, I.; Wilke, G. *Tetrahedron Lett.* **1972**, 1457. Barnett, B. L.; Kruger, C.; Tsay, Y. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 137.

(34) Acetone because of its high dielectric constant is an ideal solvent for conductivity studies.

(35) Angelici, R. J. "Synthesis and Techniques in Inorganic Chemistry"; 2nd ed.; Saiders: Philadelphia, 1977.

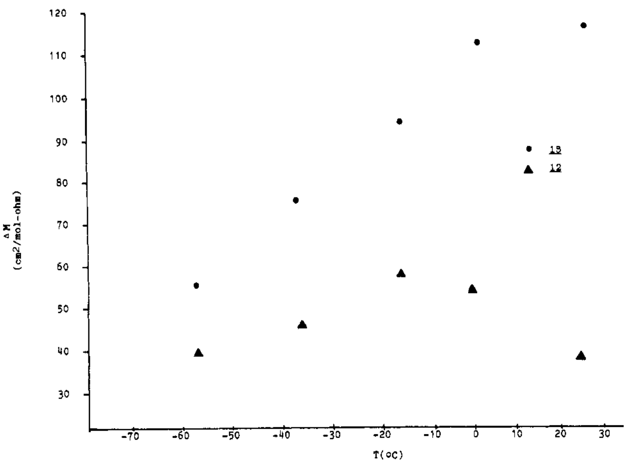


**Figure 2.** Conductivity data for **12** and **15** as a function of temperature.

(phosphine) cation" but rather one in which the $Cl^-$ is intimately associated with the complex (**12CIP**). As expected, the $PF_6^-$ salt **15** behaves like a 1:1 electrolyte.

The most interesting results are obtained on cooling a sample of $PPh_3/Pd = 8$ which exists primarily as the species **12CIP** at ambient temperature ($^1H$ NMR). Significantly, the conductivity goes through a maximum at ~−15 °C (Figure 2). The $PF_6$ salt **15** in contrast behaves normally; i.e., it shows a linear decrease in conductivity with temperature. These results agree well with the $^1H$ NMR data and again suggest an equilibration between **12CIP**, the contact ion pair or pentavalent species which conducts only weakly, and a free ion pair species (**12FIP**) which behaves like a 1:1 electrolyte, with **12FIP** being increasingly formed as the temperature decreases. The observation of low temperatures favoring free ion pairs over contact ion pairs is well-known for organic systems.[28]

Conductivity data were also obtained in $CH_2Cl_2$. They showed a temperature dependence for the conductivity of the $PPh_3/Pd = 2$ and 8 samples comparable to that observed in acetone, the only difference being a compression of the scale of values observed, as an ideal 1:1 electrolyte has a conductance of ~40 $cm^2/(\Omega\ mol)$ in $CH_2Cl_2$ at room temperature (e.g., **15** showed a value of 42 $cm^2/(\Omega\ mol)$). The $^1H$ NMR data in $CD_2Cl_2$ are in complete accord with these conductivity data, showing **12CIP** at ambient temperature, **12FIP** at low temperature, and **15** as a free ion pair at all temperatures. Significantly, the $PPh_3/Pd = 2$ and 8 samples were nonconducting in THF even at low temperatures. This is consistent with the $^1H$ NMR data obtained in THF-$d_8$ which showed only **10** and **11** and again indicates that bis(phosphine) cations as either free or contact ion pairs are not present in appreciable concentration. The bis(phosphine) cation **15** was not sufficiently soluble in THF to allow conductivity measurements to be made. A sample of the corresponding diphos $PF_6$ salt was prepared and was found to exhibit normal 1:1 electrolyte behavior in THF. Meaningful conductivity data in $CHCl_3$ could not be obtained due to the low dielectric constant of the medium.

## Chemical Reactivity

**Malonate Addition.** The palladium complexes **10**, **11** ($PPh_3/Pd = 1$), and **12CIP** ($PPh_3/Pd = 2$) were generated by addition of the appropriate amount of $PPh_3$ to the chloride dimer **5** in $CH_2Cl_2$, (to allow maximum correspondence to the NMR and conductivity data) while the preformed $PF_6^-$ salt **15** was added directly to $CH_2Cl_2$. The concentration of Pd was uniformly 0.06 M. Diethyl sodiomalonate (1.5 equiv of a 2 M solution in THF) was then added to the $CH_2Cl_2$ at ambient temperature under an $N_2$ atmosphere. The reactions were run a total of 15 h at which time an aqueous workup was performed and GLC analysis of the products conducted.

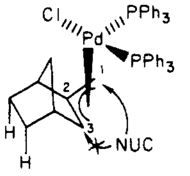
Table IV. Reactions of Nucleophiles with Complex Produced in Mixture of 5 with 4$PPh_3$ in $CH_2Cl_2$

| nucleophile | conditns[b] | % yield |
|---|---|---|
| $NaCH(CO_2Et)_2$ | rt, 18 h | 75 |
| $NaCH(COCH_3)(CO_2Et)$ | rt, 18 h | 75 |
| $NaC_5H_5$ | rt, 1 h | 65[a] |
| $(n\text{-}Bu)_3)SnOMe$ | rt, 18 h | 35 |

[a] Mixture of diene isomers. [b] rt = room temperature.

It was assumed that the species present in $CH_2Cl_2$ were identical with those characterized by $^1H$ NMR and conductivity despite the small amount of THF present. All the complexes gave malonate addition exclusively at the less substituted carbon although the yields did vary somewhat: mono(phosphine) chlorides **10** and **11**, 50%; bis(phosphine) chloride **12CIP**, 68%; and bis(phosphine) hexafluorophosphate **15** as a model for **12FIP**, 45%.

Direct ligand attack by malonate has been unequivocally established.[1,2] Attack at the less substituted terminus in this $\eta^3$ complex is doubly reinforced, first by the inherent nature of the reaction[1,2] to proceed in this fashion and second by the fact that attack at the more substituted terminus would involve an endo addition in a norbornyl system.



Comparable results were obtained by using other soft nucleophiles, e.g., β-keto ester anions, $NaC_5H_5$, and $(n\text{-}Bu)_3SnOMe$.[36] Table IV contains a summary of these results.

As all metal complexes (**10**, **11**, **12CIP**, and **15**) gave the same product in similar yields, either these nucleophiles are not useful for discerning differences in the chemistry of these species or a single reactive species is responsible for the observed chemistry. However, if **12FIP** (as modeled by **15**) is solely responsible for the observed reactivity in $PPh_3/Pd = 2$ where **12CIP** is the major species present (NMR), the rate of product formation should equal $Kk$(obsd), where $K$ is that ratio of concentrations of **12FIP**/**12CIP** and $k$(obsd) is the rate constant for the reaction of **12FIP** with malonate. The rate constant $k$(obsd) for **12FIP** can be estimated from the rate of reaction of **15** in $CH_2Cl_2$. The conductivity data in $CH_2Cl_2$ can be used to obtain a good estimate of $K$, since the conductivity of the $PPh_3/Pd = 2$ system in $CH_2Cl_2$ was measured (8.3 $cm^2/(\Omega\ mol)$) as well as the conductivity of **15** (model for **12FIP**, 42.6 $cm^2/(\Omega\ mol)$). $K$ was estimated by this method to be less than 0.2. Although quantitative kinetics were not ascertained, the rate of product formation in the reaction of the $PPh_3/Pd = 2$ system with malonate was observed to be slightly faster than that of **15** with malonate in $CH_2Cl_2$, indicating that the $PPh_3/Pd = 2$ system was *not* reacting exclusively as **12FIP**.

Hard nucleophiles are known to add by metal attack[8,37] and appear somewhat more promising in discerning be-

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[36] Keinan, E.; Roth, Z. *J. Org. Chem.* **1983**, *48*, 1769.
[37] Keinan, E.; Greenspoon, N. *Tetrahedron Lett.* **1982**, 241.

Table V. Reaction of PhLi with ($\pi$-Allyl)palladium Complexes[a]

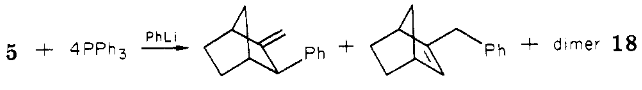
| complex | % yield of **16** and **17** | ratio of **16**/**17** | % dimers |
|---|---|---|---|
| **5** + $4PPh_3$ | 53 | 2.5 | 23 |
| **5** + $2PPh_3$ | 62 | 2.7 | 19 |
| **15** | 48 | 1.1 | 4 |

[a] 1.5 equiv of 0.04 M PhLi in THF at −10 °C for 0.5 h.

tween these allyl complexes as described below. Unfortunately, we could not compare the behavior of **12FIP** and **12CIP** in $CHCl_3$, acetone or $CH_2Cl_2$ because of the nature of the nucleophiles employed. We were able to assay the reactions of **10** and **11** (the mono(phosphine) halides) and the $PPh_3/Pd = 2$ system in THF and contrast this with **15** which served as a model for the free ion pair (**12FIP**).

**Phenyllithium Addition.** Reactions with PhLi were carried out by using 1.5 equiv of PhLi in a 0.04 M solution of complex in THF at −10 °C under a $N_2$ atmosphere. Reactions were run for 0.5 h prior to aqueous workup and GLC analysis. The results are summarized in Table V.

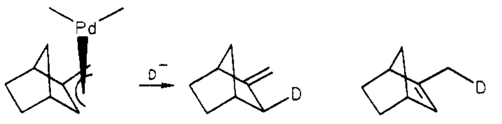
Phenyllithium addition produced the phenyl-substituted isomers **16** and **17** in good yield along with some allyl-coupled dimeric material (mixture of isomers) (**18**). The stereochemistry of **16** was determined to be exo by its conversion to the known *exo*-3-phenyl-2-norbornanone by ozonolysis.[38] The predominant product now represents attack at the more substituted center in contrast to the soft nucleophiles. Also, the exo addition process indicates that PhLi is adding via the metal followed by reductive elimination.



16 17

The mono(phosphine) halides **10** and **11** appear to behave quite similarly to the $PPh_3/Pd = 2$ system, (ratio **16**/**17** = 2.5) while **15** shows a distinctly different regio preference (ratio **16**/**17** = 1.1) and a smaller chemical yield, again supporting the $^1H$ NMR and conductivity data and indicating that the $PPh_3/Pd = 2$ species in THF is reacting comparable to a mixture of **10** and **11**.

**Hydride Addition.** $LiAlH_4$ and $NaBH_4$[8] were also examined. Hydride was found to produce excellent yields (>90%) of a mixture of norcamphene (**19**) and methylnorbornene (**20**). Use of $D_2O–NaBD_4$ demonstrated that the norcamphene produced had deuterium exclusively in the exo position ($^1H$ NMR) consistent with attack via the metal. However, this study also revealed that the products of this reaction equilibrate under the reaction conditions and no information regarding inherent regiochemical preference of $H^-$ could be discerned.



19 20

## Discussion

Our investigation of the species present on addition of 2 equiv of $PPh_3$/palladium to the $\pi$-allyl chloride dimer **5** in $CHCl_3$, $CH_2Cl_2$, and acetone indicates that it is best characterized as a contact ion pair (**12CIP**). This conclusion is based on $^1H$ NMR studies at ambient temperature which show it to be a bis(phosphine) allyl moiety and conductivity measurements which indicate that at room temperature it is nonconducting. This assignment is further supported by the low-temperature $^1H$ NMR and conductivity results which show **12CIP** is converted into a free ion pair, **12FIP**, similar to classical organic ion pair systems. The model for the spectral and conductivity measurements for **12FIP** was the $PF_6$ salt **15**.

These results clearly suggest that ambient-temperature conductivity measurements alone cannot be used as a criterion for the existence of bis(phosphine) cations because of the likely existence of contact ion pairs.

Disappointingly, the addition of soft nucleophiles allowed no significant discrimination between **12CIP** and **12FIP** (**15**) in $CH_2Cl_2$, as both give the same products in comparable yields. However, qualitative rate data indicate that the $PPh_3/Pd = 2$ system in $CH_2Cl_2$ does not react solely as **12FIP**.

Our studies in THF showed by $^1H$ NMR and conductivity that the predominant species present on the addition of 4 equiv of $PPh_3$ to **5** was the mono(phosphine) halides **10** and **11**. No evidence for **12FIP** or **12CIP** could be discerned in the low-temperature NMR or conductivity measurements. The $PF_6$ salt **15** again served as a model for **12FIP** in THF in the $^1H$ NMR and conductivity studies. Reaction of PhLi in THF showed significant differences between **15** (the free ion) and **10**, **11**, and the $PPh_3/Pd = 2$ system, while the latter three behaved similarly.

Undoubtedly, $PPh_3$ is liberated as the reaction of PhLi with the mono(phosphine) halides **10** and **11** proceeds. This will allow for their rapid equilibration and explain the correspondence with the $PPh_3/Pd = 2$ system. Recalling the Yammamoto experiment,[5] it is possible that although **12CIP** is not detected by $^1H$ NMR or conductivity in the $PPh_3/Pd = 2$ system that it is the species responsible for the observed reactions. However, we *can* eliminate **12FIP** as the predominant reactive species in THF because of the differences observed with respect to **15**.

The $PF_6$ bis(phosphine) cation **15** uniformly exhibited itself as a free ion pair system as evidenced by variable-temperature $^1H$ NMR and conductivity measurements. X-ray structure determination unequivocally established this pivotal model system as the exo complex and supplied detailed structural information.

The X-ray structure of **15** showed a closer association of the metal with the less substituted allyl terminus but more olefin character in the exocyclic C–C bond. With the assumption of a corresponding asymmetry in the solution structure of **15**, soft nucleophiles are adding to the more olefin-like center and hard nucleophiles preferentially to the more saturated center. The consistent greater lability of the phosphine positioned over the more substituted allyl terminus as discerned in the $^1H$ NMR studies may also provide an explanation for the preference of phenyl substitution at this regiocenter. These results must also be tempered however by the fact that the norbornyl framework itself is prejudicing the regiochemistry of ligand attack.

This inverse correspondence in regioselectivity between hard and soft nucleophiles as evidenced for **15** appears to be a general phenomenon,[36,37] but the explanation for this behavior remains unclear.

These results also suggest that nucleophiles such as amines that can add by either ligand or metal attack may

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[38] Kleinfelter, T. E.; Mallory, J. E.; Trent, E. S. *J. Org. Chem.* **1967**, *32*, 1734.

exhibit variable regiochemical selectivity in the addition to allyl systems as a function of mode of addition. Furthermore, the mode of addition may well be a function of the counterion to the bis(phosphine) cation, especially if the counterion forms a contact rather than a free ion pair.

## Conclusions

The complexity of mechanistic studies of π-allyl alkylations is considerable. It is apparent that the nature of the phosphine, counterion, temperature, solvent, and allyl substrate can have significant effects on the number and type of (allyl)Pd species present in solution. This situation is further compounded by our ignorance regarding the relative rates of reaction of these moieties even if they can be identified spectroscopically. That is, the major *detectable* species may not be the most *reactive* one. It is equally clear to us that conclusions based exclusively on a single physical or spectroscopic technique, especially conductivity, may be misleading as the existence of a nonconducting ion pair in these reactions now seems likely. Furthermore, the use of nucleophiles that are known to add by either ligand or metal attack as a means of discernment of the nature of the intermediates present may also unnecessarily cloud the experimental results.

## Experimental Section

**General Data.** $^1$H NMR spectra, including all low-temperature studies, were recorded on a Bruker WH-400. Chemical shifts are given in parts per million (δ) relative to internal $Me_4Si$. Multiplicities are expressed as follows: s, singlet; d, doublet; t, triplet; q, quartet; b, broad. Coupling constants are reported in hertz. Mass spectra were taken on a Du Pont 21-490B at an ionizing voltage of 70 eV. Electrical conductivities were measured with a Barnstead PM-70CB conductivity bridge equipped with a Barnstead B-10, 1.0-cm cell. Analytical gas-liquid chromatography was performed with a Perkin-Elmer 900 using a flame ionization detector. Peak areas were calculated by triangulation and cut and weigh methods. A 6 ft × $^1/_8$ in. 20% SE-30 on Chromosorb W column was used for all analytical work. Preparative gas-liquid chromatography was accomplished by using a Hewlett-Packard 5700A equipped with a thermal conductivity detector. A 10 ft × $^1/_4$ in. 20% SE-30 on Chromosorb W column was utilized for all preparative work. THF, benzene, and hexane were purified by distillation from sodium benzophonone ketyl, $CH_2Cl_2$ by distillation from $CaH_2$, and $CDCl_3$ by filtration through alumina immediately before use. Triphenylphosphine was recrystallized before use.

**The π-Allyl Chloride Dimer 5.**[8] The π-allyl chloride dimer 5 was prepared by the method of Trost from norcamphene: $^1$H NMR ($CDCl_3$) δ 3.88 (s, 1 H), 3.64 (b s, 1 H), 3.03 (b s, 1 H), 2.75 (b s, 2 H), 1.70 (m, 1 H), 1.55 (m, 2 H), 1.26 (m, 2 H), 1.10 (d, $J$ = 11.0 Hz, 1 H).

**Monophosphine Chlorides 10 and 11.** The π-allyl chloride dimer 5 (0.21 g, 0.41 mol) and triphenylphosphine (0.22 g, 0.082 mmol) were dissolved in 2.0 mL of $CH_2Cl_2$ at room temperature under an $N_2$ atmosphere. After 15 min of stirring, the solvent was removed under reduced pressure yielding a yellow solid (0.43 g, 100%). **10**: $^1$H NMR ($CDCl_3$) δ 7.69 (m, 6 H), 7.57 (m, 3 H), 7.40 (m, 6 H), 4.40 (d, $J$ = 10.2 Hz, 1 H), 3.19 (b s, 1 H), 3.01 (d, $J$ = 1.3 Hz), 2.75 (s, 1 H), 2.58 (b s, 1 H), 1.94 (d, t, $J$ = 8.0, 1.0 Hz, 1 H), 1.75 (m, 2, H), 1.32 (m, 2 H), 1.13 (d, $J$ = 8.0 Hz, 1 H). **11**: $^1$H NMR ($CDCl_3$) δ 7.69 (m, 6 H), 7.57 (m, 3 H), 7.40 (m, 6 H), 4.72 (d, $J$ = 6.3 Hz, 1 H), 3.86 (d, $J$ = 9.2 Hz, 1 H), 3.19 (b s, 1 H), 3.80 (d, $J$ = 2.0 Hz, 1 H), 1.58 (m, 1 H), 1.32 (m, 2 H), 1.23 (d, $J$ = 8.7 Hz, 1 H), 1.04 (m, 1 H), 0.95 (b s, 1 H), 0.725 (d, $J$ = 8.7 Hz, 1 H).

**The Hexafluorophosphate Complex 15.** The π-allyl chloride dimer 5 (0.133 g, 0.268 mmol) and triphenylphosphine (0.28 g, 1.07 mmol) were dissolved in $CH_2Cl_2$ (45 mL) at room temperature under an $N_2$ atmosphere, $NH_4PF_6$ (0.087 g, 0.53 mmol) was added, and the solution was stirred for 24 h. The mixture was filtered through Celite and concentrated under reduced pressure to yield a clear yellow oil. Crystallization was induced by dissolving the oil in 10 mL of benzene followed by slow addition of hexane (20 mL). The crystals were removed by filtration and dried, yielding 0.395 g (84%) of **15**: $^1$H NMR ($CDCl_3$) δ 7.30 (m, 12 H), 7.21 (m, 12 H), 7.00 (m, 6 H), 4.12 (d, $J$ = 10.2 Hz, 1 H), 3.92 (d, $J$ = 4.9 Hz, 1 H), 3.25 (d, $J$ = 9.3 Hz, 1 H), 2.64 (b s, 1 H), 1.60 (m, 1 H), 1.42 (m, 1 H), 1.28 (m, 1 H), 1.08 (m, 1 H), 1.06 (b s, 1 H), 0.95 (d, $J$ = 8.6 Hz, 1 H), 0.85 (d, $J$ = 8.6 Hz, 1 H).

**Reaction of 5 and 4PPh$_3$ with NaC$_5$H$_5$.** The π-allyl chloride dimer (0.1 g, 0.2 mmol) and $PPh_3$ (0.21 g, 0.8 mmol) were dissolved in THF (2 mL) and cooled to 0 °C under an $N_2$ atmosphere. $NaC_5H_5$ (1.1 M, 1 mL) was then added to the solution. The reaction mixture was stirred for 1 h, and then ether (10 mL) was added and the solution was washed with 10 mL of $H_2O$. The organic phase was filtered, dried, and concentrated, and the product was collected by preparative TLC on silica gel (0.045 g, 65%). $^1$H NMR indicated only the product derived from attack at the less substituted allyl terminus but as a mixture of diene isomers in the cyclopentane ring.

**Reaction of 5 and 4PPh$_3$ with (*n*-Bu)$_3$SnOMe.** The π-allyl chloride dimer 5 (0.197 g, 0.394 mmol) and triphenylphosphine (0.415 g, 1.58 mmol) were dissolved in THF (2.0 mL) under a $N_2$ atmosphere at room temperature ($n$-Bu)$_3$SnOMe (0.0512 g, 1.53 mmol) was then added, and the mixture was stirred at room temperature for 24 h. Filtration and concentration of the filtrate yielded a yellow oil from which the product was isolated by preparative GLC (45%): $^1$H NMR ($CDCl_3$) δ 5.81 (s, 1 H), 4.01 (d, d, $J$ = 12.7, 2 Hz, 1 H), 3.88 (d, $J$ = 12.7 Hz, 1 H), 3.30 (5.3 H), 2.83 (b s, 2 H), 1.63 (m, 2 H), 1.39 (d, t, $J$ = 8.7, 3 Hz, 1 H), 1.10 (d, $J$ = 8.7 Hz, 1 H), 1.00 (m, 2 H).

**Reaction of the π-Allyl Chloride Dimer 5 and 4PPh$_3$ with NaBD$_4$.** The chloride dimer 5 (0.0309 g, 0.06 mmol) and triphenylphosphine (0.033 g, 0.125 mmol) were dissolved in 2.5 mL of THF under a $N_2$ atmosphere at room temperature. The solution was stirred 15 min, and $D_2O$ (0.134 mL) was added. The mixture was then transferred into a flask containing $NaBD_4$ (0.0142 g, 0.0372 mmol) and stirred for 5 h at room temperature under a $N_2$ atmosphere. Workup consisted of addition of the reaction mixture to $H_2O$ (15 mL) and pentane (15 mL). The pentane layer was separated, washed with $H_2O$ and brine, and carefully concentrated to avoid loss of the volatile products. $n$-Heptane was added as a standard and the mixture GLC analyzed. The same procedure was used for $LiAlD_4$ except no $D_2O$ was added. $^1$H NMR analysis of the products showed both methylenenorbornane and 2-methylnorbornene. The methylenenorbornane had deuterium incorporation both at the exo-H position and in the olefin protons. Assignment of the exo and endo H's in methylene norbornane was based on careful decoupling experiments on the parent (nondeuterated) compound. The exo H appeared as a d,d,d at 2.10 ppm with a 15-Hz coupling to the endo H, a 6-Hz coupling to the bridgehead H, and a 4-Hz coupling to the H on the one carbon bridge (W coupling). The endo proton appeared at 1.82 ppm as a d,d with $J$ = 15 and 5 Hz and was not coupled to the adjacent bridgehead H. The other product of the reaction was methylnorbornene which showed D incorporation in the $CH_3$ group.

**Reaction of Metal Complexes with Phenyllithium. Typical Procedure.** The π-allyl chloride dimer (0.0206 g, 0.0414 mmol) and triphenylphosphine (0.0436 g, 0.1666 mmol) were dissolved in THF (2.07 mL) under an $N_2$ atmosphere at room temperature. The solution was stirred for 15 min, wrapped in aluminum foil, and cooled to −10 °C. After 15 min at −10 °C, the phenyllithium (0.056 mL, 2.2 M in THF) (Aldrich) was added. The solution was stirred for 30 min and then analyzed by GLC using dodecane as an internal standard. Samples for $^1$H NMR were obtained by preparative GLC. Identical procedures were used starting with **15**, **10**, and **11**. **16**: $^1$H NMR ($CDCl_3$) δ 7.24 (m, 4 H), 7.15 (m, 1 H), 5.10 (s, 1 H), 4.60 (s, 1 H), 3.37 (d, $J$ = 2.5 Hz, 1 H), 2.80 (b s, 1 H), 2.30 (b s, 1 H), 1.68 (m, 2 H), 1.14 (d, d, $J$ = 9.5, 2.5 Hz, 1 H). **17**: $^1$H NMR ($CDCl_3$) δ 7.25 (m, 4 H), 7.15 (m, 1 H), 5.50 (b s, 1 H), 3.39 (s, 1 H), 3.35 (s, 1 H), 2.77 (b s, 1 H), 2.63 (b s, 1 H), 1.55 (m, 2 H), 1.37 (d, t, $J$ = 8.7, 2.7 Hz, 1 H), 1.05 (d, $J$ = 8.7 Hz, 1 H), 1.02 (m, 1 H), 0.87 (m, 1 H). **18** (mixture of isomers): $^1$H NMR ($CDCl_3$) δ 5.55 (s, 0.53 H), 5.50 (s, 0.47 H), 4.80 (s, 1 H), 4.57 (s, 1 H), 2.77 (s, 1 H), 2.67 (s, 1 H), 2.08 (m, 1 H), 2.07 (s, 1 H), 1.95 (m, 1 H), 1.87 (m, 1 H), 1.59 (m, 4 H), 1.42 (m, 1 H), 1.37 (m, 1 H), 1.25 (m, 1 H), 1.20 (m, 1 H), 1.18 (m, 1 H), 1.07 (d, $J$ = 8.7 Hz, 1 H), 1.03 (m, 1 H), 0.97 (m, 1 H).

The exo stereochemistry of **16** was verified by its ozonolysis ($CH_2Cl_2$, −70 °C, 15 min, then $Me_2S$ workup) to provide the 3-exo-phenyl-2-norbornanone that was found to be identical with an authentic sample prepared by the method of Kleinfelter.[38]

**Reaction of Complexes with Diethyl Sodiomalonate. Typical Procedure.** The $\pi$-allyl chloride dimer **5** (0.0294 g, 0.059 mmol) and triphenylphosphine (0.062 g, 0.234 mmol) were dissolved in $CH_2Cl_2$ (1.18 mL) under a $N_2$ atmosphere at room temperature. The solution was stirred for 15 min, and then the diethyl sodiomalonate (0.466 M in THF, 0.076 mL, 0.0354 mmol) was added. The solution was stirred at room temperature 15 h and then it was partitioned between 25 mL of saturated aqueous $NH_4Cl$ and 25 mL of $CH_2Cl_2$. The organic layer was separated, washed with brine, and filtered through a Celite–silica gel pad. The $CH_2Cl_2$ was removed under reduced pressure, and the product was GLC and $^1H$ NMR analyzed. Identical procedures were used starting with **15**, **10**, and **11**: $^1H$ NMR ($CDCl_3$) $\delta$ 5.56 (b s, 1 H), 4.14 (q, $J$ = 9.3 Hz, 4 H), 3.51 (t, $J$ = 6.5 Hz, 1 H), 2.75 (b s, 1 H), 2.66 (d, $J$ = 6.5, 2 H), 2.65 (b s, 1 H), 1.58 (m, 2 H), 1.29 (d, t, $J$ = 8.5, 2.0 Hz, 1 H), 1.22 (t, $J$ = 9.3 Hz, 6 H), 1.04 (d, $J$ = 8.5 Hz, 1 H), 0.95 (d, d, $J$ = 6.5, 2.3 Hz, 2 H).

***exo*- and *endo*-3-Chloro-2-methylenenorbornane.** The corresponding norbornanone isomers were prepared by the method of Kleinfelter[38] and subjected to a Wittig reaction with methyltriphenylphosphonium bromide to give the chloromethylene isomers.

**Electrical Conductivity Studies. Ambient Temperature.** The $\pi$-allyl chloride dimer **5** (0.0249 g, 0.05 mmol) and the appropriate amount of triphenylphosphine were dissolved in $CH_2Cl_2$ (5 mL). The solution was stirred until homogeneous, and then the $CH_2Cl_2$ was removed under reduced pressure. Acetone (10.0 mL) was then added to the resulting solid, and conductivities were measured for 10.0, 5.0, 2.5, and 1.25 mM solutions (molarity calculated based on Pd). The 5.0, 2.5, and 1.25 mM solutions were obtained by successive dilutions. The measured values ($L$) were then calibrated to give $L = 1.15L$. The values for $\Lambda_{eq} = 1000\bar{L}/C$ ($cm^2/(\Omega\ mol)$) were then calculated. A plot of $\Lambda_{eq}$ vs. $(C)^{1/2}$ extrapolated to a 1.0 mM solution gave the values for $\Delta m$ ($\Lambda_{eq}$). Comparable procedures were followed for **15**.

**Low Temperature.** In the low-temperature studies of the $\pi$-allyl dimer **5** and 16 equiv of $PPh_3$ and **15** all four concentrations of solutions were prepared separately and cooled to the appropriate temperature prior to measuring conductivities. Comparable procedures were run for $CH_2Cl_2$ and THF.

**X-ray Diffraction Study of 15.** The bis(phosphine) cation **15** ($C_{44}H_{41}P_3F_6Pd$) crystallized as colorless prisms. A crystal of **15** (0.1 × 0.25 × 0.4 $mm^3$) was examined on an Enraf-Nonius CAD-4 diffractometer equipped with a Ni-filtered Cu X-ray tube ($\lambda(K\alpha_1) = 1.5405$ Å). The space group is $P2_1/n$. The setting angles of automatically centered 17 reflections ($74° < \theta < 98°$) were used to determine the cell parameters by least-squares. The cell dimensions are $a$ = 10.328 (1) Å, $b$ = 17.767 (1) Å, $c$ = 21.984 (1) Å, $\beta$ = 100.21(1)°, and $V$ = 3972.9 Å$^3$. For $Z$ = 4 the calculated density is 1.48 g cm$^{-3}$. The data were collected at room temperature by using an $\omega$–$2\theta$ scan with constant speed of 7 deg min$^{-1}$ (in $\omega$). The strong reflections were remeasured with attenuator. The scan range and aperture width were determined as a function of $\theta$ to compensate $\alpha_1$–$\alpha_2$ dispersion: $\omega$ scan width = $(0.90 + 0.35 \tan\theta)°$ and aperture width = $(3.0 + \tan\theta)$ mm. Peak backgrounds were measured by extending the scan 25% on either side of the calculated range to give a peak to background counting time of 2:1. Intensity measurements were made on reflections of the type $\pm h,k,l$ to a $2\theta$ limit of 120°. A total of 6298 reflections were collected, and these were corrected for Lorentz, polarization, and absorption effect ((Cu K$\alpha$) = 51.6 cm$^{-1}$),[39] yielding 5234 independent reflections with $F_o > 3\sigma(F_o)$. The structure was solved by using the heavy-atom technique. Refinement of atomic parameters were carried out by using least-squares techniques on $F_o$ minimizing the function $\sum\omega(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are observed and calculated structure factor amplitudes, respectively, and the weighting factor $\omega$ is given by $\omega = 2.7/(\sigma^2(F_o) + 0.00067F_o^2)$. The atomic scattering factors were calculated from the analytical expression for the scattering factor curves.[40] The $f'$ and $f''$ components of anomalous dispersion were those of Cromer and Liberman[41] and were included in the calculations for all atoms. All hydrogens were located in a difference Fourier map and were included into refinement. The final agreement factors $R_1 = \sum||F_o| - F_c/\sum|F_o| = 0.053$ and $R_2 = [\sum\omega(|F_o| - |F_c|)^2/\sum\omega F_o{}^{1/2} = 0.059$. The largest peaks in a difference Fourier map calculated from the final structure factors are 1.9 e Å$^{-3}$ and located at the fractional coordinates 0.165, 0.682, 0.3636 and 0.163, 0.680, 0.242, respectively. The next high peak is of 0.5 e Å$^{-3}$. All calculations were performed with SHELX-76 program.[42] Final atomic and bonding parameters as well as calculated and observed structure factors are given in Table II and supplementary material.

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**Registry No.** **5**, 65629-73-4; **10**, 87517-88-2; **11**, 87583-18-4; **15**, 87517-90-6; **16**, 87517-91-7; **17**, 68490-80-2; $NaC_5H_5$, 4984-82-1; $NaBD_4$, 15681-89-7; $NaCH(COCH_3)(CO_2Et)$, 19232-39-4; $(n\text{-}Bu)_3SnOMe$, 1067-52-3; $NaCH(CO_2Et)_2$, 996-82-7; methylenenorbornane, 497-35-8; 2-methylnorbornene, 694-92-8; phenyllithium, 591-51-5; 3-*exo*-phenyl-2-norbornanone, 10472-46-5; *exo*-3-chloro-2-methylenenorbornane, 87517-92-8; *endo*-3-chloro-2-methylenenorbornane, 73537-28-7.

**Supplementary Material Available:** Tables of atomic coordinates, anisotropic temperature factors, hydrogen atom coordinates, and bond angles (4 pages). Ordering information is given on any current masthead page.

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