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Journal of Organometallic Chemistry 655 (2002) 192–203

Journal of Organometallic Chemistry

www.elsevier.com/locate/jorganchem

Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]^+$ with oxygen nucleophiles and chemistry of resultant $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]^+$ complexes

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Received 8 February 2002; received in revised form 19 April 2002; accepted 19 April 2002

Abstract

The η^3-allenyl/propargyl complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (**1**OTf) undergoes addition reactions with a number of oxygen nucleophiles in CH_2Cl_2 solution at ambient temperature. With H_2O, it yields the binuclear oxygen-bridged η^3-allyl $[\{(PPh_3)_2Pt(\eta^3\text{-}CH_2CCHPh)\}_2O](OTf)_2$ (**2**$(OTf)_2$). With primary and secondary alcohols, it rapidly affords the η^3-(2-alkoxyallyl) complexes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]OTf$ (R = Et (**3**OTf), *i*-Pr (**4**OTf), CH_2CMe_3 (**5**OTf), $CH_2CH{=}CH_2$ (**7**OTf)), whereas with tertiary alcohols, in slower reactions, it gives both **2**$(OTf)_2$ and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]OTf$ (R = CMe_3, $C(Me)_2Et$ (**6**OTf)). There is no reaction at ambient temperature between **1**OTf and phenols; however, **1**OTf and PhOH afford $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OPh)CHPh)]OTf$ (**8**OTf) in the presence of NEt_3. Competition studies reveal the following reactivity order, attributed to steric effects: $Me_3CCH_2OH(1.0) < i\text{-}PrOH(1.2) < EtOH(2.1) < MeOH(4.3)$. The η^3-(2-alkoxyallyl) complexes react with NaOMe to yield the η^3-oxatrimethylemethane product $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(O)CHPh)$ (**10**), which was also obtained by reaction of **2**$(OTf)_2$ with two equivalents of NaOMe and of **1**OTf with NaOH. Complex **10** undergoes conversion to the appropriate $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]^+$ with $[Et_3O]PF_6$, $(MeO)_2SO_2$ and MeI. The η^3-(2-allyloxyallyl) **7**OTf reacts with $(PPh_3)_2Pt(C_2H_4)$ to give **10** and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]OTf$; thermolysis of **7**OTf in toluene at reflux furnishes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]OTf$, whereas heating in benzene–chloroform affords $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH{=}CHMe)CHPh)]OTf$ (**11**OTf), which results from isomerization of $OCH_2CH{=}CH_2$ to $OCH{=}CHMe$. Reaction pathways have been suggested for a number of the aforementioned transformations. All new complexes were characterized by a combination of elemental analysis, FAB mass spectrometry and ^1H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy. They were assigned structures in which the η^3-allyl oxygen and Ph groups are *syn* from the ^1H-NMR spectra.

Keywords: Platinum complexes; η^3-Allenyl–propargyl; η^3-(2-Alkoxyallyl); η^3-Oxatrimethylenemethane; Nucleophilic addition; Rearrangement

1. Introduction

η^3-Allenyl/propargyl complexes represent a growing class of organotransition-metal compounds [1–5]. Recent advances in this field include the rapidly developing chemistry of the η^3 coordinated allenyl/propargyl ligand (η^3-CH_2CCR) that features addition of a variety of nucleophilic reagents [1,2,5,6]. A number of oxygen [2,5,7], nitrogen [2,5,7d,7e,8], carbon [2,5,9], sulfur [7c], selenium [7c] and phosphorus [2,5,7a,8b] nucleophiles (NuH or Nu) have been shown to add to the central carbon atom of the η^3-CH_2CCR ligand in cationic metal complexes to afford isolable η^3-allyl (Eq. 1) or metallacyclobutene (Eq. 2) products. Reactive oxygen nucleophiles include water [5,7a,7b,7e], alcohols [5,7b,7c,7d], phenols [7c] and carboxylic acids [2], with $[Cp^*Re(CO)_2(\eta^3\text{-}CH_2CCH)]^+$ [5], $[(\eta^6\text{-}C_6H_nMe_{6-n})Mo(CO)_2(\eta^3\text{-}CH_2CCH)]^+$ [7a], $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCR)]^+$ [5,7b,7c,7d,7e] and $[(PPh_3)_2Pd(\eta^3\text{-}CH_2CCR)]^+$ [7d] representing the investigated substrate complexes.

Our group has reported that $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCR)]^+$ (R = Ph (**1**), Me) react with MeOH to afford the appropriate η^3-(2-methoxyallyl) complexes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OMe)CHR)]^+$ [7d]. We now present our results of a study on reactions of **1** with other

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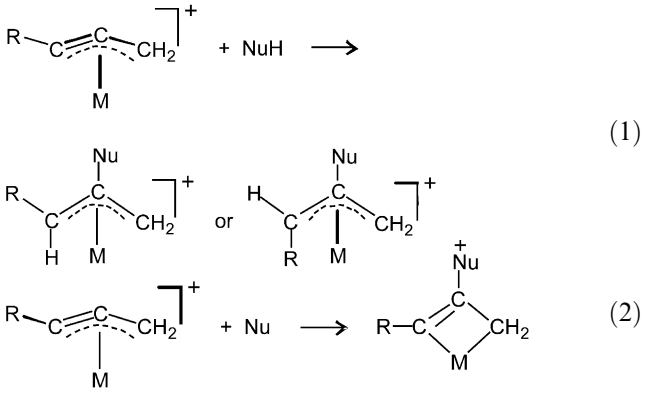
0022-328X/02/$ - see front matter
PII: S0022-328X(02)01556-5



(1)

(2)

alcohols and with phenols and water; these results differ somewhat from and expand on those of Chen and coworkers [7c] for the related $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH)]^+$ containing unsubstituted η^3-CH_2CCH in place of η^3-CH_2CCPh. Also presented here is reaction chemistry of the $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]^+$ products which features formation of the platinum η^3-oxatrimethylenemethane complex $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(O)CHPh)$ as well as rearrangements of some $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]^+$. Aspects of this investigation were communicated earlier [7e,10].

2. Experimental

2.1. General procedures and measurements

Reactions and manipulations of organoplatinum compounds were carried out under an atmosphere of dry Ar by use of standard procedures [11]. Solvents were dried [12], distilled under Ar and degassed before use. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. of Canada. M.p.s were measured on a Thomas–Hoover m.p. apparatus and are uncorrected. IR, NMR (^{1}H, ^{2}H, ^{13}C and ^{31}P) and FAB mass spectra were obtained as previously described [13,14].

2.2. Materials

Reagents were procured from various commercial sources and used as received, except as noted below. Methyl alcohol was distilled, first from CaH_2 after heating for 24 h at reflux, and then from sodium. Ethyl alcohol from a newly opened bottle of absolute grade was distilled from $Mg(OEt)_2$. Both *t*-butyl alcohol and *t*-amyl alcohol (1,1-dimethylpropanol) were distilled from CaH_2 after heating for 48 h at reflux. Phenol and neopentyl alcohol were purified by sublimation at ambient temperature (33 and 760 torr, respectively). The complexes $(PPh_3)_2Pt(C_2H_4)$ [15] and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (**1**OTf) [7d] were synthesized as reported in the literature.

2.3. .Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (*1OTf*) with oxygen nucleophiles

2.3.1. Reaction of *1OTf* with water

To a stirred solution of **1**OTf (0.179 g, 0.182 mmol) in 10 ml of CH_2Cl_2 at room temperature (r.t.) was added a large excess (0.1 ml, ca. 6 mmol) of H_2O. The mixture was stirred for 4 days, the volatiles were removed under reduced pressure and the light beige residue was recrystallized from 100 ml of 2:3 (by volume) C_6H_6–C_5H_{12}. The yield of $[\{(PPh_3)_2Pt(\eta^3\text{-}CH_2CCHPh)\}_2\text{-}O](OTf)_2$ (**2**$(OTf)_2$), a white solid, was 0.145 g (80%). IR (Nujol): no ν(OH) at 3650–3250 cm^{-1}. ^{1}H-NMR (CD_2Cl_2): δ 7.5–6.4 (m, 70H, Ph), 4.0 (d, $J_{PH} = 11$ Hz, $J_{PtH} = 47$ Hz, 2H, C*H*Ph), 3.3 (m, 2 H, *syn*-C*H*H), 2.4 (m, $J_{PtH} = 55$ Hz, 2H, *anti*-CH*H*). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ 19.6 (d, $J_{PP} = 10$ Hz, $J_{PtP} = 3652$ Hz), 15.7 (d, $J_{PP} = 10$ Hz, $J_{PtP} = 3861$ Hz). Anal. Found: C, 55.42; H, 4.10. Calc. for $C_{92}H_{76}F_6O_7P_4Pt_2S_2$: C, 55.62; H, 3.97%.

2.3.2. Reaction of *1OTf* with ethyl alcohol

Ethyl alcohol (1.5 ml, 26 mmol) was added to a stirred solution of **1**OTf (0.150 g, 0.152 mmol) in 3 ml of CH_2Cl_2 at r.t. After 5 min, all volatiles were removed under vacuum, and the residue was dissolved in 3 ml of CH_2Cl_2. Hexane (30 ml) was added to induce the precipitation of a beige product. The volume of the mixture was reduced to 15 ml, and the light beige solid was collected on a filter frit and washed with 5 ml of hexanes. The product $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OEt)CHPh)]OTf$ (**3**OTf) was dried under vacuum at 60 °C for 2 days. Yield: 0.137 g (88%). ^{1}H-NMR ($CDCl_3$): δ 7.50–6.65 (m, 35H, Ph), 3.93 (d, $J_{PH} = 10.0$ Hz, $J_{PtH} = 42.6$ Hz, 1H, C*H*Ph), 3.72 (dq, $^2J_{HH} = 9.6$ Hz, $^3J_{HH} = 7.0$ Hz, 1H, OC*H*HMe), 3.54 (dq, $^2J_{HH} = 9.6$ Hz, $^3J_{HH} = 7.0$ Hz, OCH*H*Me), 2.77 (ddd, $^2J_{HH} = 6.4$ Hz, $J_{PH} = 4.5$ Hz, $J_{PH} = 2.8$ Hz, 1H, *syn*-C*H*H of η^3-allyl), 2.50 (dd, $^2J_{HH} = 6.4$ Hz, $J_{PH} = 9.5$ Hz, $J_{PtH} = 40.5$ Hz, 1H, *anti*-CH*H* of η^3-allyl), 1.29 (t, $^3J_{HH} = 7.0$ Hz, 3H, Me). ^{13}C{^{1}H}/^{13}C-NMR ($CDCl_3$): δ 150.6 (s, *C*OEt), 136.3–121.5 (m, Ph), 71.5 (dd, $^1J_{CH} = 149$ Hz, $J_{PC} = 37$ Hz, $J_{PtC} = 72$ Hz, *C*HPh), 65.8 (t, $^1J_{CH} = 147$ Hz, *C*H_2Me), 51.4 (td, $^1J_{CH} = 158$ Hz, $J_{PC} = 35$ Hz, $J_{PtC} = 132$ Hz, *C*H_2CO), 14.5 (q, $^1J_{CH} = 128$ Hz, Me). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 18.5 (d, $J_{PP} = 10.5$ Hz, $J_{PtP} = 3758$ Hz), 14.1 (d, $J_{PP} = 10.5$ Hz, $J_{PtP} = 3769$ Hz). FAB MS: ^{195}Pt, *m*/*z* 880 (M^+), 719 ($Pt(PPh_3)_2^+$).

The foregoing reaction was also conducted on a smaller scale by using **1**OTf and EtOD. The ^{1}H-NMR spectrum (in $CDCl_3$) of the product $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OEt)CDPh)]OTf$ (**3**-d_1OTf) was identical with that of **3**OTf except for the absence of the signal of

C*H*Ph. ^{2}H-NMR (CH_2Cl_2): δ 7.0 (br s, Ph-d_1, nat. abund.), 5.0 (br s, $CHDCl_2$, nat. abund.), 3.9 (br d, C*D*Ph).

2.3.3. Reaction of 1OTf with isopropyl alcohol

Isopropyl alcohol (0.45 ml, 5.9 mmol) was added via gas-tight syringe to a stirred solution of **1**OTf (0.199 g, 0.202 mmol) in 3 ml of CH_2Cl_2. The resulting solution was stirred for 20 min at r.t., and the solvent and excess alcohol were removed under reduced pressure to leave a pale green solid. The residue was dissolved in 2 ml of CH_2Cl_2, and addition of 25 ml of hexanes resulted in the precipitation of a pale yellow product. The solid was collected on a filter frit, washed with hexanes (3 × 5 ml) and dried under vacuum at 50 °C for 3 days. Yield of [$(PPh_3)_2Pt(\eta^3$-CH_2C(O-*i*-Pr)CHPh)]OTf (**4**OTf), 0.188 g (89%). ^{1}H-NMR ($CDCl_3$): δ 7.5–6.5 (m, 35H, Ph), 4.48 (d, $J_{PH} = 10.3$ Hz, $J_{PtH} = 41.6$ Hz, C*H*Ph), 4.12 (m, 1H, C*H*Me$_2$), 3.22 (dd, $^2J_{HH} = 6.6$ Hz, $J_{PH} = 10.0$ Hz, $J_{PtH} = 35.3$ Hz, 1H, *anti*-C*H*H), 2.73 (br s, 1H, *syn*-CH*H*), 1.38 (d, $^3J_{HH} = 6.1$ Hz, 3H, Me), 1.23 (d, $^3J_{HH} = 6.1$ Hz, 3H, Me). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 150 (s, $J_{PtC} = 9.4$ Hz, *C*O-*i*-Pr), 135–120 (m, Ph), 73.3 (s, *C*HMe$_2$), 72.3 (d, $J_{PC} = 35.6$ Hz, $J_{PtC} = 70.8$ Hz, *C*HPh), 51.6 (d, $J_{PC} = 35.8$ Hz, $J_{PtC} = 139$ Hz, CH_2), 21.9 (s, Me), 20.9 (s, Me). ^{31}P{^{1}H}-NMR (CH_2Cl_2): δ 18.8 (d, $J_{PP} = 10.4$ Hz, $J_{PtP} = 3750$ Hz), 14.3 (d, $J_{PP} = 10.4$ Hz, $J_{PtP} = 3832$ Hz). FAB MS: ^{195}Pt, *m*/*z* 894 (M^+), 719 ($Pt(PPh_3)_2^+$). Anal. Found: C, 55.61; H, 4.45. Calc. for $C_{49}H_{45}F_3O_4P_2PtS$: C, 56.37; H, 4.34%.

2.3.4. Reaction of 1OTf with neopentyl alcohol

Freshly sublimed Me_3CCH_2OH (0.11 g, 1.3 mmol) dissolved in 0.5 ml of CH_2Cl_2 was added via gas-tight syringe to a stirred solution of **1**OTf (0.0514 g, 0.052 mmol) in 1.5 ml of CH_2Cl_2, and the resulting reaction mixture was stirred for 30 min at r.t. The rest of the procedure followed that in Section 2.3.3 to afford 0.0515 g (92%) of [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OCH_2CMe_3)$CHPh)]OTf (**5**OTf) as a pale green solid. ^{1}H-NMR ($CDCl_3$): δ 7.5–6.5 (m, 35H, Ph), 4.5 (d, $J_{PH} = 10.5$ Hz, $J_{PtH} = 38.5$ Hz, 1 H, C*H*Ph), 3.4 (d, $^2J_{HH} = 8.7$ Hz, 1H, C*H*HCMe$_3$), 3.35 (dd, $^2J_{HH} = 6.6$ Hz, $J_{PH} = 9.4$ Hz, $J_{PtH} = 36.2$ Hz, 1H, *anti*-C*H*H), 3.1 (d, $^2J_{HH} = 8.7$ Hz, 1H, CH*H*CMe$_3$), 2.9 (br s, 1H, *syn*-CH*H*), 1.0 (s, 9H, Me). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ 150 (s, $J_{PtC} = 8.8$ Hz, *C*OCH$_2$), 135–120 (m, Ph), 79.2 (s, OCH_2), 72.7 (d, $J_{PC} = 31.6$ Hz, $J_{PtC} = 74.4$ Hz, *C*HPh), 52.5 (d, $J_{PC} = 35$ Hz, $J_{PtC} = 125$ Hz, *C*H$_2$CO), 31.5 (s, *C*Me$_3$), 26.3 (s, Me). ^{31}P{^{1}H}-NMR ($CDCl_3$): δ 18.0 (d, $J_{PP} = 10.6$ Hz, $J_{PtP} = 3784$ Hz), 13.3 (d, $J_{PP} = 10.6$ Hz, $J_{PtP} = 3797$ Hz). FAB MS: ^{195}Pt, *m*/*z* 922 (M^+), 719 ($Pt(PPh_3)_2^+$).

2.3.5. Reaction of 1OTF with t-amyl alcohol

A solution of **1**OTf (0.0623 g, 0.063 mmol) in 40 ml of CH_2Cl_2 was added dropwise over 1 h to freshly distilled Et(Me)$_2$COH (2.8 ml, 26 mmol), and the reaction contents were stirred for an additional hour at r.t. before evaporation to dryness under reduced pressure. The yellow residue was treated with 0.2 ml of CH_2Cl_2, and the mixture was filtered. The collected white solid was identified as [{$(PPh_3)_2Pt(\eta^3$-$CH_2CCHPh)$}$_2$-O](OTf)$_2$ (**2**(OTf)$_2$) by ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The filtrate was evaporated to a yellow residue, which was washed with hexanes (3 × 10 ml) and then dissolved in 0.1 ml of C_6H_6 and precipitated from solution by addition of 20 ml of Et_2O. The yellow solid was washed with Et_2O (2 × 5 ml) and dried under vacuum at r.t. for 2 h. Yield of [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OC(Me)_2Et)$CHPh)]OTf (**6**OTf), 0.0127 g (19%). ^{1}H-NMR ($CDCl_3$): δ 7.5–6.2 (m, 35H, Ph), 4.47 (d, $J_{PH} = 9.9$ Hz, $J_{PtH} = 37.5$ Hz, 1H, C*H*Ph), 3.25 (d, $J_{PH} = 9.7$ Hz, $J_{PtH} = 35.8$ Hz, 1H, *anti*-C*H*H), 2.92 (br s, 1H, *syn*-CH*H*), 1.64 (br q, 2H, OC(Me)$_2$C*H*$_2$), 1.32, 1.30 (2s, 3H, 3H, OC(*Me*)$_2$), 0.93 (t, $^3J_{HH} = 13.4$ Hz, 3H, OC(Me)$_2$CH$_2$*Me*). ^{31}P{^{1}H}-NMR (CH_2Cl_2): δ 19.0 (d, $J_{PP} = 8.8$ Hz, $J_{PtP} = 3737$ Hz), 14.9 (d, $J_{PP} = 8.8$ Hz, $J_{PtP} = 3886$ Hz).

2.3.6. Reaction of 1OTf with allyl alcohol

Allyl alcohol (0.45 ml, 2.9 mmol), dried over $MgSO_4$, was added dropwise with stirring via gas-tight syringe over 5 min to a solution of **1**OTf (0.0738 g, 0.075 mmol) in 8 ml of CH_2Cl_2 at −15 °C. The reaction mixture was stirred for 30 min at −15–−10 °C. All volatiles were removed under reduced pressure as the reaction mixture was allowed to warm to ambient temperature. The resulting green residue was dissolved in 0.3 ml of CH_2Cl_2 and precipitated from solution by addition of 30 ml of Et_2O. The pale green residue was collected on a filter frit, washed with Et_2O (2 × 5 ml), and dried under vacuum at r.t. for 5 h. Yield of [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OCH_2CH{=}CH_2)$CHPh)]OTf (**7**OTf), 0.075 g (95%). ^{1}H-NMR ($CDCl_3$): δ 8.0–6.5 (m, 35H, Ph), 5.9 (m, 1H, C*H*=CH$_2$), 5.2 (m, 2H, CH=C*H*$_2$), 4.48 (d, $J_{PH} = 10.0$ Hz, $J_{PtH} = 39.3$ Hz, 1H, C*H*Ph), 4.2 (dq, $^3J_{HH} = 5.0$ Hz, 2H, OCH_2), 3.16 (dd, $^2J_{HH}$ ca. 6 Hz, $J_{PH} = 9.9$ Hz, $J_{PtH} = 23.5$ Hz, 1H, *anti*-C*H*H of η^3-allyl), 2.70 (br s, 1H, *syn*-CH*H* of η^3-allyl). ^{13}C{^{1}H}-NMR: δ 150 (s, $J_{PtC} = 9.4$ Hz, *C*OCH$_2$), 135–120 (m, Ph), 119 (s, CH=*C*H$_2$), 72.5 (d, $J_{PC} = 35.2$ Hz, $J_{PtC} = 69.8$ Hz, *C*HPh), 69.7 (s, OCH_2), 52.0 (d, $J_{PC} = 45.3$ Hz, $J_{PtC} = 118.2$ Hz, *C*H$_2$CO) (Signal of CH$_2$=*C*H may be masked by Ph resonances). ^{31}P{^{1}H}-NMR (CH_2Cl_2): δ 18.4 (d, $J_{PP} = 10.4$ Hz, $J_{PtP} = 3797$ Hz), 13.9 (d, $J_{PP} = 10.4$ Hz, $J_{PtP} = 3833$ Hz). FAB MS: ^{195}Pt, *m*/*z* 892 (M^+), 719 ($Pt(PPh_3)_2^+$).

2.3.7. Reaction of 1OTf with phenol

Freshly sublimed PhOH (0.0098 g, 0.10 mmol) dissolved in 1 ml of CH_2Cl_2 was added dropwise with stirring to a solution of **1**OTf (0.101 g, 0.103 mmol) in 3

ml of CH_2Cl_2. The reaction solution was then treated with a large excess of Et_3N (4 drops), resulting in an immediate change of color from yellow to red. After the mixture had been stirred for 30 min at r.t., all volatiles were removed under reduced pressure. The pale yellow residue (0.107 g) was dissolved in CH_2Cl_2 (0.4 ml), and Et_2O (50 ml) was added to precipitate a gummy orange solid. The solvent was removed by syringe, and the residue was washed consecutively with Et_2O (2 × 50 ml), C_6H_5Me (2 × 30 ml) and THF (2 × 5 ml) to furnish a pale yellow solid which was dried under vacuum at r.t. for 4 days. Yield of [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OPh)CHPh)$]OTf (**8**OTf), 0.0729 g (66%). ^{1}H-NMR (CD_2Cl_2): δ 7.5–6.5 (m, 40H, Ph), 4.85 (d, $J_{PH} = 9.8$ Hz, $J_{PtH} = 35.4$ Hz, 1H, C*H*Ph), 3.3 (dd, $^2J_{HH}$ ca. 6 Hz, $J_{PH} = 9.5$ Hz, $J_{PtH} = 32.9$ Hz, 1H, *anti*-C*H*H), 2.35 (br s, 1H, *syn*-CH*H*). $^{13}C\{^1H\}$-NMR (CD_3OD): δ 147 (s, $J_{PtH} = 8.9$ Hz, *C*OPh), 135–120 (m, Ph), 74.6 (d, $J_{PC} = 33.1$ Hz, $J_{PtC} = 48.2$ Hz, *C*HPh), 54.6 (d, $J_{PC} = 33.8$ Hz, $J_{PtC} = 127.3$ Hz, CH_2CO). $^{31}P\{^1H\}$-NMR (CH_2Cl_2): δ 18.9 (d, $J_{PP} = 10.2$ Hz, $J_{PtP} = 3764$ Hz), 14.2 (d, $J_{PP} = 10.2$ Hz, $J_{PtP} = 3983$ Hz). FAB MS: ^{195}Pt, *m/z* 928 (M^+), 719 ($Pt(PPh_3)_2^+$).

2.4. Competition reactions of [$(PPh_3)_2Pt(\eta^3$-$CH_2CCPh)$]OTf (1OTf) with ROH and R′OH

The reaction of **1**OTf with a mixture of MeOH and EtOH illustrates the procedure employed.

A well stirred mixture of MeOH (0.103 ml, 2.6 mmol) and EtOH (0.150 ml, 2.6 mmol) was added quickly by syringe to a stirred solution of **1**OTf (0.0530 g, 0.054 mmol) in 2 ml of dry CH_2Cl_2. The resulting solution was stirred for 20 min at r.t., and then all the volatiles were removed under reduced pressure. The yellow solid residue was purified by dissolution in 0.5 ml of CH_2Cl_2 and precipitation by addition of 5 ml of hexanes. The precipitate was dried under vacuum at r.t. for 2 days. The product mixture was examined by ^{1}H-NMR spectroscopy before and after purification to ensure that no significant change in composition occurred as a result of solubility difference. The ^{1}H- and $^{31}P\{^1H\}$-NMR spectra showed the presence of both [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OMe)CHPh)$]OTf (**9**OTf) [7d] and [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OEt)CHPh)$]OTf (**3**OTf) in the mixture, ca. in a 2:1 ratio. The relative intensities of the signals of C*H*Ph of **9**OTf (1.38, 1H) and of Me of **3**OTf (1.97, 3H) were used to determine the exact ratio of the two products.

Similar procedures were employed for reactions of **1**OTf with mixtures of MeOH and *i*-PrOH and of MeOH and Me_3CCH_2OH. A 50- and a 20-fold excess of each alcohol over **1**OTf was used in the former and the latter reaction, respectively. Both [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OMe)CHPh)$]OTf (**9**OTf) and [$(PPh_3)_2Pt(\eta^3$-$CH_2C(O$-*i*-Pr)$CHPh)$]OTf (**4**OTf), and both [$(PPh_3)_2Pt(\eta^3$-$CH_2(OMe)CHPh)$]OTf (**9**OTf) and [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OCH_2CMe_3)CHPh)$]OTf (**5**OTf), were observed in the respective mixtures of products by ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopy, with **9**OTf being the major product in each case. The exact ratios of products were determined from the relative intensities of the signals of OMe of **9**OTf, of the lower-field resonating Me of **4**OTf and of CMe_3 of **5**OTf.

2.5. Preparation of $(PPh_3)_2Pt(\eta^3$-$CH_2C(O)CHPh)$ (10)

2.5.1. Reactions of [$(PPh_3)_2Pt(\eta^3$-$CH_2C(OR)CHPh)$]OTf (R = Me (9OTf), Et (3OTf), i-Pr (4OTf)) with NaOMe

A solution of **9**OTf (0.286 g, 0.281 mmol) in 10 ml of CH_2Cl_2 was treated with NaOMe (0.015 g, 0.28 mmol) in ca. 1 ml of MeOH, and the contents were stirred for ca. 12 h. The mixture was filtered, the filtrate was evaporated to dryness, and the residue was recrystallized from CH_2Cl_2–C_5H_{12}. The pale beige solid was dried under vacuum at 55 °C for 5 days. Yield of **10**: 0.179 g (74%), m.p. 208 °C (dec.). ^{1}H-NMR ($CDCl_3$): δ 7.6–6.6 (m, 35H, Ph), 3.94 (d, $J_{PH} = 11.6$ Hz, $J_{PtH} = 80.4$ Hz, 1H, C*H*Ph), 2.53 (m, 1H, *syn*-C*H*H), 2.33 (m, $J_{PtH} = 36$ Hz, 1H, *anti*-CH*H*). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 177.9 (t, $J_{PC} = 4.9$ Hz, $J_{PtC} = 151$ Hz, CO), 135–123 (m, Ph), 66.7 (dd, $J_{PC} = 57$, 3.6 Hz, $J_{PtC} = 305$ Hz, *C*HPh), 49.9 (dd, $J_{PC} = 52$, 4.6 Hz, $J_{PtC} = 305$ Hz, CH_2). $^{31}P\{^1H\}$-NMR ($CDCl_3$): δ 21.3 (d, $J_{PP} = 5.1$ Hz, $J_{PtP} = 3107$ Hz), 19.9 (d, $J_{PP} = 5.1$ Hz, $J_{PtP} = 2964$ Hz). FAB MS: ^{195}Pt, *m/z* 851 (M^+). Anal. Found: C, 63.26; H, 4.60. Calc. for $C_{45}H_{38}OP_2Pt$: C, 63.45; H, 4.50%.

Complex **10** was also obtained from **3**OTf or **4**OTf and NaOMe by similar procedures.

2.5.2. Reaction of [{$(PPh_3)_2Pt(\eta^3$-$CH_2CCHPh)$}$_2$O](OTf)$_2$ (2(OTf)$_2$ with NaOMe

A solution of NaOMe (0.0094 g, 0.174 mmol, two equivalents) in 2 ml of MeOH was added with stirring to **2**$(OTf)_2$ (0.1727 g, 0.0869 mmol) partially dissolved in 15 ml of CH_2Cl_2. The resulting solution was stirred for ca. 12 h, all volatiles were removed under reduced pressure and the residue was dissolved in 1 ml of CH_2Cl_2. The $^{31}P\{^1H\}$-NMR spectrum showed **10** as the only phosphorus-containing product.

2.5.3. Reaction of [$(PPh_3)_2Pt(\eta^3$-$CH_2CCPh)$]OTf (1OTf) with KOH

To a solution of **1**OTf (0.1535 g, 0.156 mmol) in 20 ml of CH_2Cl_2 was added a large excess (typically one pellet) of KOH, and the mixture was stirred while being monitored by $^{31}P\{^1H\}$-NMR spectroscopy. The reaction reached completion in 10 days. The mixture was filtered, and the filtrate was evaporated to dryness. Dissolution in minimal CH_2Cl_2 and addition of hexanes

induced the precipitation of **10**, which was identified spectroscopically. Yield: ca. 0.11 g (83%).

Use of 1:1 (by volume) CH_2Cl_2–THF as the solvent decreases reaction time to ca. 24 h owing to increased solubility of KOH. However, additional THF decreases solubility of **1**OTf to the point that the reaction slows down.

2.6. Reactions of $(PPh_3)_2Pt(\eta^3\text{-}CH_2C(O)CHPh)$ (10) with alkylating reagents

2.6.1. Reaction of 10 with $[Et_3O]PF_6$

To a solution of **10** (0.0902 g, 0.11 mmol) in 3 ml of CH_2Cl_2 was added one equivalent of $[Et_3O]PF_6$ (0.0263 g, 0.11 mmol) in 2 ml of CH_2Cl_2, and the resulting mixture was stirred at r.t. for 1 h. Examination of the reaction solution by $^{31}P\{^1H\}$-NMR spectroscopy revealed complete conversion to $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OEt)CHPh)]^+$ (**3**).

2.6.2. Reaction of 10 with dimethylsulfate

A solution of **10** (0.0488 g, 0.057 mmol) in 0.5 ml of $CDCl_3$ in an NMR tube was treated by syringe with ca. 10-fold excess (0.01 ml) of $(MeO)_2SO_2$ at r.t. The reaction was followed by $^{31}P\{^1H\}$-NMR spectroscopy and went cleanly to completion in ca. 5 h to afford $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OMe)CHPh)]^+$ (**9**).

2.6.3. Reaction of 10 with methyl iodide

A solution containing **10** (0.125 g, 0.15 mmol) and MeI (0.10 ml, 0.16 mmol) in 10 ml of CH_2Cl_2 was maintained at reflux temperature for 12 h and then was allowed to cool to ambient temperature. The mixture was filtered, and the filtrate was concentrated to 1 ml. The $^{31}P\{^1H\}$-NMR spectrum indicated the presence of **10** and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OMe)CHPh)]^+$ (**9**) in ca. 3:1 ratio, as well as $[Ph_3PMe]^+$ [16].

2.7. Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH_2CH{=}CH_2)CHPh)]OTf$ (7OTf) with $(PPh_3)_2Pt(C_2H_4)$

To a solution of 0.019 g (0.025 mmol) of $(PPh_3)_2Pt(C_2H_4)$ in 0.1 ml of $CDCl_3$ in an NMR tube was added by syringe 0.025 g (0.024 mmol) of **7**OTf in 0.8 ml of $CDCl_3$, and the contents were shaken for 10 min at r.t. An immediate color change from yellow to light brown was observed. The ^1H- and $^{31}P\{^1H\}$-NMR spectra showed the presence of **10** and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]^+$ [17] in a 1:1 ratio.

2.8. Thermolysis of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH_2CH{=}CH_2)CHPh)]OTf$ (7OTf)

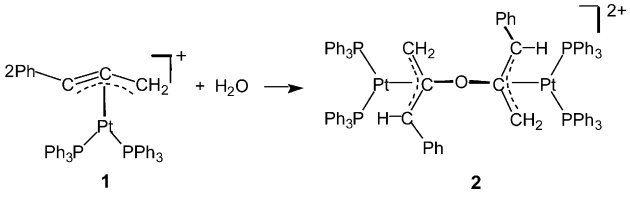
A slurry of **7**OTf (0.1027 g, 0.099 mmol) in C_6H_5Me (50 ml) was heated at reflux with vigorous stirring in a flask equipped with a reflux condenser. After all the solid had dissolved, progress of the reaction was monitored by $^{31}P\{^1H\}$-NMR spectroscopy. Conversion of **7** to a single PtP product, identified as $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]^+$ [17], was complete in ca. 2 days.

In another experiment, **7**OTf (0.043 g, 0.041 mmol) dissolved in 0.6 ml of 1:5 (by volume) $CDCl_3$–C_6D_6 in a pyrex tube equipped with a stopcock was heated in an oil bath at 80 °C for 48 h and then allowed to cool to r.t. The cloudy yellow solution was treated with 2 ml of CH_2Cl_2 to dissolve most of the solid, and the mixture was filtered. To the filtrate was slowly added with stirring 30 ml of hexanes to precipitate a pale yellow solid, which was collected on a filter frit, washed with hexanes (2×5 ml) and dried for several hours in vacuum. Yield of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH{=}CHMe)CHPh)]OTf$ (**11**OTf), 0.0307 g (71%). ^1H-NMR ($CDCl_3$): δ 8.0–6.5 (m, 35H, Ph), 6.15 (d, $^3J_{HH} = 7$ Hz, 1H, OCH), 5.00 (quin, $^3J_{HH}$ ca. 7 Hz, 1H, C*H*Me), 4.75 (d, $J_{PH} = 10$ Hz, $J_{PtH} = 33.5$ Hz, 1H, C*H*Ph), 3.35 (dd, $^2J_{HH} = 7$ Hz, $J_{PH} = 10$ Hz, $J_{PtH} = 43$ Hz, 1H, *anti*-C*H*H), 3.02 (br s, 1H, *syn*-CH*H*), 1.87 (d, $^3J_{HH} = 7$ Hz, 3H, Me). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ 146 (s, $J_{PtC} = 9.0$ Hz, *C*OCH), 138 (s, OCH), 135–125 (m, Ph), 111 (s, *C*HMe), 72.5 (d, $J_{PC} = 33.6$ Hz, $J_{PtC} = 57.8$ Hz, *C*HPh), 53.5 (d, $J_{PC} = 33.7$ Hz, $J_{PtC} = 123.6$ Hz, CH_2), 10.0 (s, Me). $^{31}P\{^1H\}$-NMR (CH_2Cl_2): δ 18.1 (d, $J_{PP} = 9.4$ Hz, $J_{PtP} = 3876$ Hz), 13.7 (d, $J_{PP} = 9.4$ Hz, $J_{PtP} = 3920$ Hz).

3. Results and discussion

3.1. Reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (1OTf) with water

Treatment of **1**OTf in CH_2Cl_2 at room temperature with a large excess of H_2O affords the binuclear $[\{(PPh_3)_2Pt(\eta^3\text{-}CH_2CCHPh)\}_2O](OTf)_2$ (**2**$(OTf)_2$) as a white solid in 80% yield (Eq. 3).



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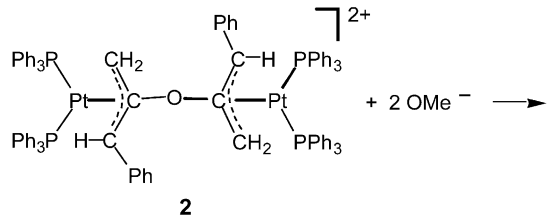
The product, which is somewhat soluble in CH_2Cl_2 and essentially insoluble in $CHCl_3$ and other common organic solvents, was characterized by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy and elemental analysis. The ^1H-NMR signals at δ 4.0, 3.3 and 2.4 and the coupling constants J_{PH} and J_{PtH} (cf. Section 2.3.1) are characteristic of the C*H*Ph, *syn*-C*H*H and *anti*-CH*H* protons, respectively, in various complexes $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(X)CHPh)]^+$ (X = O-donor group)

where X and Ph are *syn* [7d,7e,10]. In the $^{31}P\{^{1}H\}$-NMR spectrum two signals are observed, at δ 19.6 and 15.7, with $J_{PP} = 10$ Hz and $J_{PtP} = 3652$ and 3861 Hz, also in the ranges expected for $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(X)CHPh)]^+$ [7d,7e,10]. The absence of a ν(OH) absorption in the IR spectrum rules out the formulation of **2** as a 2-hydroxyallyl complex, $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OH)CHPh)]^+$. The assigned structure is further supported by treatment of **2** with two equivalents of NaOMe to afford **10** (cf. Section 3.3) as the only Pt complex (Eq. 4).



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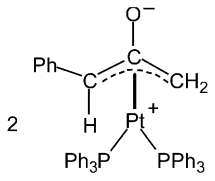

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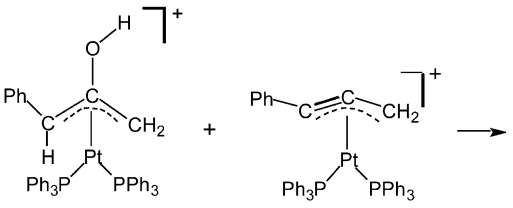

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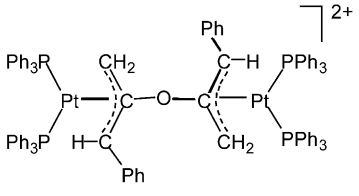

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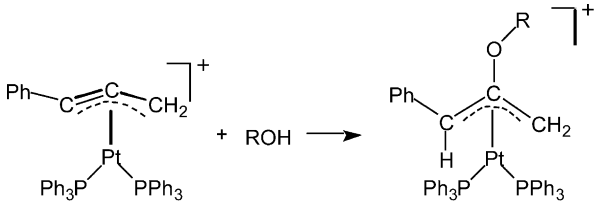
Reaction of **1**OTf with H_2O under various other conditions, for example, use of equimolar amounts of the reactants in CH_2Cl_2–THF, also yielded **2**$(OTf)_2$. No evidence was obtained for the presence of a η^3-(2-hydroxyallyl) product. These results stand in contrast to those obtained for aquation of other η^3-allenyl/propargyl complexes, viz. $[(\eta^6\text{-}C_6H_nMe_{6-n})Mo(CO)_2(\eta^3\text{-}CH_2CCH)]^+$ [7a] and $[Cp^*Re(CO)_2(\eta^3\text{-}CH_2CCH)]^+$ [5], where the η^3-(2-hydroxyallyl) products were obtained instead. However, the reaction with H_2O of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH)]^+$, the unsubstituted η^3-CH_2CCH analog of **1**, afforded both $[\{(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH_2)\}_2O]^{2+}$ and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OH)CH_2)]^+$ in the relative amounts that varied with experimental conditions [7b]. The observation of the oxo-bridged binuclear platinum product in that study as well as in the present work may be explained by the initial formation of a η^3-(2-hydroxyallyl) complex and its subsequent rapid reaction with the η^3-allenyl/propargyl reagent (Eq. 5). In fact, reaction of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH)]^+$ with $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OH)CH_2)]^+$ was shown to produce $[\{(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH_2)\}_2O]^{2+}$ [7b].

3.2. Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCPh)]OTf$ (**1**OTf) with alcohols and phenols

Reaction of **1**OTf with a large excess of the primary or secondary alcohol EtOH, *i*-PrOH or Me_3CCH_2OH in CH_2Cl_2 solution occurs within minutes at room temperature to afford the appropriate η^3-(2-alkoxyallyl) complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]OTf$ (R = Et (**3**OTf), *i*-Pr (**4**OTf) or Me_3CCH_2 (**5**OTf)) as a light yellow or beige solid in ca. 90% isolated yield (Eq. 6). The



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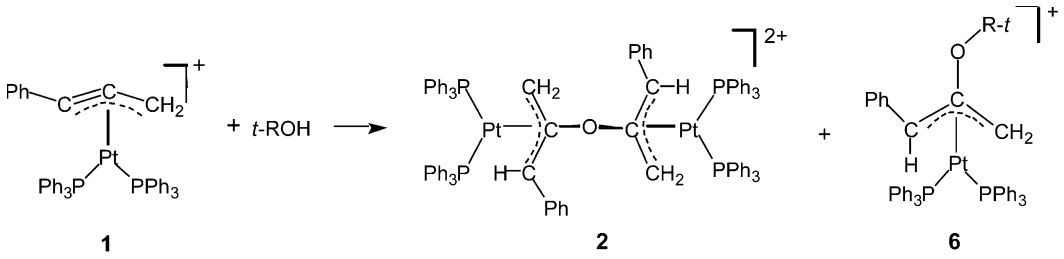
(6)

corresponding reaction of **1**OTf with $CH_2{=}CHCH_2OH$ in CH_2Cl_2, conducted similarly but at −15–−10 °C, gave $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH_2CH{=}CH_2)CHPh)]OTf$ (**7**OTf) essentially quantitatively. In contrast, the tertiary alcohols $Et(Me)_2COH$ and Me_3COH require longer than an hour to completely react with **1**OTf at ambient temperature and afford both **2**$(OTf)_2$ and the appropriate η^3-(2-alkoxyallyl) complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OR)CHPh)]OTf$ (R = $Et(Me)_2C$ (**6**OTf), Me_3C) (Eq. 7).



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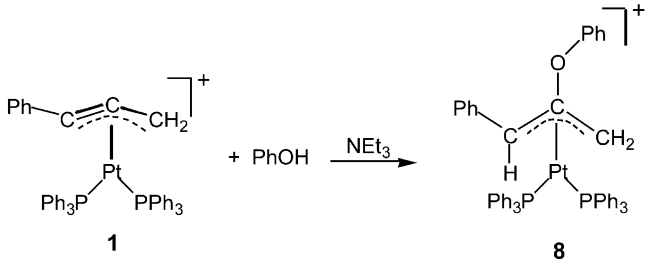
The yield of the η^3-(2-alkoxyallyl) complex can be optimized (ca. 1:1 alkoxyallyl/**2**) by slow addition of a dilute solution of **1**OTf in CH_2Cl_2 to a large excess of the alcohol. Phenol, *p*-methoxyphenol and *p*-nitrophenol do not react with **1**OTf in CH_2Cl_2 at room temperature over several hours. However, addition of triethylamine in excess to a CH_2Cl_2 solution of phenol and **1**OTf gives $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OPh)CHPh)]OTf$ (**8**OTf) as a pale yellow solid in 66% yield in ca. 30 min (Eq. 8). Interestingly, $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CCH)]^+$, the unsubstituted η^3-CH_2CCH analog of **1**, reacts with



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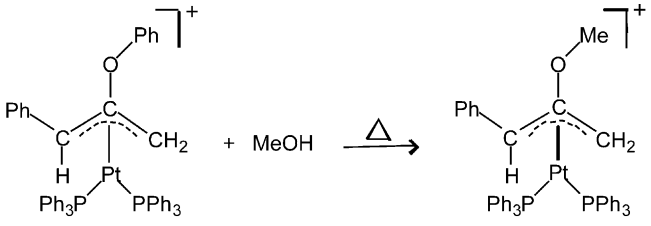
phenol in the absence of base, albeit more slowly than with primary or secondary alcohols or with Me_3COH, to give $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OPh)CH_2)]^+$ [7c].

The η^3-(2-alkoxyallyl) complexes **3**OTf, **4**OTf, **5**OTf and the previously reported [7d] $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OMe)CHPh)]OTf$ (**9**OTf) are thermally stable compounds. For example, **4**OTf undergoes only slight decomposition when heated in THF at reflux temperature for 2 months (monitored by ^{31}P-NMR spectroscopy). Furthermore, heating **4**OTf in water results in very little decomposition. The η^3-(2-alkoxyallyl) complexes also remain intact upon prolonged contact with alcohols; for example, there is no reaction between **9**OTf and ethyl alcohol at ambient temperatures over ca. 2 days. However, the η^3-(2-phenoxyallyl) **8**OTf reacts with methyl alcohol on heating to give **9**OTf (Eq. 9); there is also slow reaction at room temperature.



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Complexes **3**OTf–**8**OTf were characterized by a combination of IR and NMR (^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H}) spectroscopy, FAB mass spectrometry and elemental analysis. All of the FAB mass spectra showed a strong peak corresponding to *m*/*z* for (M^+). The ^{1}H- and ^{13}C{^{1}H}-NMR spectra are consistent with the presence of a η^3-$CH_2C(OR)CHPh$ ligand in which the OR and Ph groups are *syn*. Accordingly, proton resonances occur in the ranges δ 4.85–3.93 (d, J_{PH} = 9.8–10.5 Hz, with ^{195}Pt satellites, J_{PtH} = 35.4–42.6 Hz), 3.35–2.50 (dd, $^2J_{HH}$ ca. 6–6.6 Hz, J_{PH} = 9.4–10.0 Hz, with ^{195}Pt satellites, J_{PtH} = 23.5–40.5 Hz) and 2.92–2.35 (generally, br s). They are assigned to C*H*Ph, *anti*-C*H*H and *syn*-CH*H*, respectively. These assignments receive support from the following observations: (i) the presence of substantial ^{195}Pt–H coupling (vide supra) for the signals at δ 4.85–3.93 and 3.35–2.50, which suggest *anti* positions for both protons [18]; (ii) an appreciable value of J_{HH} (6–6.6 Hz) for the resonance at δ 3.35–2.50, which is attributed to geminal coupling; and (iii) the absence of *W*-coupling [19] expected for *syn* allylic hydrogens of C_1 and C_3, which was ascertained by selective decoupling experiments on **3**OTf. The foregoing ^{1}H-NMR data are in good agreement with those obtained for the η^3-(2-methoxyallyl) complex **9**OTf, where the same orientation of OR and Ph was inferred [7d].

In the ^{31}C{^{1}H}-NMR spectra, resonances of the η^3-allyl *C*OR, *C*HPh and CH_2 carbon atoms are observed at δ 150–147, 74.6–71.5 and 54.6–51.4, respectively. Whereas the *C*HPh and CH_2 signals appear as doublets owing to phosphorus–carbon coupling involving one PPh_3 ligand (J_{PC} = 31.6–37 and 33.8–45.3 Hz, respec-

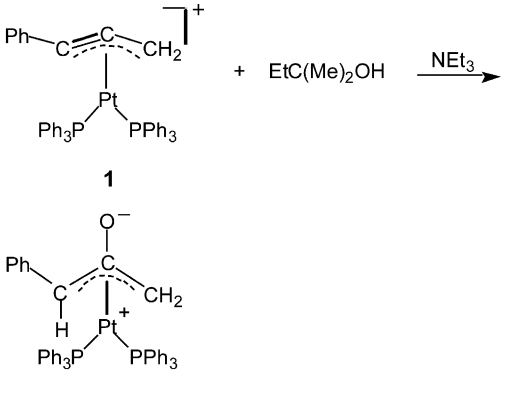
tively), no such interaction is evident for the *C*OR carbon. All three signals generally occur with observable ^{195}Pt satellites: $J_{PtC} = 8.8–9.4$ Hz for *C*OR, 48.2–74.4 Hz for *C*HPh and 118.2–139 Hz for CH_2. Again, there is good accord with corresponding data for related platinum complexes [7b,7c,7d,8c,9a].

Among further noteworthy features in the ^{1}H- and ^{13}C{^{1}H}-NMR spectra of complexes **3**OTf–**8**OTf is diastereotopy of the otherwise equivalent nuclei owing to the presence of the chiral C*C*(Pt)HPh center. As a result, two signals are observed for each of OC*H*$_2$Me of **3**OTf, OCH*Me*$_2$ of **4**OTf, OC*H*$_2$CMe$_3$ of **5**OTf, OC(*Me*)$_2$Et of **6**OTf and OC*H*$_2$CH=CH$_2$ of **7**OTf in the respective ^{1}H-NMR spectra, and for OCH*Me*$_2$ of **4**OTf in the ^{13}C{^{1}H}-NMR spectrum. The ^{31}P{^{1}H}-NMR spectra consist of two doublet signals ($J_{PP} = 8.8–10.6$ Hz) at δ 19.0–18.0 and 14.3–13.3 with ^{195}Pt–P coupling ($J_{PtP} = 3737–3983$ Hz) as a result of the terminal carbon atoms of η^3-allyl being in different environments. For the η^3-(2-allyloxyallyl) complex **7**OTf, the ^{1}H- and ^{13}C{^{1}H}-NMR signals of the OCH$_2$CH=CH$_2$ group are similar in position and appearance to those of allyl alcohol. The coupling constants and splitting patterns given in Section 2.3.6 were elucidated by selective decoupling experiments.

A mechanism consistent with the *anti* addition of MeOH to the η^3-CH$_2$CCPh of **1** was proposed earlier (Scheme 1) [7d]. Briefly, it involves: (i) attack of MeOH at the central carbon atom to generate a methoxy-substituted metallacyclobutene intermediate; (ii) loss of the OH proton to the platinum center; and (iii) transfer of this hydrogen to the *C*Ph carbon atom away from the OMe group. This general pathway has also been suggested for addition of ROH to other metal η^3-allenyl/propargyl complexes [2,5] and applies to the reactions of **1**OTf with the primary and secondary alcohols investigated here (Eq. 6) because of a similar stereochemical outcome. Treatment of **1**OTf with EtOD affords **3**-d_1OTf where the D atom is positioned *anti* to OEt, as inferred from the ^{1}H- and ^{2}H-NMR spectra. This result is consistent with the aforementioned mechanism and indicates that no scrambling of ligand hydrogens occurs during the addition of alcohol.

The formation of the η^3-(2-alkoxyallyl) complexes in the reaction of **1**OTf with tertiary alcohols (cf. Eq. 7) likely proceeds by a similar pathway from stereochemical evidence. However, the mechanism by which the co-product **2**(OTf)$_2$ arises is less apparent. This binuclear complex might be generated by reaction of **1**OTf with water present in the alcohol, although such a possibility would appear unlikely since the alcohol was carefully dried and purified as reported in Section 2.2. Alternatively, **2**(OTf)$_2$ could arise from reaction of **1**OTf with a η^3-(2-hydroxyallyl) complex, [(PPh$_3$)$_2$Pt(η^3-CH$_2$C(OH)-CHPh)]OTf (cf. Eq. 5), generated in the reaction. Formation of the latter would require elimination of alkene from the reacting alcohol. This could possibly occur by initial addition of ROH to the central carbon atom of η^3-CH$_2$CCPh followed by agostic interaction of the alcohol β-H with the metal leading to formation of Pt–H and elimination of appropriate alkene. Transfer of this hydrogen to the *C*Ph carbon atom would then afford such a η^3-(2-hydroxyallyl) intermediate. This sequence of transformations is set out in Scheme 2.

Several experiments were performed to shed light on the aforementioned proposal. Intermediate **A** in Scheme 2 has two possible sources of H for transfer to produce the 2-alkoxyallyl or 2-hydroxyallyl: the hydroxyl H (cf. Scheme 1) and alkyl β-H, respectively. If the reaction is carried out in the presence of a non-nucleophilic base, then one could generate a deprotonated form of **A**, and the hydroxylic hydrogen would no longer be available for transfer to give the η^3-(2-alkoxyallyl). Accordingly it was found that if **1**OTf and *t*-amyl alcohol were allowed to react in the presence of NEt$_3$ in excess, only the elimination product **10** was obtained (Eq. 10). However, the



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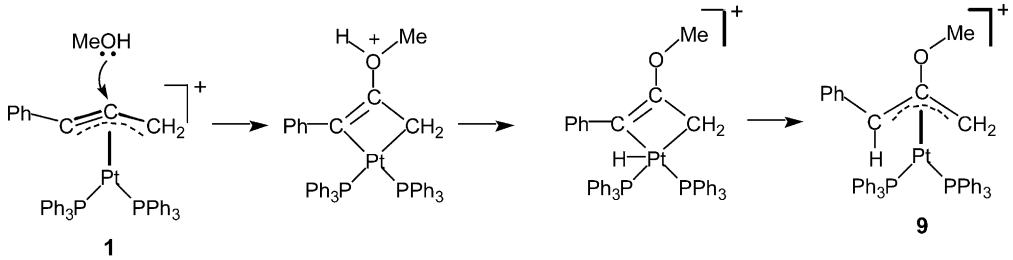
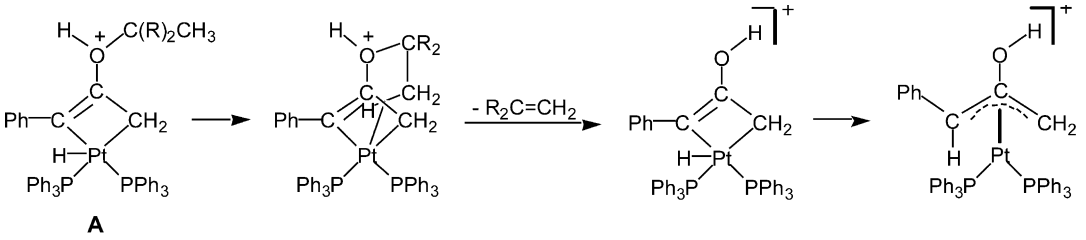


Scheme 1.



Scheme 2.

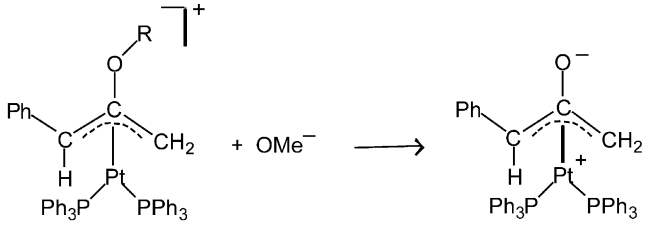
η^3-(2-*t*-amyloxyallyl) **6**OTf reacts neither with NEt_3 nor with $[HNEt_3][OC(Me)_2Et]$. Thus the elimination to give **10** must be occurring at some intermediate stage of the reaction in Eq. 10, and not from the product **6**.

To further test the foregoing mechanism of formation of **2**$(OTf)_2$ from **1**OTf and *t*-amyl alcohol, attempts were made at detection of 2-methylbut-1-ene or 2-methylbut-2-ene during the reaction. However, ^{1}H-NMR spectra of the volatile organic mixture showed no evidence of vinylic hydrogens of an alkene. Because of this result, the question of mechanism remains unresolved.

The relative reactivity of **1**OTf toward various alcohols was determined by competition studies using mixtures of two alcohols as described in Section 2.4. These experiments showed that the rate of reaction at ambient temperature increases in the order $Me_3CCH_2OH < i$-PrOH < EtOH < MeOH in the ratios 1.0:1.2:2.1:4.3. The difference in reactivity among the four alcohols is quite modest and may be attributed to their steric properties. Interestingly, in a parallel study Chen and coworkers reported [7c] that the order of reactivity in the addition of alcohols to $[(PPh_3)_2Pt(\eta^3$-$CH_2CCH)]BF_4$ follows a similar pattern, viz. $Me_3COH < i$-PrOH < EtOH < MeOH, with the relative rates being 1.0:5.8:10.0:17.5. The quantitative rate profiles of the two platinum η^3-allenyl/propargyl complexes are almost identical for MeOH, EtOH and *i*-PrOH. In contrast, Me_3COH, which reacts only ca. six times more slowly than *i*-PrOH with $[(PPh_3)_2Pt(\eta^3$-$CH_2CCH)]BF_4$, is significantly less reactive than *i*-PrOH toward **1**OTf. This greater difference in reactivity observed for the latter complex may be a result of considerable steric repulsion between the phenyl group of its η^3-CH_2CCPh ligand and the bulky Me_3COH.

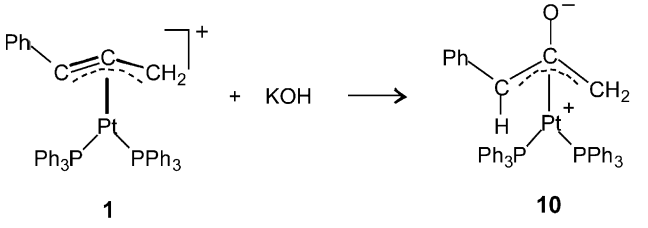
3.3. Preparation and reactions of $(PPh_3)_2Pt(\eta^3$-$CH_2C(O)CHPh)$ (10)

In an attempt to introduce another methoxy group, in a terminal position of the η^3-hydrocarbyl ligand of $[(PPh_3)_2Pt(\eta^3$-$CH_2C(OMe)CHPh)]^+$ (**9**), **9**OTf was allowed to react with NaOMe in CH_2Cl_2–MeOH. However, instead of addition of OMe^-, dealkylation of the OMe of **9** took place to afford the platinum η^3-oxatrimethylenemethane complex $(PPh_3)_2Pt(\eta^3$-$CH_2C(O)CHPh)$ (**10**) (Eq. 11). Similar results were obtained by using the η^3-(2-ethoxyallyl)



(11)

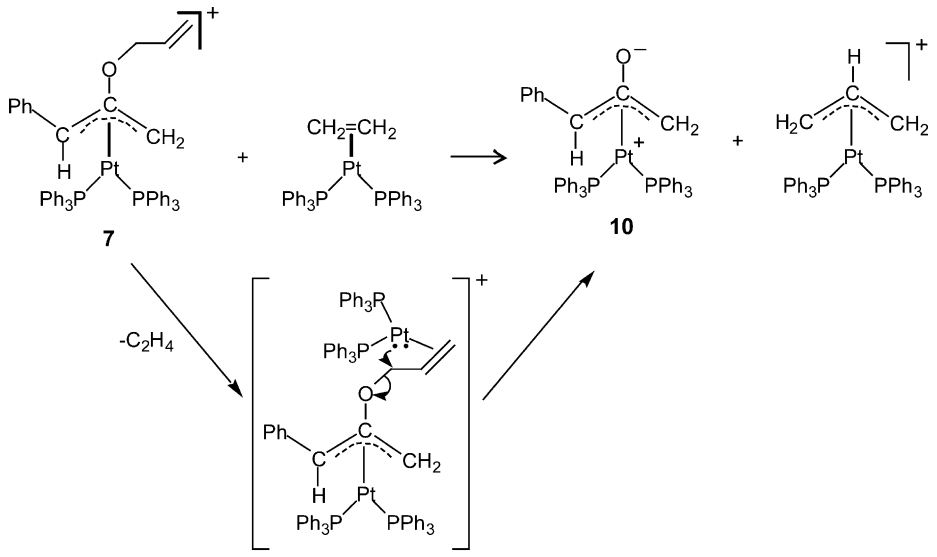
(**3**OTf), η^3-(2-isopropoxyallyl) (**4**OTf) and η^3-(2-*t*-amyloxyallyl) (**6**OTf) complexes in place of **9**OTf. Also, in related work, Kurosawa, Ikeda and coworkers employed reactions of $[(PPh_3)_2M(\eta^3$-$CH_2C(OCH_2O$-$Me)CH_2)]X$ (M = Pd, Pt; X = Cl, PF_6) with NaOMe or NaOH to synthesize $(PPh_3)_2M(\eta^3$-$CH_2C(O)CH_2)$ [20]. In all of these transformations, the metal η^3-$(CH_2C(OR)CHR')$ (R′ = Ph, H) complex behaves as an alkyloxonium salt, readily losing its oxygen-bound R^+. A reported variation on this methodology is deprotonation of cationic metal η^3-(2-hydroxyallyl) complexes [20,21]. In the present study, complex **10** was also prepared by reaction of **2**$(OTf)_2$ with two equivalents of NaOMe (cf. Eq. 4) and of **1**OTf with KOH (Eq. 12). Of the methods reported



(12)

here, the one of choice is that presented in Eq. 10 because of simplicity, purity of product and high yield.

Complex **10** was characterized by ^{1}H-, $^{13}C\{^1H\}$- and $^{31}P\{^1H\}$-NMR spectroscopy, FAB mass spectrometry and elemental analysis. The NMR data show strong similarities to the corresponding data of the precursor η^3-(2-alkoxyallyl) complexes, except for the absence of the appropriate signals of OR. The appearance of three

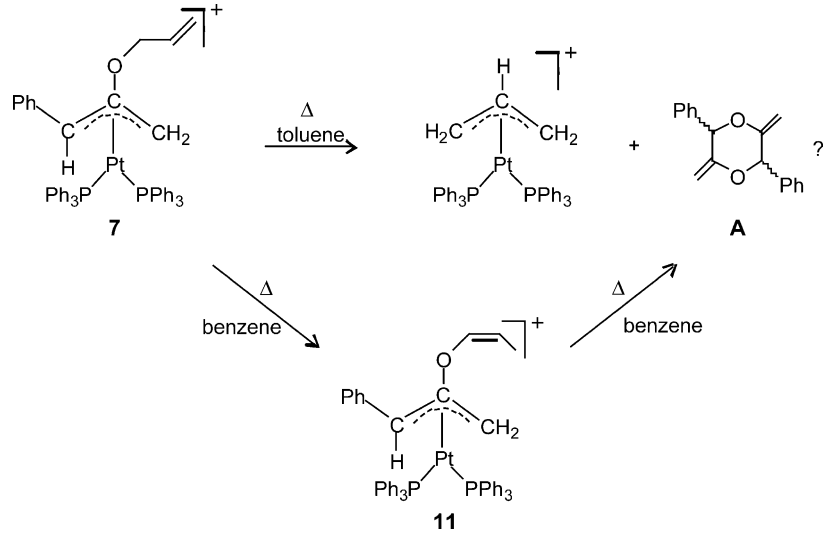


Scheme 3.

proton resonances of η^3-$CH_2C(O)CHPh$ at δ 3.94, 2.53 and 2.33, two with the relatively large coupling constants J_{PtH} of 80 and 34 Hz, indicates that the Ph group is *syn* to the oxygen [18], as for the η^3-(2-alkoxyallyl) complexes. The $^{13}C\{^1H\}$-NMR signals of CO, *C*HPh and CH_2 occur at δ 177.9 (t, 151), 66.7 (dd, 305) and 49.9 (dd, 305), respectively, with observable spin–spin coupling to both ^{195}Pt (given in Hz in parentheses) and ^{31}P. In general, the NMR spectroscopic data of **10** compare well with those of a series of complexes $L_2Pt(\eta^3$-$CH(R)C(O)CHR)$ ($L = PPh_3$, $AsPh_3$, other phosphines, $\frac{1}{2}$bipy; R = H, Ph, C(O)Me, CO_2Me), obtained by Kemmitt and coworkers [21,22] via synthetic methods very different from those developed in this study.

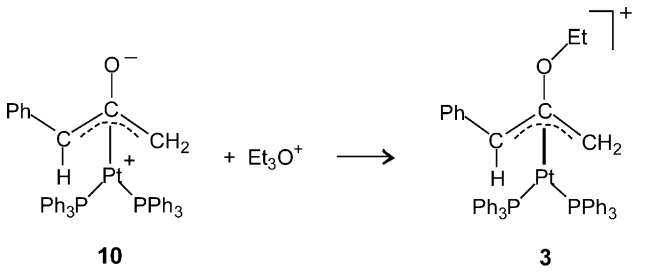
The bonding in these platinum oxatrimethylenemethane complexes is best described as a hybrid of slipped metal η^3-allyl and puckered metallacyclic resonance structures [7e,22]. This conclusion is derived from X-ray structural [20,21] and NMR spectroscopic studies [7d,10,20,21]. Interestingly, unlike most of the $L_2Pt(\eta^3$-oxatrimethylenemethane) complexes, **10** shows stereochemically rigid behavior in its ^1H- and $^{13}C\{^1H\}$-NMR spectra at ambient temperatures. However, the complexes $L_2Pt(\eta^3$-$CH(R)C(O)CHR)$ investigated by Kemmitt and coworkers generally undergo scrambling of the *syn* and *anti* groups of CHR, and this observed fluxionality has been attributed to inversion of the puckered metallacyclic ring [21,22].

Complex **10** undergoes alkylation to regenerate $[(PPh_3)_2Pt(\eta^3$-$CH_2C(OR)CHPh)]^+$. Thus, ethylation has been effected essentially quantitatively by use of $[Et_3O]PF_6$ in CH_2Cl_2 at room temperature (Eq. 13), and methylation by use of an excess of $(MeO)_2SO_2$ in



Scheme 4.

$CDCl_3$, also at



10 **3**

(13)

ambient temperature. In contrast, reaction of **10** with MeI in CH_2Cl_2 at reflux did not proceed cleanly, and after 12 h gave ca. 3:1 unreacted **10** and **9**, as well as $[Ph_3PMe]^+$.

3.4. Reactions of $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH_2CH{=}CH_2)CHPh]OTf$ (7OTf)

Since allyl groups are readily transferred to metal under a variety of conditions [23], it was of interest to ascertain whether **7**OTf would react with $(PPh_3)_2Pt(C_2H_4)$. When equimolar amounts of the aforementioned complexes were combined in chloroform at room temperatue, clean conversion occurred within 10 min to afford **10** and $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]^+$, characterized by ^1H- and $^{31}P\{^1H\}$-NMR spectroscopy. This reaction probably proceeds by replacement of $\eta^2\text{-}CH_2{=}CH_2$ with the $CH_2{=}CHCH_2O$ of **7** followed by cleavage of the $CH_2{-}O$ bond as shown in Scheme 3.

A structural similarity exists between platinum η^3-(2-alkoxyallyl) complexes and organic vinyl ethers. Since allyl vinyl ethers undergo [3,3] sigmatropic rearrangement reactions [24], it was of interest to explore possible analogous reactivity of **7**. In that vein, **7**OTf was heated in toluene at reflux, but no products of a sigmatropic rearrangement could be detected. Instead, the η^3-allyl complex $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]OTf$ was isolated as the sole metal-containing product, but non-volatile organic compounds could not be observed. A possible organic product might be dioxane **A** (Scheme 4), formed by dimerization of released $CH_2C(O)CHPh$ and unstable to reaction conditions. Compounds similar to **A** have been observed in thermally induced organic oxyallyl dimerization reactions [25]; in this study, however, no evidence was found for such a coupling product.

In an attempt to detect organic reaction products, **7**OTf was heated at a lower temperature in benzene–chloroform. This thermolysis yielded a single platinum product, which was isolated in 71% yield as a pale yellow solid and identified spectroscopically as $[(PPh_3)_2Pt(\eta^3\text{-}CH_2C(OCH{=}CHMe)CHPh)]OTf$ (**11**OTf) (cf. Scheme 4). The ^1H-NMR signals at δ 4.75 (C*H*Ph), 3.35 (*anti*-C*H*H) and 3.02 (*syn*-CH*H*) and the $^{13}C\{^1H\}$-NMR signals at δ 146 (*C*OCH), 72.5 (*C*HPh) and 53.5 (CH_2) are similar in position and splitting pattern to those of the other platinum η^3-$CH_2C(OR)CHPh$ complexes prepared in this study. The remaining ^1H and $^{13}C\{^1H\}$ resonances of the η^3-$CH_2C(OR)CHPh$ ligand are in accord with the OR group being OCH=CHMe, which resulted from isomerization of the $OCH_2CH{=}CH_2$ in **7**. Organic C=C double bond isomerization is quite commonly effected by platinum and other metal catalysts [26]. Further heating of **11**OTf in benzene at reflux affords $[(PPh_3)_2Pt(\eta^3\text{-}CH_2CHCH_2)]OTf$ as expected, although the reaction is much slower than that in toluene at reflux.

Acknowledgements

This study was supported in part by the National Science Foundation and The Ohio State University.

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