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Oxidative Addition as a Route to Organometallic Polymers

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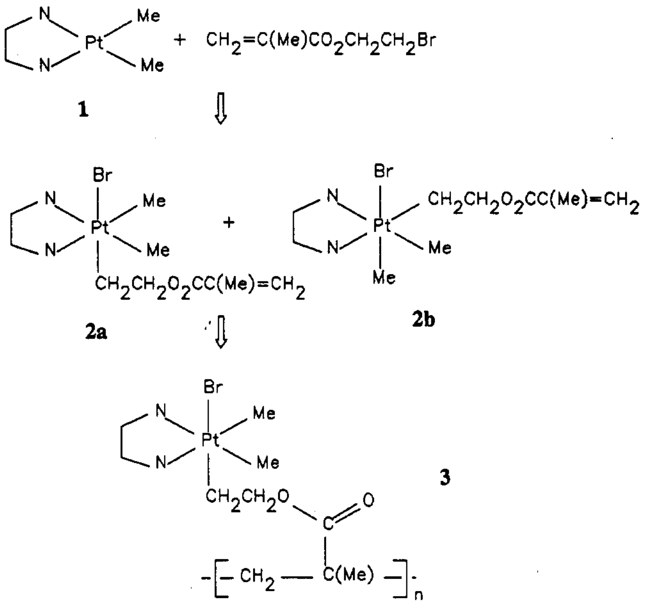
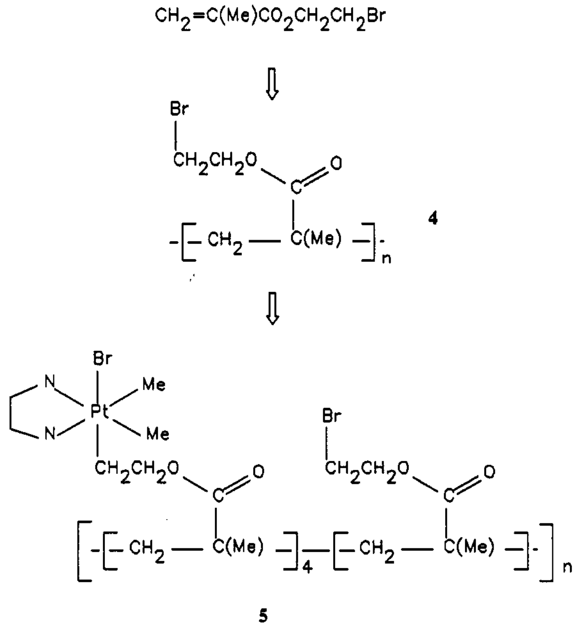
Summary: The ease of oxidative addition of alkyl halides to [$PtMe_2$(2,2′-bipyridine)] and related compounds has been exploited to give a new route to organometallic polymers. A C–X bond (X = Cl, Br) is incorporated into a vinyl monomer, and the organometallic polymer may then be prepared by oxidative addition of the monomer to platinum(II) followed by free-radical polymerization or, with a lower platinum incorporation, by polymerization of the monomer followed by oxidative addition to platinum(II). The platinum-containing polymers from [$PtMe_2$(bpy)] are insoluble, but those from [$PtMe_2$(4,4′-di-*tert*-butyl-2,2′-bipyridine)] are soluble in organic solvents.

Scheme I



Scheme II



In most polymers containing transition elements, the metal is bound to the polymer by coordination to amine, phosphine, η-cyclopentadienyl, η-arene, or related donors.[2] This communication reports new polymers and monomers in which the metal is bonded to the polymer or polymerizable monomer through a metal–carbon σ-bond formed by oxidative addition. An example of the synthetic method is shown in Scheme I, which takes advantage of the high reactivity of [$PtMe_2$(bpy)] toward oxidative addition of alkyl halides.[3]

Oxidative addition of the C–Br bond of 2-bromoethyl methacrylate to [$PtMe_2$(bpy)] (1)[3] gave complex **2a**, by trans addition, along with some **2b** formed by cis addition.[4] Subsequent free-radical polymerization, using an AIBN initiator in chlorobenzene solution, gave the insoluble polymer **3**.[5] An attempt to prepare the polymer **3** was also made by polymerization of the organic monomer followed by oxidative addition of poly(2-bromoethyl methacrylate) (**4**; M_n = 57000, M_w = 213000, dispersity 3.73) using excess [$PtMe_2$(bpy)], but in this case only ca. 80% of the bromoethyl groups were metalated in the final polymer **5** (Scheme II; note that structure **5** is idealized and a more random arrangement of metalated units is likely). Hence, the fully metalated polymer can only be obtained from the metalated monomer **2**. The platinum-containing polymers have low solubility in all common organic solvents, and it is possible that precipitation of the partially metalated polymer prevents complete platination.

As expected, metalation of the polymer has a great effect on its physical properties. The monomer **2** melts with decomposition at 166 °C, and the polymer **4** has a glass transition in the range 65–79 °C, as determined by dif-

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[4] Typical characterization for complex **2**: Anal. Calcd for $C_{18}H_{23}BrN_2O_2Pt$: C, 37.6; H, 4.0; N, 4.9. Found: C, 37.7; H, 3.8; N, 4.9. MS: *m/e* 494. IR: ν(CO) = 1711, ν(C=C) = 1634 cm^{-1}. ^1H NMR: **2a**, δ 1.36 [s, 6 H, ^2J(PtH) = 70 Hz, MePt], 1.68 [s, 3 H, =CMe], 3.44 [t, 2 H, OCH_2], 5.41, 5.64 [m, each 1 H, =CH_2]; **2b**, δ 0.50 [s, 3 H, ^2J(PtH) = 72 Hz PtMe], 1.39 [s, 3 H, ^2J(PtH) = 70, PtMe], 1.95 [s, 3 H, =CMe] 1.84 and 2.23 [m, each 1 H, $PtCH_2$], 4.35 and 4.73 [m, each 1 H, OCH_2], 5.59 and 6.09 [m, each 1 H, =CH_2].

[5] Polymer **3**: Anal. Calcd for $C_{18}H_{23}BrN_2O_2Pt$: C, 37.6; H, 4.0; N, 4.9. Found: C, 37.1; H, 3.9; N, 4.6. **5**: Anal. Found: C, 37.1; H, 4.1; N, 4.3. The corresponding polymer with 4,4′-*t*-Bu_2bpy was soluble and gave δ(^1H) 8.8 [1 H, bpy H^3], 8.7 [1 H, bpy H^5], 7.9 [1 H, bpy H^6], 1.5 [9 H, *t*-Bu], 4.6 [CH_2O], 0.8–1.2 [broad, MeC and MePt]. In addition, a resonance at δ 0.54 [*J*(PtH) = 74 Hz, MePt] indicates units arising from cis oxidative addition. Polymers have been prepared with several different platinum contents; details will be given in the full paper.

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Table I

organic monomer	platinum monomer	trans/cis
$BrCH_2CH_2O_2CC(Me){=}CH_2$	$[PtBrMe_2\{CH_2CH_2O_2CC(Me){=}CH_2\}(bpy)]$	60/40[a]
$BrCH_2C(CO_2Me){=}CH_2$	$[PtBrMe_2\{CH_2C(CO_2Me){=}CH_2\}(bpy)]$	95/5
$3\text{-}(ClCH_2)C_6H_4CH{=}CH_2$[b]	$[PtClMe_2(3\text{-}CH_2C_6H_4CH{=}CH_2)(bpy)]$	99/1
$ClCOCH{=}CH_2$	$[PtClMe_2(COCH{=}CH_2)(bpy)]$	75/25

[a] Isomers correspond to the geometry at platinum (see text) and can be separated by recrystallization. The isomer ratio was determined by ^1H NMR spectroscopy. [b] Monomer contains 30% 4-$(ClCH_2)C_6H_4CH{=}CH_2$.

ferential scanning calorimetry. However, the polymers 3 and 5 exhibit a broad endothermic transition over the range 60–160 °C, with the peak at 115 °C, and the melting endotherm begins at 210 °C and peaks at 245 °C. When samples of polymers 3 and 5 were heated to 150 °C for 30 min and then cooled and reheated, the broad endotherm in the region 60–160 °C was not observed. Thus, it appears that polymers 3 and 5 precipitate in a strained conformation which relaxes on heating. Polymer 4 undergoes complete weight loss over the temperature range 335–395 °C, but 3 decomposes to leave a residue of platinum over the much wider temperature range 270–450 °C.

The synthetic method outlined above is generally applicable, so long as the organic monomer contains both a functional group which can take part in polymerization and a carbon–bromine or carbon–chlorine bond which can undergo oxidative addition. Some vinyl monomers and their products of oxidative addition with $[PtMe_2(2,2'\text{-bipyridine})]$ are given in Table I. In all cases, the oxidative addition occurred with mostly trans stereochemistry and, in addition, platinum-containing polymers could be synthesized by oxidative addition to the polymerized organic monomers. It is not necessary for the organic polymer to be soluble in organic solvents in order for oxidative addition to occur. Thus, Merrifield's resin, which is a cross-linked styrene(chloromethyl)styrene copolymer (1% cross-linked with divinylbenzene, with 1 mequiv of Cl/g of polymer) reacted, as a suspension in acetone, with excess $[PtMe_2(bpy)]$ to give the platinum-containing polymer in which essentially all of the chloromethyl groups were reacted.[6] All of the platinum-containing polymers described above are very sparingly soluble in organic solvents, even when the extent of platinum incorporation is <10% of the available functional groups. However, the corresponding polymers with 4,4′-di-*tert*-butyl-2,2′-bipyridine have sufficient solubility for solution characterization,[5] and efforts are being made to prepare derivatives with more highly alkylated bipyridine derivatives in order to prepare still more soluble polymers.

A major advantage of the oxidative-addition route to metal-containing monomers is the ease of reaction and the wide range of functional groups which can be incorporated. This work has focused on vinyl monomers, but platinum-containing monomers with ester, nitrile, amide, and carboxylic acid functionalities, suitable for studies of condensation polymerization, have also been synthesized by this method.

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[6] Anal. Calcd for $C_9H_8\cdot 0.15C_{21}H_{23}ClN_2Pt$: C, 74.4; H, 5.9; N, 2.1. Found: C, 72.9; H, 6.6; N, 2.1.

Novel Route to C=Si Double Bonds via a Peterson-Type Reaction[1]

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Summary: Reaction of $(Me_3Si)_3SiLi\cdot 3THF$ (1) with adamantanone in hexane or benzene leads via a Peterson-type elimination reaction to the silene bis(trimethylsilyl)adamantylidenesilane (3), which spontaneously dimerizes in a head-to-head fashion (80–90% yield) to 1,1,2,2-tetrakis(trimethylsilyl)dispiro[3,3′,4,4′-biadamantane-1,2-disilacyclobutane] (2). When it is warmed, 2 reverts to 3, which was trapped by 1-methoxybutadiene or methanol. The X-ray structure of 2 is reported. The four-membered ring is strongly puckered and has unusually long C–C and C–Si bond lengths of 1.647 and 2.008 Å, respectively. Reaction of 1 with 4-*tert*-butylcyclohexanone also proceeds via the corresponding silene, which dimerizes to 1,1,2,2-tetrakis(trimethylsilyl)-1-(4-*tert*-butylcyclohexyl)-2-(4-*tert*-butylcyclohexenyl)disilane.

Silicon chemistry is one of the fastest growing fields of organic chemistry.[2] Of special interest are compounds with multiple bonds to silicon,[3] of which we focus here on silenes, i.e. $R_2C{=}SiR_2$. Compelling evidence that a silene might exist as a transient intermediate was first presented only in 1967.[4] The first "indefinitely" stable silene was isolated by Brook et al. in 1981,[5a] and this was followed by two X-ray structure determinations[5b,c] and intensive research on silenes which led to many important developments.[3] Yet, the arsenal of methods available for synthesizing silenes is limited.[3] We now report that the reaction of $(Me_3Si)_3SiLi\cdot 3THF$ (1)[6] with certain ketones

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[1] Reported in part at the European Symposium of Organic Reactivity (ESOR III), Gotheburg, Sweden, July 7–12, 1991, proceedings p 124.

[2] For a comprehensive review, see: *The Chemistry of Organosilicon Compounds*; Patai, S., Rappoport, Z. Eds.; Wiley: Chichester, U.K., 1989.

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