NMR tube. The ^1H NMR spectra, run within 15 min of preparing the solutions, were nearly identical, showing compound **3** present in ca. 90% purity contaminated by unidentified PMe_3-containing material, but traces of decomposition products were present in the sample which had no CD_3CN. Four hours later the NMR spectrum of the sample which had been treated with CD_3CN was largely unchanged, with at least 75% of the initial amount of compound **3** remaining. But the sample which had not been treated with CD_3CN had decomposed extensively. Only small amounts of compound **3** remained (ca. 9%). Approximately equal amounts of compound **4** and $RhH_2(PMe_3)_4^+$ [hydrido NMR signal, δ −10.6 d (137 Hz) of pseudoquartets (15 Hz), superimposable on the signal of an authentic sample[10,27]] were present, each approximately 29%, together with PMe_3 signals of unidentified Rh(III) compound(s). Also present was methyl vinyl ether (ca. 29%) and methyl ethyl ether (ca. 33%). Amounts of species present were determined (±5 percentage points) by ^1H NMR integration and are reported as percentages of compound **3** originally present. ^1H NMR of methyl vinyl ether (CD_2Cl_2):[28] OCH_3, δ 3.54, s; =CH(OMe) 6.54, d of d (14.3, 6.8); $=CH_2$ 4.01, d of d (6.8, 2.2), 4.18, d of d (14.3, 2.2). ^1H NMR of methyl ethyl ether (CD_2Cl_2): OCH_3, δ 3.30, s; OCH_2, 3.42, q; CH_3, 1.71, t (7.0).

For the isotope crossover studies, $^{13}CH_3$-labeled compound **3** (0.04 g) in CD_2Cl_2 was treated with methyl ethyl ether (more than 1.5 equiv, prepared from MeI and NaOEt) and allowed to decompose. NMR analysis of the solution revealed $^{13}CH_3CH_2OMe$, unlabeled methyl ethyl ether, and $^{13}CH_2$=CH(OMe). No $^{12}CH_3{}^{13}CH_2OMe$, $^{12}CH_2{}^{13}CH(OMe)$, nor $^{12}CH_2{}^{12}CH(OMe)$ could be detected (estimated detection limits 5%). ^{13}C NMR of $^{13}CH_2{}^{12}CH(OMe)$ (CD_2Cl_2):[28] δ 86.8; $J(^{13}C-H)$ = 161, 156, 9.5 Hz. ^{13}C NMR of $^{13}CH_3{}^{12}CH_2OMe$ (CD_2Cl_2): δ 16.5; $J(^{13}C-H)$ = 129, 3 Hz.

Decomposition of Compound 2 by Phosphine Redistribution Catalysis. A solution of compound **2** (0.025 g) in CD_2Cl_2 was treated with a small amount (less than 0.002 g) of compound **4**. After 2 h the solution contained compound **2** (40% of the original amount), methyl vinyl ether and methyl ethyl ether (each 28%), and compound **3** (4%). In a repeat of this experiment the reaction went to completion within 4 h. A solution of compound **2** alone in CD_2Cl_2 did not measurably react during this time.

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Registry No. **1**, 92670-91-2; **2**, 103225-66-7; **3**, 103225-67-8; **4**, 103225-69-0; **5**, 92670-94-5; **6**, 103225-71-4; **7**, 103225-73-6; **8**, 103225-75-8; **9**, 92670-92-3; $RhMe(PMe_3)_4$, 92670-95-6; $[RhCl(C_8H_{14})_2]_2$, 12279-09-3; $BrCH_2OCH_3$, 13057-17-5; $BrSiMe_3$, 2857-97-8.

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Preparation and Reactions of Cyclopentadienylplatinum Complexes: Coupling with Coordinated Cyclooctadiene

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Cleavage of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$ with TlC_5H_5 produces $[Pt(\eta^5\text{-}C_5H_5)Ph(PPh_3)]$, but in low yield. Reaction of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ with PPh_3 in THF solution gives $[Pt(\eta^1{:}\eta^2\text{-}C_8H_{12}{\cdot}C_5H_5)Ph(PPh_3)]$ (**1**) in which the cyclopentadienyl and cyclooctadiene moieties are coupled. In ether **1** and $[Pt(\eta^5\text{-}C_5H_5)Ph(PPh_3)]$ are both formed. Treatment of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ with dppe or appe in ether solution results in displacement of cyclooctadiene, but the reaction with dppe in THF yields $[Pt(\eta^1\text{-}C_5H_5)Ph(dppe)]$ and a coupling product. The products are characterized by elemental analysis and by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy.

Introduction

We have recently shown that $[Pd(C_6H_4N{=}NPh)(\eta^5\text{-}C_5H_5)]$ undergoes a hydrogen–deuterium exchange reaction at the cyclopentadienyl ring when treated with nucleophiles such as tertiary phosphines in suitable deuterated solvents.[1] A mechanism involving $C_5H_5^-$ dissociation was suggested by us, and support for this proposal arises from the recent isolation and structural characterization[2] of $[Re(CH_3)(NO)(PMe_3)_4]^+C_5H_5^-$. Our preliminary studies indicated that these H–D exchange phenomena are not limited to palladium complexes containing chelating ligands.[1] In order to determine whether $C_5H_5^-$ dissociation from palladium, or platinum, indeed occurs, we sought to prepare complexes of the type $[M(\eta^5\text{-}C_5H_5)RL]$ (M = Pd, Pt; L = tertiary phosphine) and to investigate their reactions with nucleophiles, the platinum complexes being more amenable to study by NMR spectroscopy.

There are a number of compounds of this form which contain chelating ligands,[3-6] but isolable compounds of the type $[M(\eta^5\text{-}C_5H_5)RL]$ are rare,[7-10] and only three such platinum compounds are known.[7] Since $[Pt(\eta^5\text{-}C_5H_5)XL]$ (X = halide) compounds are much more difficult to prepare than their palladium analogues, alternative precursors

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to the desired compounds were studied. These included the halide-bridged dimers $[Pt_2(\mu\text{-}X)_2Ph_2L_2]$[11] and the previously unreported η^1-cyclopentadienyl complex $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$. These investigations are the subject of this paper.

Experimental Section

The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Varian XL-300, Bruker WP-200, or JEOL FX-100 instrument. Proton and carbon chemical shifts are relative to internal $(CH_3)_4Si$, and phosphorus shifts are relative to external 85% H_3PO_4, more positive shifts representing deshielding. Elemental analyses were performed by Galbraith Microanalytical Laboratories, Knoxville, TN.

All reactions were carried out under an argon atmosphere. Phosphorus ligands were obtained from Alfa Products or Aldrich and used without further purification. $[PtClPh(cod)]$[12] and $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$[11] were prepared according to established procedures.

Preparation of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$. Solid TlC_5H_5 (0.589 g, 2.19 mmol) was added to a THF solution of $[PtClPh(cod)]$ (0.905 g, 2.18 mmol), and the mixture was stirred in the dark for 2 h. The yellow solution was filtered and evaporated to dryness. The residue was extracted with ether (20 mL), and the solution was filtered and evaporated to ca. 2 mL. Cooling to −78 °C gave the product as yellow crystals which were filtered and washed with ether (2 mL) at −78 °C: yield 0.757 g (78%); mp 100 °C. Anal. Calcd for $C_{19}H_{22}Pt$: C, 51.23; H, 4.98. Found: C, 51.22; H, 5.12. ^1H NMR ($CDCl_3$): δ 6.05 (J_{PtH} = 44 Hz, C_5H_5), 4.4 (br) and 4.6 (br, CH), 2.3 (br, CH_2), 6.9–7.4 (C_6H_5).

Preparation of $[Pt(\eta^5\text{-}C_5H_5)Ph(PPh_3)]$. Benzene (15 mL) was added to a mixture of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$ (0.583 g, 0.512 mmol) and TlC_5H_5 (0.301 g, 1.12 mmol). After being stirred for 3 h, the yellow solution was filtered and evaporated to dryness. The residue was dissolved in toluene, and the solution was filtered and treated with petroleum ether. Cooling to −20 °C for several days gave the product as yellow crystals (0.135 g, 22%). Anal. Calcd for $C_{29}H_{25}PPt$: C, 58.09; H, 4.20. Found: C, 58.36; H, 4.29. ^1H NMR ($CDCl_3$): δ 5.75 (d, J_{PH} = 1.4 Hz, J_{PtH} = 10.7 Hz, C_5H_5), 6.6 (m, C_6H_5), 7.0–7.5 (PPh_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 12.3 ($^1J_{PtP}$ = 5680 Hz).

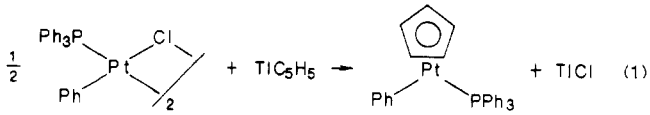
Preparation of $[Pt(\eta^1\text{:}\eta^2\text{-}C_8H_{12}\text{-}C_5H_5)Ph(PPh_3)]$ (1). Triphenylphosphine (0.124 g, 0.473 mmol) was added to a THF solution of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ (0.210 g, 0.472 mmol). After 1 h the solution was evaporated to dryness. The pale yellow residue was extracted with ether (10 mL), and the solution was filtered and reduced in volume until the product precipitated as a white solid (0.222 g, 67%). Anal. Calcd for $C_{37}H_{37}PPt$: C, 62.79; H, 5.27. Found: C, 62.44; H, 5.49. ^1H NMR ($CDCl_3$): δ 4.6 (br, shoulders due to unresolved ^{195}Pt coupling, CH), 5.83, 6.03, 6.09, 6.19, 6.34 (C_5H_5 ring, olefinic CH), 1.5–3.0 (complex, CH_2 and aliphatic CH), 6.7–7.5 (C_6H_5). $^{13}C\{^1H\}$ NMR: δ 95.8 (J_{PtC} = 63.5 Hz, CH), 99.2 (J_{PtC} = 53.6 Hz, CH), 18–46 (complex, aliphatic carbons), 121–137 (olefinic and aromatic carbons). $^{31}P\{^1H\}$ NMR: δ 22.8 ($^1J_{PtP}$ = 1318 Hz).

Preparation of $[Pt(\eta^1\text{-}C_5H_5)Ph(dppe)]$ (2). To an ether solution (50 mL) of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ (0.704, 1.58 mmol) was added dppe (0.629 g, 1.58 mmol), and the mixture was stirred for 6 h. The white product was filtered and washed with ether (10 mL); yield 0.383 g (33%). Anal. Calcd for $C_{37}H_{34}P_2Pt$: C, 60.40; H, 4.66. Found: C, 60.26; H, 4.67. (Removal of the solvent and spectroscopic examination of the residue indicated that it was largely $[Pt(\eta^1\text{-}C_5H_5)Ph(dppe)]$.) ^1H NMR ($CDCl_3$): δ 5.68 (dd, J_{PH} = 3.7 Hz and 1.2 Hz, J_{PtH} = 37.4 Hz, C_5H_5) 1.8–2.1 (m, CH_2), 6.7–7.6 (m, C_6H_5). $^{13}C\{^1H\}$ NMR: δ 114.0 (d, J_{PC} = 11.7 Hz, J_{PtC} = 63.0 Hz, C_5H_5), 127–137 (C_6H_5) (resonances due to CH_2 not detected). $^{31}P\{^1H\}$ NMR: δ 44.9 ($^1J_{PtP}$ = 1814 Hz, P trans to Ph), 40.9 ($^1J_{PtP}$ = 2578 Hz, P trans to C_5H_5).

Preparation of $[Pt(\eta^1\text{-}C_5H_5)Ph(appe)]$ (3). To an ether solution (10 mL) of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ (0.106 g, 0.238 mmol) was added appe (0.105 g, 0.238 mmol). The latter dissolved, and within a few minutes a white precipitate appeared. After 3 h the product was filtered: yield 0.074 g (40%). Anal. Calcd for $C_{37}H_{34}AsPPt$: C, 57.00; H, 4.40. Found: C, 56.50; H, 4.58. (Removal of the solvent and spectroscopic examination of the residue revealed that it was largely $[Pt(\eta^1\text{-}C_5H_5)Ph(appe)]$.) $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 114.0 (d, J_{PC} = 10.3 Hz, J_{PtC} = 58.6 Hz, C_5H_5), 26.8 (m, CH_2), 126–136 (C_6H_5). $^{31}P\{^1H\}$ NMR: δ 40.9 ($^1J_{PtP}$ = 2647 Hz, P trans to C_5H_5).

Results and Discussion

When the chloride-bridged dimer $[Pt_2(\mu\text{-}Cl)_2Ph_2(PPh_3)_2]$ is treated with TlC_5H_5 in benzene solution, the η^5-cyclopentadienyl complex $[Pt(\eta^5\text{-}C_5H_5)Ph(PPh_3)]$ is formed (eq 1). The product is obtained as yellow, air-stable crystals



from toluene–petroleum ether at −20 °C. In the ^1H NMR spectrum of the complex, the cyclopentadienyl resonance at δ 5.75 appears as a doublet due to coupling to ^{31}P, and the small J_{PtH} is typical of a η^5-cyclopentadienyl group.[7,13] The $^{31}P\{^1H\}$ NMR spectrum exhibits a single resonance at δ(P) 12.3 with a very large $^1J_{PtP}$ value of 5680 Hz. The complex is obtained in low yield by this route, however, and monitoring the reaction by $^{31}P\{^1H\}$ NMR spectroscopy reveals that a number of other species are formed. The analogous reaction of $[Pt_2(\mu\text{-}Cl)_2Ph_2(PEt_3)_2]$ results in decomposition.

An alternative potential route to $[Pt(\eta^5\text{-}C_5H_5)RL]$ complexes appeared to be by displacement of 1,5-cyclooctadiene from $[Pt(\eta^1\text{-}C_5H_5)R(cod)]$ by tertiary phosphine, followed by $\eta^1 \rightarrow \eta^5$ rearrangement of the cyclopentadienyl moiety. $[Pt(\eta^1\text{-}C_5H_5)Me(cod)]$ has been shown to react with carbon monoxide to yield $[Pt(\eta^5\text{-}C_5H_5)Me(CO)]$,[13] but reactions with phosphines appeared to be more complicated. We have prepared the previously unreported complex $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ in a manner analogous to that reported by Clark and Shaver for the corresponding methyl compound.[13] The product is obtained in good yield as yellow, air-stable crystals by cooling an ether solution to −78 °C. In its ^1H NMR spectrum the cyclopentadienyl protons exhibit a coupling to platinum of 44 Hz, typical of a η^1-ring.[7,13]

When a THF solution of $[Pt(\eta^1\text{-}C_5H_5)Ph(cod)]$ is treated with 1 molar equiv of PPh_3, a single complex is produced, which is obtained as a white solid from ether solution. Its analysis indicates PPh_3 addition occurs without loss of any of the original ligands. The $^{31}P\{^1H\}$ NMR spectrum of this complex exhibits a single resonance with platinum satellites. The small value of $^1J_{PtP}$ is indicative of PPh_3 lying trans to a substituent of high trans influence,[14] such as an alkyl or aryl group. The ^1H NMR spectrum contains a broad resonance at δ 4.6, with shoulders due to unresolved coupling to platinum, and integration reveals that this signal represents two protons. Thus one of the platinum–olefin interactions remains intact, and the $^{13}C\{^1H\}$ NMR spectrum shows that the two carbon atoms of the coordinated olefin are nonequivalent with separate signals being observed at δ(C) 95.8 and 99.2, each exhibiting coupling to platinum. No η^1-cyclopentadienyl resonance is observed in the ^1H or $^{13}C\{^1H\}$ NMR spectrum, but several olefinic CH resonances are present in the former in the

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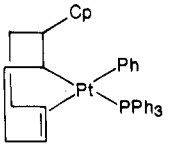
range δ 5.8–6.4. These NMR data appear to be consistent with structure 1. The stereochemistry at the carbon atom



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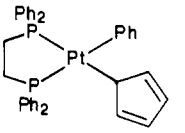
to which the cyclopentadienyl group is attached is uncertain. Due to the complexity of the aliphatic region in the ^1H and $^{13}C\{^1H\}$ spectra, resonances due to the platinum-bound CH group are not assignable. The number of olefinic CH resonances indicates the presence of more than one isomer of the coupled cyclopentadienyl group. Comparison with the ^1H NMR spectra of isomeric methylcyclopentadienes[15] suggests that the 1- and 2-substituted rings are present, though the 5-substituted isomer may also be involved. The complexity of the aromatic region does not permit assignment of carbon resonances to the cyclopentadiene moiety.

Addition of PEt_3 to a THF-d_8 solution of [Pt(η^1-C_5H_5)Ph(cod)] yields an analogous complex. Its $^{31}P\{^1H\}$ NMR spectrum exhibits a single resonance at δ(P) 14.0 ($^1J_{PtP}$ = 1398 Hz), a broad resonance at δ 4.3 with unresolved coupling to platinum is observed in the ^1H NMR spectrum, and two platinum-bound olefinic carbons are seen in the $^{13}C\{^1H\}$ NMR spectrum at δ(C) 94.3 (J_{PtC} = 68 Hz) and 96.9 (J_{PtC} = 50 Hz). In this case the 120–140 ppm region is less complex, and six intense resonances are observed. Three of these will be due to the proton-bearing carbons of the phenyl ring (the platinum-bound carbon is not readily detected); indeed, two of the peaks show coupling to platinum (δ(C) 128.6 (J_{PtC} = 85 Hz); δ(C) 136.0 (J_{PtC} = 35 Hz)), providing further evidence that it is the cyclopentadienyl moiety and not the phenyl group, which is transferred from platinum to the coordinated cyclooctadiene. Three of the remaining four resonances could be due to either a 1- or 2-substituted cyclopentadiene.[16] In this case only one isomer appears to be formed, at least at short reaction times.

When the reaction of [Pt(η^1-C_5H_5)Ph(cod)] with PPh_3 is performed in ether solution, a mixture of [Pt(η^1:η^2-C_8H_{12}·C_5H_5)Ph(PPh_3)] (1) and [Pt(η^5-C_5H_5)Ph(PPh_3)] results. After solvent removal and dissolution in $CDCl_3$, the $^{31}P\{^1H\}$ NMR spectrum indicates that the products are present in a 1:1 ratio. Thus, in ether solution, a reaction involving $\eta^1 \rightarrow \eta^5$ rearrangement of the cyclopentadienyl moiety competes effectively with the coupling reaction described above. Since THF is better able to support ionic intermediates, we suggest that this solvent dependence may be rationalized if the coupling reaction proceeds by displacement of $C_5H_5^-$, followed by attack of this anion on the coordinated olefin. If so, the attack is likely to be from the face opposite the metal, and studies are continuing to determine the stereochemistry of the product.

With the bidentate ligands 1,2-bis(diphenylphosphino)ethane (dppe) and 1-(diphenylarsino)-2-(diphenylphosphino)ethane (appe) novel η^1-cyclopentadienyl complexes are obtained. When an ether solution of [Pt(η^1-C_5H_5)Ph(cod)] is treated with 1 molar equiv of dppe, a white precipitate is formed, which is identified as [Pt(η^1-C_5H_5)Ph(dppe)] (2). Its ^1H NMR spectrum exhibits a cyclopentadienyl resonance at δ 5.68, which appears as



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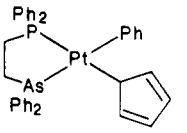

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a doublet of doublets due to coupling to cis and trans P atoms, for which the magnitude of the coupling to ^{195}Pt is indicative of a η^1-cyclopentadienyl ring.[7,13] In the $^{13}C\{^1H\}$ NMR spectrum the cyclopentadienyl resonance appears as a doublet; coupling to the cis P atom is unresolved. The $^{31}P\{^1H\}$ NMR spectrum of the complex shows two resonances with $^1J_{PtP}$ values similar to those reported for [Pt(η^1-C_5H_5)Me(dppe)].[17] (The two-bond phosphorus–phosphorus coupling is too small to be resolved, which is often the case in Pt–dppe complexes.[17-19]) The $^1J_{PtP}$ value for the P atom trans to Ph is 1814 Hz, whereas that for the P atom trans to the cyclopentadienyl group is 2578 Hz. When the corresponding reaction with appe is carried out, a white precipitate is again formed. Spectroscopic examination reveals that the product is [Pt(η^1-C_5H_5)Ph(appe)] (3) in which the P atom is trans to the C_5H_5 ring, as would be expected on the basis of the trans influences of the ligands involved.[14,17] The cyclopentadienyl resonance in the $^{13}C\{^1H\}$ NMR spectrum appears as a doublet due to coupling to the trans P atom, and the $^1J_{PtP}$ value is indicative of a phosphino moiety trans to a η^1-C_5H_5 ring.

When $CDCl_3$ solutions of [Pt(η^1-C_5H_5)Ph(dppe)] or [Pt(η^1-C_5H_5)Ph(appe)] are allowed to stand for several days at ambient temperature, quantitative conversion to [PtClPh(dppe)] or [PtClPh(appe)][18] occurs. The reaction of [Pt(η^1-C_5H_5)Ph(dppe)] with $CDCl_3$ is catalyzed by $PMePh_2$, and with 1 molar equiv of $PMePh_2$ the [PtPh(dppe)($PMePh_2$)]$^+$ cation is produced quantitatively. The latter is presumably present as its chloride salt, and its $^{31}P\{^1H\}$ NMR spectrum is identical with that of [PtPh(dppe)($PMePh_2$)]BPh_4, obtained by treatment of [PtClPh(dppe)] with $PMePh_2$ in the presence of $NaBPh_4$ (δ(P_A) 44.4 ($^1J_{PtP_A}$ = 1719 Hz); δ(P_B) 48.3 ($^1J_{PtP_B}$ = 2660 Hz); δ(P_C) 3.2 ($^1J_{PtP_C}$ = 2715 Hz); $^2J_{P_AP_B}$ not observed, $^2J_{P_AP_C}$ = 19 Hz, $^2J_{P_BP_C}$ = 371 Hz).

If the reaction of [Pt(η^1-C_5H_5)Ph(cod)] with dppe is performed in THF solution, examination of the solution by $^{31}P\{^1H\}$ NMR spectroscopy indicates formation of an approximately 1:1 ratio of [Pt(η^1-C_5H_5)Ph(dppe)] and a second Pt–dppe complex (δ(P_A) 41.3 ($^1J_{PtP_A}$ = 1836 Hz); δ(P_B) 37.5 ($^1J_{PtP_B}$ = 1397 Hz)). We have been unable to separate these complexes satisfactorily, but the magnitudes of the two coupling constants appear to be consistent with a compound of the type [Pt(η^1-C_8H_{12}·C_5H_5)Ph(dppe)] in which the second olefinic group is uncoordinated. Such a formulation is consistent with the earlier observation that coupling of the cyclopentadienyl and cyclooctadiene moieties occurs more readily when THF is used as solvent (vide supra).

In an attempt to prepare an analogous compound containing monodentate phosphines, [Pt(η^1:η^2-C_8H_{12}·C_5H_5)Ph(PPh_3)] was treated with triphenylphosphine. No reaction occurs, however, indicating that PPh_3 is unable to displace the olefinic moeity of the η^1:η^2-C_8H_{12}·C_5H_5 ligand. A similar result is found when PEt_3 is added to a [Pt(η^1:η^2-C_8C_{12}·C_5H_5)Ph(PEt_3)] solution.

We are currently studying the solvent dependence of the reactions of [Pt(η^1-C_5H_5)R(cod)] complexes with phos-

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phorus ligands, as well as investigating the mechanism of these unusual coupling reactions. The results of these studies will be reported in due course.

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Preparation of Vinylstannanes via the Peterson Reaction

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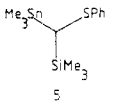
The condensation of anions derived from (phenylthio)(tri-*n*-butylstannyl)(trimethylsilyl)methane (**2a**), *tert*-butyl (tri-*n*-butylstannyl)(trimethylsilyl)acetate (**2b**), and (tri-*n*-butylstannyl)(trimethylsilyl)methane (**2c**) with carbonyl compounds was used to compare the Peterson and tin eliminations. In all cases, the silicon moiety was eliminated to give the vinylstannane **4**.

A recent paper,[1] describing the elimination of silicon from a β-silyl-β-stannylalkoxide (**1**) derived from condensation of an α-silyl-α-stannyl ester enolate with a carbonyl compound, prompts us to report our results in this area.

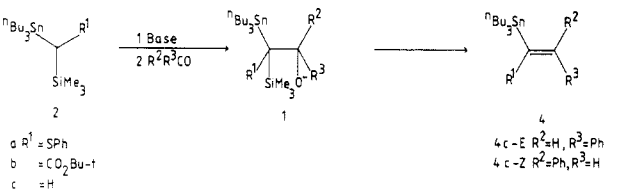
The Peterson reaction[2] has found acceptance as a useful alternative to the Wittig reaction. By contrast, the tin analogue of this elimination has found little use in synthesis although it is known[3] and has been shown to exhibit stereochemical control.[4] Previous studies suggested that the route outlined in Scheme I could provide a general method to vinylstannanes.[1,5]

Our initial studies were carried out with the sulfide **2a** which is readily available from (phenylthio)(trimethylsilyl)methane (**3**).[6] Anion formation with potassium diisopropylamide (KDA), or lithium diisopropylamide (LDA) in the presence of hexamethylphosphoric triamide (HMPA), followed by condensation with a nonenolizable carbonyl compound gave the vinylstannanes (**4a**, R^2 = Ph, R^3 = H, 63%; R^2 = R^3 = Ph, 27%). No stereoselectivity was seen, nor was any vinylsilane detected (NMR, GLC, TLC); the balance of material was **2a** together with a small amount (ca. 10%) of **3**. Enolizable carbonyl compounds were deprotonated by the anion which is also a base. Some aldehydes (e.g., hexanal), however, did give low yields of **4a** (<20%); the amount of destannylation increased in these cases. The trimethylstannyl compound **5** has been shown to react in an analogous manner, although the yields were higher with enolizable aldehydes.[5]



5

Scheme I



The α-silyl-α-stannyl ester **2b** was prepared by a similar method to that already described[7] from *tert*-butyl (trimethylsilyl)acetate.[1] The tin moiety had to be introduced last to circumvent the problem of O-silylation. The α-stannyl esters were relatively difficult to purify; significant destannylation occurred under mild conditions, such as chromatography on silica. Again, the anion was prepared by treatment with KDA or LDA–HMPA and gave good yields with nonenolizable carbonyl compounds (**4a**, R^2 = Ph, R^3 = H, 72%; R^2 = R^3 = Ph, 46%) but tended to act as a base with enolizable aldehydes and ketones.

Finally, the unsubstituted derivative (tri-*n*-butylstannyl)(trimethylsilyl)methane (**2c**) was prepared by condensation of ((trimethylsilyl)methyl)magnesium chloride with tri-*n*-butyltin chloride in 95% yield; this procedure has the advantage of cheaper reagents than the previously reported route.[8] Deprotonation of **2c** proved troublesome; not a surprising observation as bis(trimethylsilyl)methane is also difficult to deprotonate,[5] and use of alkyllithiums result in transmetalation of a stannyl group.[9] No reaction occurred between **1c** and LDA, but deprotonation was achieved with KDA—albeit in 45% yield as detected by deuteration; some destannylation (ca. 20%) also occurred. Condensation of this anion derived from **1c** with benzaldehyde led to the vinylstannane (**4c**, R^2, R^3 = H, Ph; 35%; an *E*:*Z* ratio of 1:1 by NMR). No vinylsilane was detected. Reactions with enolizable carbonyl compounds resulted in deprotonation of the latter.

Small amounts of destannylated alkenes were detected from the reactions of **2a** and **2c**. This observation suggests

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