# The Direct Synthesis of $\eta^3$-ArCH$_2$PdCl Compounds by the Oxidative Addition of ArCH$_2$–Chlorine Bonds to Palladium Atoms[1]
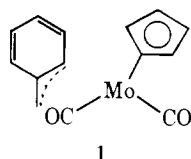
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**Abstract:** Oxidative addition of benzyl chloride and substituted benzyl chlorides to palladium atoms yields $\eta^3$-benzylpalladium chloride dimers. The parent compound, bis(1,2,3-$\eta^3$-benzyl)di-$\mu$-chloro-palladium(II) quantitatively adds four molecules of triethylphosphine by first forcing the $\eta^3$-benzyl $\eta^1$-benzyl transformation and then breakage of the Pd–Cl bridges to form *trans*-bis(triethylphosphine)(benzyl)chloropalladium(II). Bis(1,2,3,-$\eta^3$-benzyl)di-$\mu$-chloro-palladium(II) is fluxional even at −90 °C, but possesses good thermal stability (toward decomposition) and exhibits other spectral properties characteristic of allylic type bonding. It readily carbonylates, reacts with potassium acetate, and serves as a catalyst for benzylation of methylacrylate by benzyl chloride. Similar $\eta^3$-benzylpalladium compounds were prepared from 4-methylbenzyl chloride, 2-chloro-2-phenyl-1,1-trifluoroethane, and 3,4-dimethylbenzyl chloride. The 3,4-dimethylbenzyl derivative demonstrated temperature dependent behavior in the NMR, showing complete nonequivalence of benzyl protons at −61 °C. The spectra indicate that the fluxionality at higher temperatures is probably due to a rapid $\pi \to \sigma$ ($\eta^3 \to \eta^1$) equilibrium allowing C$_1$–C$_2$ rotation, and thus equivalence of benzyl (C$_1$) protons. In further synthetic work, chloro substituted $\eta^3$-benzylpalladium was found to be isolable, but quite unstable relative to previous compounds discussed. Also, 2-chloromethylpyridine apparently yielded a heteroatom $\eta^3$-benzyl compound.

In earlier papers we have reported the synthesis of "coordinatively unsaturated RPdX species.[3,4] Variance in R has a dramatic effect on thermal stability, as noted for the following compounds: C$_6$F$_5$PdBr, 100 °C; C$_6$H$_5$PdBr, <−100 °C; C$_6$H$_5$CH$_2$PdCl, 105 °C; CF$_3$PdI, 90 °C; CH$_3$PdBr, <−100 °C; CF$_3$CF$_2$PdI, >25 °C; CH$_3$CH$_2$PdBr, <−100 °C. Normal alkyl and aryl derivatives are very unstable materials, whereas the corresponding perfluorinated groups yielded surprisingly stable compounds.

One nonperfluoro R group, the benzyl group, yielded an unusually stable RPdX species, however. This group lends totally different properties to RPdX when compared with CH$_3$, C$_2$H$_5$, or C$_6$H$_5$. Indeed, when the results are examined closely, it is concluded that the benzyl group must be bonded to palladium in a very unusual manner. On examination of the literature, some precedent for "allylic" or $\eta^3$-bonding is found, especially in ($\eta^3$-C$_6$H$_5$CH$_2$)Mo(Cp)(CO)$_2$ (1) and some related materials.[5,6] Thus, it seemed useful to investigate the



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C$_6$H$_5$CH$_2$PdCl compound further, and to look at some substituted benzyls by the metal atom (vapor) technique.[7] This paper reports on these studies.

## Results and Discussion

**Benzyl Chloride.** The result of the cocondensation of benzyl chloride with palladium vapors was the formation of a deep red matrix from which a red powder could be isolated from toluene. This compound was assigned molecular structure 2 on the basis



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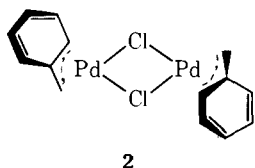
of its ^{1}H NMR, IR, UV, and molecular weight, and upon the basis of a triethylphosphine addition compound prepared by

adding triethylphosphine to a solution of the red product.[4] The assigned structure (2) can account for the unexpectedly high stability of the alkyl complex.

Details of the addition of triethylphosphine to 2 are probed by ^{1}H NMR in Figure 1, which displays the methylene (CH$_2$) adsorptions. The spectrum of 2 shows marked similarities to the ^{1}H NMR spectra of similar molybdenum[5,6a] and palladium[6c] compounds. The CH$_2$ protons give rise to a sharp single peak (Figure 1a); after 1 mol of triethylphosphine was added to 2, a decrease in the intensity of the signal for the ortho protons ($\delta$ 7.2) was observed and the benzylic protons became nonequivalent (Figure 1b). The addition of a second mole of triethylphosphine resulted in the loss of nonequivalence of the benzylic protons, and a splitting of CH$_2$ by phosphorus (Figure 1c). Likewise, the ortho protons moved downfield and joined



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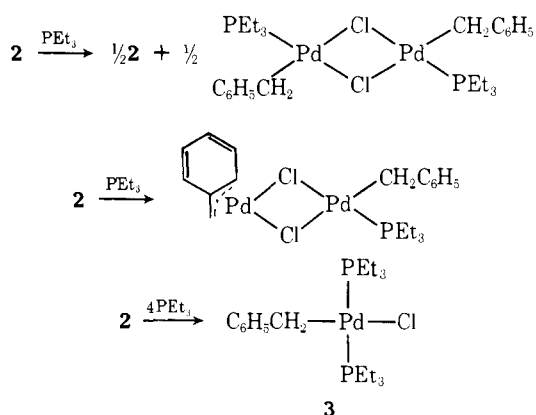
the meta and para protons, which implied a return to aromaticity. Further addition of the phosphine yielded the exact spectrum for *trans*-bis(triethylphosphine)(benzyl)chloropalladium(II) (3). If indeed this phosphine addition sequence is correct, it is different from the path followed by allylpalladium halide dimers where bridge cleavage generally occurs first, followed by a $\pi \to \sigma$ rearrangement on addition of further phosphine.

Previous reports indicate that temperature-dependent ^{1}H NMR behavior is sometimes but not always observed for $\eta^3$-benzyl systems.[5,6] For 2, no temperature-dependent behavior was observed, even as low as −91 °C. Since we have
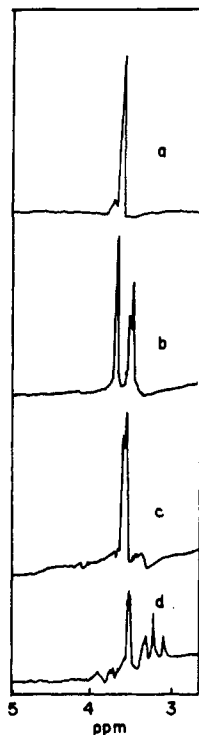
**Figure 1.** The benzylic CH$_2$ $^1$H NMR adsorptions recorded during addition of triethylphosphine to bis($\eta^3$-benzyl)di-$\mu$-chloro-dipalladium(II) (**2**), in CD$_2$Cl$_2$ solvent. (a) With no triethylphosphine added. (b) Addition of 1 equiv of triethylphosphine. The doublet at $\delta$ 3.43 is the methylene protons of a $\sigma$-bonded benzyl group split by a cis-phosphorus atom. (c) Addition of 2 equiv of triethylphosphine. (d) Addition of 3 equiv of triethylphosphine. The triplet at $\delta$ 3.20 is the methylene protons of trans-bis(triethylphosphine)benzylpalladium chloride (**3**).
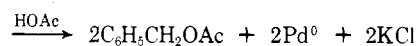
found the expected temperature dependence in a substituted benzyl system (vide infra), the implication is that **2** is extremely fluxional, even near −90 °C.

Other spectroscopic investigations of **2** support the $\eta^3$-bonding scheme. In the UV, large changes are observed between the UV spectrum of C$_6$H$_5$CH$_2$Cl ($\lambda_{max}$ 2600 Å), **3** (2650 m, 3100 sh, 3440 s), and **2** (2380 s, 2900 m, 3850 w). Infrared spectra indicate that bands which could be attributed to aryl C–H in-plane bending or stretching modes for **3** (1155 and 1180 cm$^{-1}$) and benzyl chloride (1158 and 1182 cm$^{-1}$) were either not observed, or significantly shifted for **2**. The aryl C–C stretching frequencies for **2** are either missing or shifted for **2** (1448 and 1482 cm$^{-1}$) when this IR spectrum is compared to either benzyl chloride (1588, 1498, and 1452 cm$^{-1}$) or **3** (1595, 1492, and 1458 cm$^{-1}$). These changes in spectroscopic properties indicate that the aromatic character of the phenyl rings in **2** is greatly different from either benzyl chloride or **3**.

Compound **2** was moderately air sensitive, and only slightly water sensitive, although aqueous base brought about immediate decomposition. It was found to be stable in degassed glacial acetic acid over a 3 week period at 25 °C. However, upon addition of a small amount of potassium acetate, the material rapidly decomposed. Fitton and McKeon find similar reactivity for [(((C$_6$H$_5$)$_3$P)$_2$PdCl(CH$_2$C$_6$H$_5$)].[8]

($\eta^3$-C$_6$H$_5$CH$_2$PdCl)$_2$ + 2KOAc

**2**

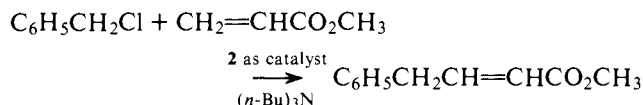$\xrightarrow{\text{HOAc}}$ 2C$_6$H$_5$CH$_2$OAc + 2Pd$^0$ + 2KCl

Bis($\eta^3$-benzyl)di-$\mu$-chloro-dipalladium(II) (**2**) is very reactive with many donor ligands. Triphenyl- and triethylphosphine and pyridine all react rapidly with **2** to form the stable L$_2$PdCl(CH$_2$C$_6$H$_5$) adducts ($\sigma$-CH$_2$C$_6$H$_5$) in quantitative

yields. However, the weaker bidendate ligand norbornadiene did not react with **2** at room temperature.

In order to compare **2** with the intermediate, "benzylpalladium chloride", proposed by Heck and Nolley,[9] we subjected **2** to the exact reaction conditions outlined by these workers. The reaction in question is the catalytic benzylation of methyl acrylate with benzyl chloride to form methyl 4-phenyl-3-butenoate. In the previous work it was proposed that some "active Pd" species is formed from PdCl$_2$, which then reacts to form "benzylpalladium chloride" as the reactive intermediate in the benzylation reaction. Indeed, the reaction proceeded quite well in the presence of **2**. However, stoichiometric addition of **2** to methyl acrylate has not yet been studied.

C$_6$H$_5$CH$_2$Cl + CH$_2$=CHCO$_2$CH$_3$

$\xrightarrow[\text{($n$-Bu)$_3$N}]{\text{2 as catalyst}}$ C$_6$H$_5$CH$_2$CH=CHCO$_2$CH$_3$

Carbonylation of **2** proceeded readily at room temperature in methylene chloride, with methyl $\alpha$-phenylacetate and palladium metal being observed as products, upon the addition of methanol. Similar carbonylation activities for allylpalladium compound have been found.[10]
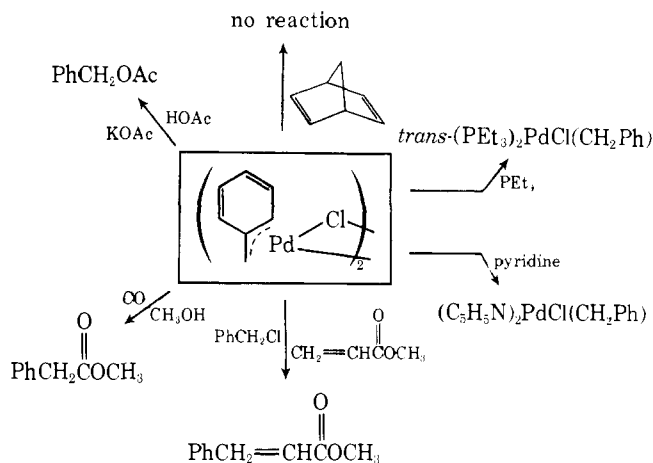


A unique and annoying feature of **2** and substituted variations of **2** is their tendency to become less and less soluble in organic solvents with age. This is not a matter of slow decomposition of the aging crystals since both fresh and aged samples of **2** react with triethylphosphine quantitatively to form the L$_2$(Cl)PdCH$_2$C$_6$H$_5$ adduct. An x-ray powder pattern of a fresh sample of **2** revealed a unit cell size of 11.44 Å where upon the same sample was aged for 3 weeks and then revealed a unit cell size of 18.99 Å. In a similar time span the solubility of **2** in toluene changed from moderate to very poor solubility. Thus, slow formation of trimers, and higher telomers in the solid state appears evident. So far we have been unsuccessful at preparing a single crystal of **2**, or a related substituted system suitable for single-crystal x-ray analysis, and this failure is probably due in part to this unique slow telomerization. Similar observations have been made in the case of organolanthanides.[11]
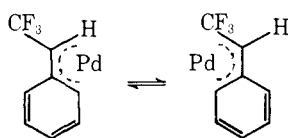
**4-Methylbenzyl Chloride.** The $^1$H NMR spectrum of the product of the cocondensation of 4-methylbenzyl chloride and palladium vapors, bis($\eta^3$-4-methylbenzyl)di-$\mu$-chloro-dipalladium(II) (**4**), was very similar to that of the parent compound ($\eta^3$-C$_6$H$_5$CH$_2$PdCl)$_2$ (**2**).

This compound was also extremely air sensitive in solution but could be handled for short periods as a solid in the air. The solubility of this compound was the same as **2**; that is, when freshly prepared it was soluble in a variety of organic solvents, but it became very insoluble in a few weeks.

The addition of triethylphosphine resulted in the formation of trans-bis(triethylphosphine)-4-methylbenzylpalladium

chloride in quantitative yield. Other properties and yields of compound **4** are listed in Tables I and II.

**2-Chloro-2-phenyl-1,1,1-trifluoroethane.** The cocondensation of 2-chloro-2-phenyl-1,1,1-trifluoroethene (CF₃CHClPh) with palladium vapors resulted in a yellowish orange compound, bis($\eta^3$-trifluoromethylbenzyl)di-$\mu$-chloro-dipalladium(II) (**5**). A poor ¹H NMR spectrum was obtained, and certain similarities to the previously discussed ¹H NMR spectrum were noted. The proton on the $\alpha$-carbon was not entirely resolved because of the compound's poor solubility and because of the broad splitting pattern due to the three fluorine atoms on the adjacent trifluoromethyl group. The ¹⁹F NMR spectrum of this compound revealed two types of fluorine atoms, one comprising ca. 80% of the sample (doublet, $J = 8$ Hz) at 87.82 ppm (relative to CCl₃F) and the other comprising ca. 20% of the sample (doublet, $J = 8$ Hz) at 70.49 ppm. The infrared spectrum revealed two very strong C–F stretching frequencies (1107 and 1225 cm⁻¹). It is possible that an equilibrium between two forms of the compound had been established.



This compound was found to be air sensitive in solution but could be handled in the air as a solid for short periods. Other properties and the yield of compound **5** are listed in Tables I and II.

**3,4-Dimethylbenzyl Chloride.** The cocondensation of 3,4-dimethylbenzyl chloride with palladium vapors yielded bis($\eta^3$-3,4-dimethylbenzyl)di-$\mu$-chloro-dipalladium(II) (**6**). When



**6**
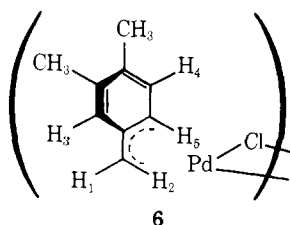
a CDCl₃ solution of **6** was cooled, temperature-dependent behavior in the ¹H NMR spectrum was observed (Figure 2). The two ortho protons are at approximately the same chemical shift at room temperature, but, as the temperature decreases, the doublet (proton 3) moves upfield and the singlet (proton 5) moves downfield. In ¹H NMR studies of palladium allyl complexes, generally, the protons closest to the palladium atom are the most shielded, and absorb furthest upfield.[10] These literature results imply, not unexpectedly, that the most stable low temperature configuration for **6** is that form in which the methyl groups are farthest from the palladium. At lower temperatures the two benzylic protons become nonequivalent.

As the benzylic protons become nonequivalent, the ortho protons continue to become more widely different in their chemical shifts. These concurrent changes in chemical shift imply that only one equilibrium process is being slowed, and hence must explain both effects (benzylic proton and ortho proton changes). One such process would be a $\pi \rightarrow \sigma \rightarrow \pi$ equilibrium, with a $\sigma$-bonded benzyl group as a short-lived higher energy intermediate. As a C₁–C₂ rotation would be rapid, H₁ and H₂ would be equivalent on an NMR time scale as long as the $\pi \rightarrow \sigma \rightarrow \pi$ rearrangement was rapid. As the temperature is lowered, it would become more difficult for such a process to occur, and, in this case, a preferred conformation would become favored. The $\pi$-system with the CH₃ groups
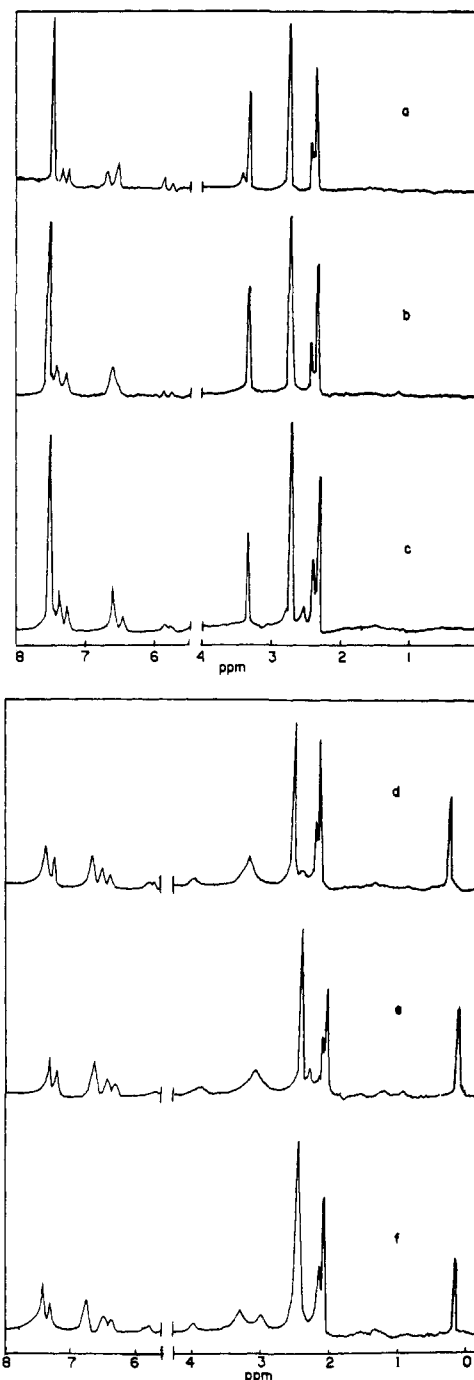


**Figure 2.** The temperature-dependent ¹H NMR spectra of bis($\eta^3$-3,4-dimethylbenzyl)di-$\mu$-chloro-dipalladium(II) (**6**), in CDCl₃ solvent. (a) At 40 °C assignments are: s, $\delta$ 7.50, benzene; d($J = 8$ Hz), 7.27, H₄; d, 6.56, H₃ and H₅; s, 3.05, H₁ and H₂; s, 2.47, 4-methyl protons; s, 2.08, 3-methyl protons. (b) At −2 °C the singlet at 6.58 is H₃ and H₅. (c) At −31 °C the doublet at $\delta$ 6.53 is H₃ and H₅. (d) At −47 °C the singlet at $\delta$ 6.70 is H₃, the doublet ($J = 8$ Hz) at $\delta$ 6.48 is H₅. (e) At −50 °C. (f) At −61 °C. The broad singlets at $\delta$ 3.32 and 3.00 are H₁ and H₂, which have become nonequivalent.

farthest away from Pd would be expected to be sterically favored, and would finally become so favored at very low temperatures that H_A and H_B would become nonequivalent. A C₁–C₂ rotation in the $\pi$-bonded species would not necessarily occur, even at room temperature, when H₁, H₂ equivalence is indicated, according to this proposal (see scheme below).

It seems unlikely that these low temperature ¹H NMR results could be explained by the occurrence of favored cis or

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**Table I.** Properties of $\eta^3$-Benzylpalladium Compounds

| Compound | IR spectrum (cm$^{-1}$) (KBr pellet) | UV Spectrum (Å)[a] (CHCl$_3$ solution) | ($\delta$) $^1$H NMR | Decomposition pt (°C) |
|---|---|---|---|---|
| ($\eta^3$-benzylPdCl)$_2$ (2) | 455 m, 511 m, 571 s, 615 m, 682 s, 692 s, 725 (sh), 742 vs, 750 (sh), 760 (sh), 805 w, 825 m, 855 w, 911 m, 1005 (sh), 1025 (sh), 1070 s, 1210 m, 1255 m, 1268 (sh), 1315 w, 1481 m, 1448 m, 1470 m, 1482 m, 1530 w, 2930 w, 3030 m | 2380 s, 2900 m, 3850 w | ref 4 | 100–110 |
| ($\eta^3$-4-methylbenzylPdCl)$_2$ (4) | 380 (sh), 390 w, 408 w, 427 w, 447 w, 484 w, 526 s, 636 w, 699 m, 737 vs, 816 vs, 915 (sh), 924 w, 1013 w, 1042 w, 1115 w, 1188 w, 1256 w, 1346 w, 1403 w, 1452 w, 1617 w, 3000 w | 2400 s, 2625 (sh), 2920 (sh), 3970 w | CDCl$_3$ (d, 7.77) meta (d, 7.25) ortho (s, 3.53) CH$_2$ (s, 2.65) CH$_3$ | 75–80 |
| ($\eta^3$-7-trifluoromethylbenzylPdCl)$_2$ (5) | 450 w, 454 w, 478 w, 495, 519 s, 552 (sh), 585 w, 613 s, 650 m, 675 w, 699 vs, 735 (sh), 757 vs, 814 m, 832 w, 866 s, 894 s, 914 s, 970 (sh), 986 m, 1020 w, 1077 (sh), 1107 vs, 1176 (sh), 1225 vs, 1325 w, 1430 m, 1485 m, 1526 w, 1542 w, 1561 w, 1577 w, 1667 w, 1711 w, 1765 w, 1855 w, 2165 s, 3000 m | 2390 s, 2980 m, 3920 | CD$_2$Cl$_2$ (d of d, 7.83) meta and para (s, 7.25) ortho (m, 3.47) methine | 124–126 |
| ($\eta^3$-3,4-dimethylbenzylPdCl)$_2$ (6) | 379 w, 560 w, 590 w, 690 w, 735 w, 785 w, 830 m, 858 m, 876 w, 965 w, 1005 (sh), 1032 m, 1280 m, 1348 w, 1386 w, 1455 (sh), 1485 m, 1620 w, 3000 w | 2415 s, 2940 m, 3930 w | Figure 2 | 96–99 |
| ($\eta^3$-4-chlorobenzylPdCl)$_2$ (7) | 315 w, 335 w, 395 w, 410 w, 575 m, 655 m, 820 m, 934 w, 1020 w, 1075 (sh), 1095 m, 1260 m, 1335 w, 1400 w, 1950 m, 1977 m, 2950 w | 2400 s, 2970 (sh), 3280 (sh), 3800 w | | 90–92[b] |
| ($\eta^3$-5-chlorobenzylPdCl)$_2$ (8) | 355 w, 392 w, 516 m, 582 m, 598 m, 685 m, 714 m, 725 (sh), 810 vs, 862 (sh), 870 (sh), 1030 (sh), 1072 vs, 1100 vs, 1218 w, 1216 m, 300 w | 2360 s, 2450 s, 2910 (sh), 3915 w | | 80–83[b] |
| ($\eta^3$-6-chlorobenzylPdCl)$_2$ (9) | 336 m, 360 (sh), 410 w, 437 w, 575 w, 649 w, 673 w, 736 (sh), 755 s, 810 w, 834 w, 873 w, 971 w, 1028 w, 1054 m, 1115 w, 1282 w, 1337 w, 1428 w, 1465 w, 1528 w, 1590 (sh), 1597 w, 1863 w, 1967 w, 2930 w | 2490 s, 2680 (sh), 2965 (sh), 3550 w | | 81–87[b] |
| ($\eta^3$-2-CH$_2$C$_6$H$_4$N)(2-(ClCH$_2$)C$_5$H$_4$N)PdCl (10) | 310 w, 329 (sh), 357 m, 3832, 405 w, 433 (sh), 453 m, 472 (sh), 535 w, 586 m, 629 w, 650 m, 660 w, 692 m, 713 m, 752 (sh), 762 vs, 778 (sh), 830 m, 932 m, 998 w, 1032 (sh), 1040 (sh), 1065 m, 1105 w, 1122 w, 1158 m, 1180 (sh), 1218 (sh), 1232 (sh), 1242 m, 1258 (sh), 1260 m, 1304 m, 1388 (sh), 1412 (sh), 1438 (sh), 1443 s, 1482 vs, 1529 (sh), 1560 (sh), 1567 (sh), 1573 s, 1580 (sh), 1607 vs, 1628 (sh), 1638 (sh), 1658 w, 1712 w, 2882 m, 2940 (sh), 2970 (sh), 2980 m, 3032 m, 3080 m, 3110 (sh) | 2480 s, 2650 (sh), 3020 (sh), 3850 w | | 140 |

[a] Extinction coefficients not obtained as a portion of each sample was generally insoluble. [b] Temperature range in which decomposition appeared to be complete with sample heated at approximately 1°/min. Sample slowly decomposed at lower temperature.

**Table II.** Yields and Elemental Analysis of $\eta^3$-Benzylpalladium Compounds

| Compound | Isolation method[a] | Elemental analysis (%) | | | | | | Yield (%)[b] |
|---|---|---|---|---|---|---|---|---|
| | | C | | H | | Cl | | |
| | | Calcd | Found | Calcd | Found | Calcd | Found | |
| $(\eta^3\text{-}C_6H_5CH_2PdCl)_2(2)$ (2) | A | 36.18 | 36.23 | 3.02 | 3.16 | 15.21 | 15.27 | 39.4 |
| $(\eta^3\text{-}4\text{-}CH_3C_6H_4CH_2PdCl)_2$ (4) | A | 38.9 | 39.0 | 3.67 | 3.70 | — | — | 31.2 |
| $(\eta^3\text{-}C_6H_5CH(CF_3)PClCl)_2$ (5) | A | 31.92 | 32.30 | 2.00 | 2.24 | — | — | 14.2 |
| $(\eta^3\text{-}3,4\text{-}(CH_3)_2C_6H_5CH_2PdCl)_2$ (6) | B | 43.8 | 43.4 | 4.41 | 4.33 | — | — | 41.0 |
| $(\eta^3\text{-}4\text{-}ClC_6H_4CH_2PdCl)_2$ (7) | A | c | c | c | c | c | c | 8.7 |
| $(\eta^3\text{-}5\text{-}ClC_6H_4CH_2PdCl)_2$ (8) | A | c | c | c | c | c | c | 12.3 |
| $(\eta^3\text{-}6\text{-}ClC_6H_4CH_2PdCl)_2$ (9) | A | c | c | c | c | c | c | 13.4 |
| $(\eta^3\text{-}2\text{-}CH_2C_5H_4N)(2\text{-}(ClCH_2)C_5H_4N)PdCl$ (10)[d] | A | 39.87 | 39.09 | 3.34 | 3.40 | — | — | 38.0 |

[a] See Experimental Section. [b] Yields uncorrected for metal loss, based on amount of palladium vaporized. [c] Not obtained as the sample was not sufficiently stable. [d] THF soluble, not toluene soluble.
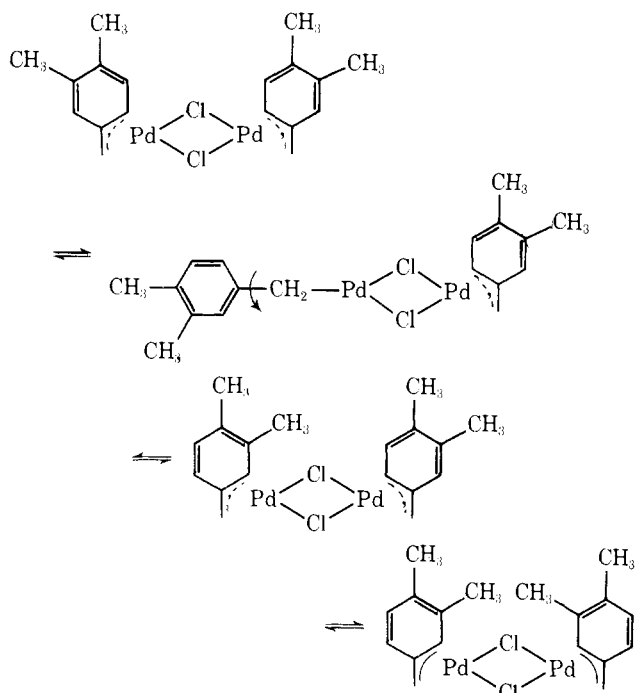


trans isomers of these dimers, since in either case, the two halves can be related by simple symmetry operations.
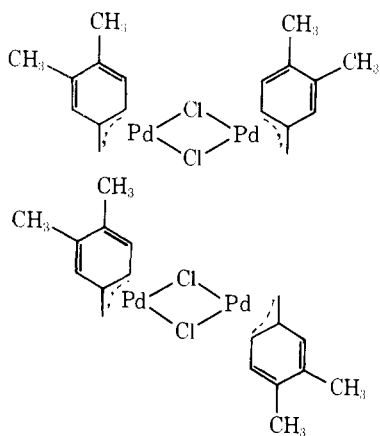


The solubility of **6** was much greater than that of the other complexes prepared, and it became insoluble only on standing for extended periods (approximately 2 months). As the $^1$H NMR spectrum shows, and from elemental analysis, a certain quantity of benzene was found as solvent of coordination, and the compound analyzed for $C_{20}H_{24}Pd_2Cl_2$ or $(C_{18}H_{22}Pd_2Cl_2\cdot\frac{1}{3}(C_6H_6))$. The compound was soluble in benzene, toluene, chloroform, methylene, chloride, and ace-

tone. Other properties and the yield of compound **6** are listed in Tables I and II.

**Chlorobenzyl Chlorides.** In the three experiments attempted, using 4-chlorobenzyl chloride, 3-chlorobenzyl chloride, and 2-chlorobenzyl chloride, compounds were isolated that displayed similar infrared spectra to the previously mentioned materials. These compounds, bis($\eta$-4-chlorobenzyl)di-$\mu$-chloro-dipalladium(II) (**7**), bis($\eta^3$-5-chlorobenzyl)di-$\mu$-chloro-dipalladium(II) (**8**), and bis($\eta^3$-6-chlorobenzyl)di-$\mu$-chloro-dipalladium(II) (**9**), respectively, were unstable to storage although the spectra obtained displayed similarities to those described above. The low stability was not surpising as a similar compound prepared by Stevens and Shier was also found to be extremely unstable.[6c]

**2-Chloromethylpyridine.** The cocondensation of 2-chloromethylpyridine with palladium vapors yielded a different type of compound than those described above. Based on the elemental analysis and infrared spectrum, it is probable that the structure involves a $\eta^3$-bonded azabenzyl group bond and an N-bonded pyridine group **10** or **11**. The infrared spectrum



10                    11
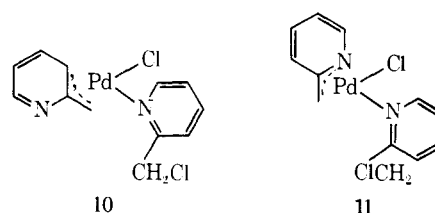
indicated that a $CH_2$-Cl bond was still intact (762 cm$^{-1}$) and the elemental analysis agreed with the above structures. An alternate structure, **12**, involving a C–Pd $\sigma$ bond is also possi-



12
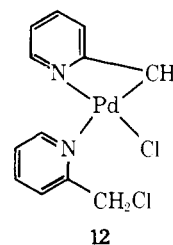
ble, although the formation of a four-membered ring would not seem likely. Other properties of this compound are listed in Tables I and II.

**Attempted Preparations.** It was noted that three substrates, (chloromethyl)-2-methylbenzene, (chloromethyl)-3-methylbenzene, and (chloromethyl)-3-trifluoromethylbenzene, when cocondensed with palladium vapors did not yield any isolable benzyl palladium compounds. Even the addition of triethylphosphine at −196 °C did not result in the isolation of any palladium organometallic compounds. The only palladium containing compound isolated was PdCl₂ or its triethylphosphine complex. Gas chromatographic analysis of the substrates

showed peaks attributable to 1,2-diarylethanes (coupling products). We can offer no explanation at this time as to why these particular substituted benzyl chlorides did not yield stable benzyl organometallics.

## Conclusions

The compounds described above are novel compounds, in that they are readily prepared by direct cocondensation of a suitable chloromethyl arene with palladium vapors, and are the simplest compounds having a $\eta^3$-benzyl group prepared to date. These materials are chemically similar to allyl complexes, and yet their chemistry and/or stabilities are greatly affected by certain substituents. Further work, particularly x-ray structural work, is warranted.

## Experimental Section

**Analytical Methods.** Quantitative analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.; Dornis and Kolbe, Hohenweg, West Germany; Instranal Laboratory, Inc., Rensselau, N.Y.; and Midwest Microlabs, Ltd., Indianapolis, Ind. Analysis of pertinent compounds are listed in Tables I and II, along with yields and infrared and ultraviolet spectra. The $^1$H spectra were obtained on a Varian A-60, and the $^{19}$F spectrum was taken on a JEOLCO PS-100. The infrared spectra were recorded on a Beckmann IR-12 and ultraviolet spectra were recorded on a Cary 14. All solvents were dried and stored under an argon atmosphere. The chloromethyl arenes were used as supplied.

**Yields.** The percent yields are based on palladium vaporized and are uncorrected for metal loss (20-40%) to electrodes supports, wide spread depositions, etc. The yields, in general, were low, but palladium metal is reasonably inexpensive, and unreacted metal can be reclaimed.

**Metal Atom Apparatus.** Our metal atom reactors have been described in previous publications.[7] In this study palladium vapors were generated by electrical resistive heating of aluminum oxide coated tungsten wire crucibles (Sylvania Emissive Products, CS-1002A). Power input was generally in the range of 200-300 W (7-8 V at 30-40 A), depending upon the age of the crucible, which, with proper care, would last 20-25 evaporations.

**Reaction Procedures (Methods A and B and Examples).** In all cases, it was necessary to heat all portions of the reactor in which the (chloromethyl)arenes were inletted, as the rate of addition of the vapor would have been too low otherwise. In general a 20-40-fold excess of the chloromethyl arenes was used.

**Method A** (for preparation of thermally stable compounds with reasonably volatile substrates). **Example, Preparation of Bis($\eta^3$-benzyl)di-$\mu$-chloro-dipalladium(II) (2).** Palladium vapor (0.598 g, 5.62 mmol) and benzyl chloride (11.5 g, 90 mmol) were cocondensed at $-196$ °C. The liquid nitrogen bath was removed and the reactor was allowed to warm to room temperature with magnetic stirring while open to the vacuum pumpout line. After complete removal of the excess substrate (ca. 4 h), the reactor was pressurized to atmospheric pressure with argon and was washed with four 25-mL portions of toluene. Each aliquot was removed by syringe and transferred to Schlenk apparatus where it was filtered. The combined solution was concentrated under reduced pressure and a 25-mL portion of pentane was added to the solution. A dark red powder separated from solution. Excess solution was removed by syringe and the powder was washed twice with 25-mL portions of pentane, and dried by pumping (yield 0.63 g, 39.4%). (Yields are quite variable.)

**Method B** (for preparation of compounds from substrates with low volatility). **Example, Preparation of Bis($\eta^3$-3,4-dimethylbenzyl)di-$\mu$-chloro-dipalladium(II) (6).** Palladium vapors (0.150 g, 1.41 mmol) and (chloromethyl)-2,4-dimethylbenzene (4.3 g, 27.8 mmol) were cocondensed at $-196$ °C. After codeposition was complete, the liquid nitrogen bath was removed and the reactor, which has been isolated from the vacuum line, was warmed to room temperature with stirring. The reactor was pressurized to atmospheric pressure with argon and a 25-mL portion of toluene was added to the mixture in the reactor by syringe. The solution was stirred for a few minutes and then syringed from the reactor into a Schlenk tube equipped with a glass frit, and filtered. The same procedure was followed with three other toluene washes. The combined solutions were placed on a vacuum line and excess substrate and solvent were removed under vacuum. The relatively short path between the trap on the vacuum line and the round

bottom was heated to approximately 80 °C to facilitate removal of the relatively involatile substrate. After substrate removal was complete, the residues were taken up in 75 mL of toluene, filtered, and concentrated under reduced pressure. Pentane (10 mL) was added to the concentrated solution, and the excess solvent was decanted, using a syringe and needle, from the resulting red powder. Three pentane washes (10 mL each) were added and removed by syringe. After drying the resultant red powder for 8 h under vacuum 0.138 g (41.0% yield) of bis($\eta^3$-3,4-dimethylbenzyl)di-$\mu$-chloro-dipalladium(II) was obtained.

**Preparation of *trans*-Bis(triethylphosphine)benzylchloropalladium(II).** Benzyl chloride (3.8 g, 30 mmol) and palladium vapors (0.146 g, 1.37 mmol) were cocondensed as in method A, above. After vacuum removal of excess substrate, triethylphosphine (0.78 g, 6.63 mmol) was condensed directly into the reactor. Excess triethylphosphine was removed under vacuum and then the reactor was vented to the air. The reactor was rinsed with hexane (4-25 mL portions) and the washes were combined, decolorized with Norit, and then filtered. The volume of the solution was reduced to approximately 25 mL by blowing nitrogen over the top of the solution. The flask was stoppered and stored overnight at approximately $-10$ °C. The resulting yellowish white crystals were collected by suction filtration, washed with cold hexane, and then air dried (0.15 g, 23% yield). The compound was identified by its $^1$H NMR spectrum ($\delta$ 1.10, p; 1.81, hept; 2.66, t ($J$ = 7.5 Hz); 7.05, d ($J$ = 5.0 Hz); 7.35 d ($J$ = 5.0 Hz), and its elemental analysis (calcd for $C_{19}H_{37}ClP_2Pd$: C, 48.63; H, 7.95; Cl, 7.55. Found: C, 48.50; H, 7.83; Cl, 7.41).

**Reaction of 2 with Carbon Monoxide.** A solution of **2** (0.33 g, 0.72 mmol) in 20 mL of toluene was placed in a Schlenk tube which had been fitted with a gas dispersion tube. Carbon monoxide was bubbled through the solution for 5 min (precipitation of metal appeared to cease after 2 min). Methanol (1.2 mmol) was added to the toluene solution. GLC analysis indicated that methyl phenylacetate (68% yield) and benzyl chloride (24% yield) were isolated as products.

**The Reaction of 2 with Potassium Acetate.** To a Schlenk tube was added **2** (0.377 g, 0.81 mmol) and 10 mL of freeze-thaw degassed glacial acetic acid. The red solution stood for 4 days with no detectable decomposition or formation of benzyl acetate. Solid potassium acetate (0.082 g, 0.8 mmol) was added to the acetic acid solution, resulting in rapid decomposition of ($\eta^3$-$C_6H_5CH_2PdCl)_2$ as evidenced by the formation of palladium metal. GLC analysis (5 ft × ¼ in. SE30, 20%) and a mass spectrum identified benzyl acetate (65% yield) as the only organic product.

**X-ray Powder Pattern of 2.** Samples were sealed in thin wall capillary tubes in a glove bag under an argon atmosphere, waxed temporarily, and then sealed with a flame. The samples were exposed to nickel filtered copper K$\alpha$ radiation (1.5418 Å) for 2.5 h.

**The Effect of ($^3\eta$-$C_6H_5CH_2PdCl)_2$ (2) as a Catalyst in the Reaction between Methyl Acrylate and Benzyl Chloride.** To a Schlenk tube was added benzyl chloride (4.5 mL, 40 mmol) tributylamine (9.5 mL, 40 mmole), freshly distilled methyl acrylate (4.5 mL, 50 mmol) and ($^3\eta$-$C_6H_5CH_2PdCl)_2$ (0.073 g, 0.16 mmol), under argon. The mixture stood for 72 h at room temperature, but did not form any detectable products. The Schlenk tube was then fitted with a Friedrichs condenser and heated on a steam bath for 24 h. At the end of this time, methyl 4-phenyl-3-butenoate was found in approximately 30% yield (based on benzyl chloride). The product was collected by GLC and identified by its mass spectrum.

## References and Notes

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# Oxidative-Addition Reactions of the Na₂Fe(CO)₄ Supernucleophile

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**Abstract:** A kinetic and mechanistic study of oxidative-addition of alkyl halides and tosylates to $Na_2Fe(CO)_4$ is presented which demonstrates a two-electron $S_N2$ oxidative-addition mechanism in both tetrahydrofuran (THF) and $N$-methylpyrrolidinone (NMP) with no detectable competing one-electron atom abstraction and/or radical chain mechanism. Evidence is presented delineating the importance of ion-pairing on the oxidative-addition reactions of transition metal anions. This study includes a wide variety of relative alkyl halide and tosylate substrate reactivities, activation parameters, the effect of added crown ethers, cryptands, and counterions (as $K_2Fe(CO)_4$), and salt effects. Also included are common-ion depression, stereochemical, conductivity, and crown ether or cryptand conductometric titration studies. The conductometric titrations using crown ethers or cryptands as titrants represent a new, simple, semiquantitative method for the determination of ion association constants. Data are presented which account for the dramatic $2 \times 10^4$ oxidative-addition rate increase in NMP vs. THF by the extent of dissociation of $Na_2Fe(CO)_4$, the more dissociated species being kinetically much more reactive. In NMP, $Na_2Fe(CO)_4$ dissociates predominantly to the solvent-separated supernucleophilic ion pair $[Na^+:S:Fe(CO)_4{}^{2-}]^-$ (S = solvent), the kinetically dominant species, with no kinetic contribution by free $Fe(CO)_4{}^{2-}$. In THF, $Na_2Fe(CO)_4$ is much less dissociated, with tight-ion paired $NaFe(CO)_4{}^-$ the kinetically important species. Values for the first and second $Na^+$ dissociation constants, in both THF and NMP, are presented. The results of recent x-ray studies of $Na_2Fe(CO)_4 \cdot 1.5$dioxane, $K_2Fe(CO)_4$, and $(cryptate \cdot Na^+)_2Fe(CO)_4{}^{2-}$ (cryptate = 4,7,13,16,21,24-hexaoxyl-1,10-diazabicyclo[8.8.8]hexacosane) are summarized and discussed.

The recent concept of oxidative-addition has enjoyed both a broad and unifying appeal in organotransition metal chemistry.[1] Mechanistic studies of oxidative-addition of alkyl halides[2] to $d^7$ transition metal compounds have resulted in the delineation of a one-electron atom abstraction mechanism of oxidative-addition.[3] Studies of $d^8$ complexes suggest a one-electron[1d,4] (atom abstraction and/or radical chain) in addition to a well-documented two-electron ($S_N2$)[5] oxidative-addition mechanism, depending upon the transition metal compound, the alkyl halide addendum, and the experimental conditions. These mechanisms have been the point of some controversy.[4,6] Oxidative-additions to $d^{10}$ complexes are in general less well studied,[7] but recent work[1d,8] again suggests both one- and two-electron mechanisms for alkyl halide additions although these studies are also controversial.[8e] Detailed kinetic studies of $d^{10}$ systems have appeared only for relatively reactive substrates such as $CH_3I$ or $C_6H_5CH_2Br$.

Reactions employing initial oxidative-addition to $Na_2Fe(CO)_4$ were previously shown to be useful in the conversion of aliphatic halides and sulfonates into aldehydes,[9a] unsymmetrical ketones,[9b] carboxylic acids,[9c] esters,[9c] and amides[9c] (Scheme I). The use of $Na_2Fe(CO)_4$ in organic as well as inorganic synthesis has recently been reviewed.[10]

Previously we reported the dramatic effect of ion-pairing upon the alkyl migration reactions[11] of $[RFe(CO)_4]^-$ (Scheme I). Herein we report the characterization of $Na_2Fe(CO)_4$ as a supernucleophile,[5d] the importance of ion-pairing[12a] in the oxidative-addition reactions of this transition metal anion, elucidation of the extent of dissociation and kinetically dominant form of $Na_2Fe(CO)_4$ in both THF[13] and NMP,[13] and a full kinetic and mechanistic investigation of its oxidative-addition reactions.

**Scheme I.** Synthetic Organic Conversions Using $Na_2Fe(CO)_4$
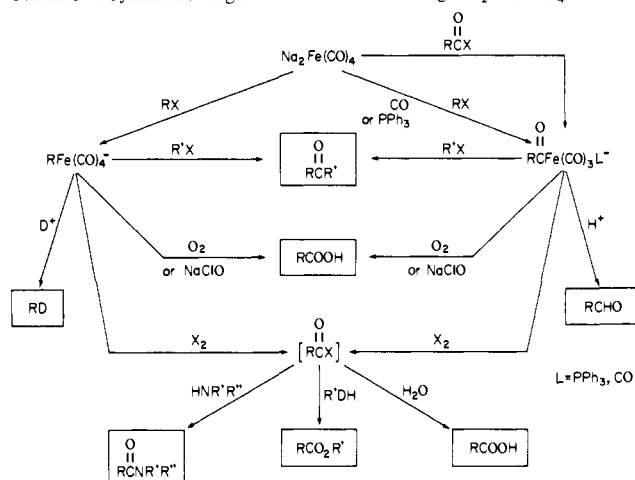


Oxidative-addition of alkyl halides or sulfonates to $Na_2Fe(CO)_4$, $d^{10}$, coordinatively saturated iron($-II$), yields a stable saturated $d^8$ alkyl iron(0) product (Scheme I), previously isolated and fully characterized as the air stable[13,14] salt $PPN^+[RFe(CO)_4]^-$. A recent x-ray diffraction study[15] of $PPN^+[CH_3CH_2CH_2Fe(CO)_4]^-$ shows a trigonal-bipyramidal structure ($C_{3v}$ symmetry) with the alkyl group in the apical position, and an iron–carbon bond length of 2.20 (2) Å. The pattern of $\nu_{CO}$ frequencies in solution suggests that the $C_{3v}$ symmetry is also maintained in solution,[14] although the single CO $^{13}C$ NMR signal[16] at ambient temperature of the CO's implies rapid scrambling of axial and equatorial groups, characteristic of many pentacoordinate complexes.[17] In the